EUROPEAN COMMISSION

Integrated Pollution Prevention and Control (IPPC)

Reference Document on Best Available Techniques in the Non Ferrous Metals Industries

December 2001

Executive Summary

This reference document on best available techniques in the non-ferrous metal industry reflects the information exchange carried out according to Article 16 (2) of Council Directive 96/61/EC. The document has to be seen in the light of the preface that describes the objective of the document and its use.

To deal with the complex area of the production of non-ferrous metals, an approach was adopted to cover production of the metals from both primary and secondary raw materials together in one document and to deal with the metals in 10 groups. Those groups are:

- Copper (including Sn and Be) and its Alloys.
- Aluminium.
- Zinc, Lead and Cadmium, (+ Sb, Bi, In, Ge, Ga, As, Se, Te).
- Precious Metals.
- Mercury.
- Refractory Metals.
- Ferro Alloys.
- Alkali and Alkaline Earth Metals.
- Nickel and Cobalt.
- Carbon and Graphite.

Carbon and graphite production was also included as a separate group as many such processes are associated with primary aluminium smelters. Processes for roasting and sintering of ores and concentrates and for the production of alumina were also included within these groups where applicable. Mining and ore treatment at the mine site are not covered in the document

In the document, information is presented in twelve chapters covering: general information in Chapter 1, common processes in Chapter 2 and then metallurgical production processes for ten groups of metals in Chapters 3 to 12. Chapter 13 presents the conclusions and recommendations. Annexes covering costs and international regulations are also included. The common processes in Chapter 2 are divided as follows:

- Use of the chapter - complex installations.
- Use and reporting of emission data.
- Management, design and training.
- Receipt, storage and handling of raw materials.
- Pre-processing and pre-treatment of raw materials and transfer to production processes.
- Metal production processes - furnace types and process control techniques.
- Gas collection and air abatement techniques.
- Effluent treatment and water re-use.
- Minimisation, recycling and treatment of process residues (including by-products and waste).
- Energy and waste heat recovery.
- Cross media issues.
- Noise and vibration.
- Odour.
- Safety aspects.
- De-commissioning.

Each of Chapters 2 to 12 includes sections on applied processes and techniques, present emission and consumption levels, techniques to consider in the determination of BAT and BAT conclusions. For Chapter 2 the BAT conclusions are only drawn for material handling and storage, process control, gas collection and abatement, dioxin removal, sulphur dioxide recovery, mercury abatement and effluent treatment/water re-use. The BAT conclusions contained in all of the chapters should be consulted for a complete understanding.

1. Non-Ferrous Metal Industry

At least 42 non-ferrous metals plus ferro alloys and carbon and graphite are produced in EU and are used in a variety of applications in the metallurgical, chemical, construction, transport and electricity generation/transmission industries. For example high purity copper is essential for electricity generation and distribution and small amounts of nickel or refractory metals improve the corrosion resistance or other properties of steel. They are also used in many high technology developments, particularly in the defence, computing, electronic and telecommunications industries.

Non-ferrous metals are produced from a variety of primary and secondary raw materials. Primary raw materials are derived from ores that are mined and then further treated before they are metallurgically processed to produce crude metal. The treatment of ores is normally carried out close to the mines. Secondary raw materials are indigenous scrap and residues and may also undergo some pre-treatment to remove coating materials.

In Europe, ore deposits containing metals in viable concentrations have been progressively depleted and few indigenous sources remain. Most concentrates are therefore imported from a variety of sources worldwide.

Recycling constitutes an important component of the raw material supplies of a number of metals. Copper, aluminium, lead, zinc, precious metals and refractory metals, among others, can be recovered from their products or residues and can be returned to the production process without loss of quality in recycling. Overall, secondary raw materials account for a high proportion of the production, thus reducing the consumption of raw materials and energy.

The product of the industry is either refined metal or what is known as semis or semi manufactures, i.e. metal and metal alloy cast ingots or wrought shapes, extruded shapes, foil, sheet, strip, rod etc.

The structure of the industry varies metal by metal. No companies produce all non-ferrous metals although there are a few pan-European companies producing several metals, e.g. copper, lead, zinc, cadmium etc.

The size of the companies producing metals and metal alloys in Europe varies from a few employing more than 5000 people and a large number having between 50 and 200 employees. Ownership varies between pan-European and national metals groups, industrial holdings groups, stand-alone public companies and private companies.

Some metals are essential as trace elements but at higher concentrations are characterised by the toxicity of the metal, ion or compounds and many are included under various lists of toxic materials. Lead, cadmium and mercury are of the greatest concern.

2. Environmental Issues for the Industry

The main environmental issues for the production of most non-ferrous metals from primary raw materials are the potential emission to air of dust and metals/metal compounds and of sulphur dioxide to if roasting and smelting sulphide concentrates or using sulphur-containing fuels or other materials. The capture of sulphur and its conversion or removal is therefore an important factor in the production of non-ferrous metals. The pyrometallurgical processes are potential sources of dust and metals from furnaces, reactors and the transfer of molten metal.

Energy consumption and the recovery of heat and energy are important factors in the production of non-ferrous metals. They depend on the efficient use of the energy content of sulphidic ores, the energy demand of the process stages, the type and supply method of energy used and the use of effective methods of heat recovery. Working examples are given in Chapter 2 of the document.

The main environmental issues associated with the production of non-ferrous metals from secondary raw materials are also related to the off-gases from the various furnaces and transfers that contain dust, metals and in some process steps, acid gases. There is also the potential for the formation of dioxins due to the presence of small amounts of chlorine in the secondary raw materials; the destruction and/or capture of dioxin and VOCs is an issue that is being pursued.

The main environmental issues for primary aluminium are the production of poly-fluorinated hydrocarbons and fluorides during electrolysis, the production of solid waste from the cells and the production of solid waste during the production of alumina.

The production of solid waste is also an issue for the production of zinc and other metals during the iron removal stages.

Other processes often use hazardous reagents such as HCl, HNO_3, Cl_2 and organic solvents for leaching and purification. Advanced processing techniques are able to contain these materials and recover and re-use them. Reactor sealing is an important issue in this respect.

In the majority of cases these process gases are cleaned in fabric filters and so the emissions of dust and metal compounds such as lead are reduced. Gas cleaning using wet scrubbers and wet electrostatic precipitators is particularly effective for process gases that undergo sulphur recovery in a sulphuric acid plant. In some cases where dust is abrasive or difficult to filter, wet scrubbers are also effective. The use of furnace sealing and enclosed transfers and storage is important in preventing fugitive emissions.

In summary the main issues for the production processes for each of the groups of metals comprise the following components:

- For the production of copper: SO_2, dust, metal compounds, organic compounds, wastewater (metal compounds), residues such as furnace linings, sludge, filter dust and slag. Dioxin formation during treatment of secondary copper materials is also an issue.
- For the production of aluminium: fluorides (incl. HF), dust, metal compounds, SO_2, COS, PAH, VOCs, green house gases (PFCs and CO_2), dioxins (secondary), chlorides and HCl. Residues such as bauxite residue, Spent Pot Lining, filter dust and salt slag and wastewater (oil and ammonia).
- For the production of lead, zinc and cadmium: dust, metal compounds, VOCs (including dioxins), odours, SO_2, other acid gases, wastewater (metal compounds), residues such as sludge, the iron rich residues, filter dust and slag.
- For the production of precious metals: VOCs, dust, metal compounds, dioxins, odours, NO_x, other acid gases such as chlorine and SO_2. Residues such as sludge, filter dust and slag and wastewater (metal compounds and organic compounds).
- For the production of mercury: mercury vapour, dust, metal compounds, odours, SO_2, other acid gases, wastewater (metal compounds), residues such as sludge, filter dust and slag.
- For the production of refractory metals, hardmetal powder and metal carbides: dust, solid hardmetal and metal compounds, wastewater (metal compounds), residues such as filter dust, sludge and slag. Process chemicals such as hydrogen fluoride (HF) are used for processing tantalum and niobium and are highly toxic. This needs to be taken into account in the handling and storage of these materials.
- For the production of ferro-alloys: dust, metal compounds, CO, CO_2, SO_2, energy recovery, wastewater (metal compounds), residues such as filter dust, sludge and slag.

- For the production of alkali and alkaline earth metals: chlorine, HCl, dioxin, SF_6, dust, metal compounds, CO_2, SO_2, wastewater (metal compounds), residues such as sludge, aluminate, filter dust and slag.
- For the production of nickel and cobalt: VOCs, CO, dust, metal compounds, odours, SO_2, chlorine and other acid gases, wastewater (metal compounds and organic compounds), residues such as sludge, filter dust and slag.
- For the production of carbon and graphite: PAHs, hydrocarbons, dust, odours, SO_2, wastewater prevention, residues such as filter dust.

3. Applied Processes

The range of raw materials available to the various installations is wide and this means that a variety of metallurgical production processes is used. In many instances the process choice is governed by the raw materials. The following tables summarise the furnaces used for the production of non-ferrous metals:

Furnace	Metals Used	Material Used	Comment
Steam coil dryer Fluid bed dryer Flash dryer	Cu and some others	Concentrates	
Rotary Kiln	Most metals for drying. Fuming ZnO. Calcining alumina, Ni and ferro alloys. Burning of photographic film for precious metal production. De-oiling Cu and Al scrap	Ores, concentrates and various scrap and residues.	Drying, calcining and fuming applications. Use as an incinerator.
Fluidised bed.	Copper and zinc Al_2O_3	Concentrates. $Al(OH)_3$	Calcining and roasting.
Up Draught sintering machine.	Zinc and lead.	Concentrates and secondary.	Sintering.
Down Draft sintering machine	Zinc and lead.	Concentrates and secondary.	Sintering.
Steel Belt sintering machine	Ferro-alloys, Mn, Nb.	Ore.	Other applications possible
Herreshoff	Mercury. Molybdenum (rhenium recovery)	Ores and concentrates.	Roasting, calcining.

Drying, roasting, sintering and calcining furnaces

Furnace	Metals Used	Material Used	Comment
Enclosed refractory lined crucibles	Refractory metals, special ferro-alloys	Metal oxides	
Open Pit	Refractory metals, special ferro-alloys.	Metal oxides	
Baiyin	Copper	Concentrates	
Electric Arc Furnace	Ferro alloys	Concentrates, ore	
Contop/Cyclone	Copper	Concentrates	
Submerged Electric Arc Furnace	Precious metals, copper, ferro alloys.	Slag, secondary materials, concentrates.	For the production of ferro-alloys the open, semi closed and closed types are used.
Rotary	Aluminium, lead, copper, precious metals	Scrap and other secondary, blister copper	Oxidation and reaction with substrate.
Tilting Rotary Furnace	Aluminium	Scrap and other secondary	Minimises salt flux use.
Reverberatory	Aluminium, copper, others	Scrap and other secondary, black copper	Smelting of Cu concentrates elsewhere in the World.
Vanyucov	Copper	Concentrates	
ISA Smelt/Ausmelt	Copper, lead,	Intermediates, concentrates and secondary materials.	
QSL	Lead	Concentrates and secondary	
Kivcet	Lead Copper	Concentrates and secondary	
Noranda	Copper	Concentrates	
El Teniente	Copper	Concentrates	
TBRC TROF	Copper (TBRC), Precious metals	Most secondary inc. slimes	
Mini Smelter	Copper/lead/tin	Scrap	
Blast Furnace and ISF	Lead, lead/zinc, copper, precious metals, high carbon ferro-manganese.	Concentrates, most secondary	For ferro-manganese production it is only used together with energy recovery.
Inco Flash Furnace	Copper, nickel	Concentrates	
Outokumpu Flash Smelter	Copper, nickel	Concentrates	
Mitsubishi process	Copper	Concentrates and anode scrap	
Peirce Smith	Copper (converter), Ferro-alloys, Metal Oxide Production	Matte and anode scrap	
Hoboken	Copper (converter)	Matte and anode scrap	
Outokumpu Flash Converter	Copper (converter)	Matte	
Noranda Converter	Copper (converter)	Matte	
Mitsubishi Converter	Copper (converter)	Matte	

Smelting and refining furnaces

Furnace	Metals Used	Material Used	Comment
Induction	Most	Clean metal and scrap.	Induced stirring assists alloying. Vacuum can be applied for some metals
Electron Beam	Refractory metals	Clean metal and scrap.	
Rotary	Aluminium, lead	Various scrap grades.	Fluxes and salts used for complex matrices.
Reverberatory	Aluminium (primary and secondary)	Various scrap grades.	Bath or hearth configuration can vary. Melting or holding
Contimelt	Copper	Copper anode, clean scrap and blister copper.	Integrated furnace system.
Shaft	Copper	Copper cathode and clean scrap.	Reducing conditions.
Drum (Thomas)	Copper	Copper scrap	Melting, fire refining
Heated Crucibles (indirect kettles)	Lead, zinc	Clean scrap.	Melting, refining, alloying.
Direct heated crucibles	Precious metals	Clean metal	Melting, alloying.

Melting Furnaces

Hydrometallurgical processes are also used. Acids and alkalis (NaOH, sometimes also Na_2CO_3) are used to dissolve the metal content of a variety of calcines, ores and concentrates before refining and electro-winning. The material to be leached is usually in the form of the oxide, either as an oxidic ore or an oxide produced by roasting. Direct leaching of some concentrates or mattes is also performed at both elevated and atmospheric pressure. Some copper sulphide ores can be leached with sulphuric acid or other media, sometimes using natural bacteria to promote oxidation and dissolution, but very long residence times are used.

Air, oxygen, chlorine or solutions containing ferric chloride can be added to leaching systems to provide the appropriate conditions for dissolution. The solutions that are produced are treated in a number of ways to refine and win the metals. Common practice is to return the depleted solutions to the leaching stage, where appropriate, to conserve acids and alkaline solutions.

4. Current Emissions and Consumption

The range of raw materials is also a significant factor and affects the use of energy, the amount of residues produced and the quantity of other materials used. An example is the removal of impurities such as iron into slags; the amount of impurity present governs the amount of slag produced and the energy used.

Emissions to the environment depend on the collection or abatement systems that are used. The current ranges reported for a number of abatement processes during the exchange of information are summarised in the following table:

Abatement Technique	**Reported emissions**			**Specific emission** (amount per t of metal produced)
	Component	**minimum**	**maximum**	
Fabric filter, hot EP and cyclone.	Dust (Metals dependent on composition)	< 1 mg/Nm^3	100 mg/Nm^3	100 - 6000 g/t
Carbon filter	Total C	< 20 mg/Nm^3		
Afterburner (including temperature quench for dioxin)	Total C	< 2 mg/Nm^3	100 mg/Nm^3	10 - 80 g/t
	Dioxin (TEQ)	< 0.1 ng/Nm^3	5 ng/Nm^3	5 - 10 µg/t
	PAH (EPA)	< 1 µg/Nm^3	2500 µg/Nm^3	
	HCN	< 0.1 mg/Nm^3	10 mg/Nm^3	
Wet or semi-dry scrubber	SO_2	< 50 mg/Nm^3	250 mg/Nm^3	500 - 3000 g/t
	Hydrocarbon	<10 mgC/Nm^3	200 mgC/Nm^3	
	Chlorine	< 2 mg/Nm^3		
Alumina scrubber	Dust	< 1 mg/Nm^3	20 mg/Nm^3	
	Hydrocarbon	< 1 mgC/Nm^3	50 mgC/Nm^3	
	PAH (EPA)	< 20 µg/Nm^3	2000 µg/Nm^3	
Chlorine recovery	Chlorine	< 5 mg/Nm^3		
Optimised combustion Low NO_x burner	NO_x	10 mg/Nm^3	500 mg/Nm^3	
Oxidising scrubber	NO_x		< 100 mg/Nm^3	
Sulphuric acid plant reported as conversion of SO_2	double contact	99.3 %	99.7%	1 - 16 kg/t
	single contact	95	99.1%	
Cooler, EP, lime/carbon adsorption and fabric filter	PAH (EPA)	0.1 mg/Nm^3	6 mg/Nm^3	
	Hydrocarbons	20 mgC/Nm^3	200 mgC/Nm^3	

Reported range of current emissions

Process gases are captured and then cleaned in fabric filters to reduce the emissions of dust and metal compounds such as those of lead. Modern filter fabrics offer significant improvements in performance, reliability and life. Afterburners and carbon absorption are used to remove dioxins and VOCs.

Uncaptured gases or fugitive emissions, however, are not treated. Dust emissions also occur from storage, handling and the pre-treatment of raw materials where fugitive dust emissions also play an important role. This is true for both primary and secondary production, as their significance can be much greater than captured and abated emissions. Careful plant design and process operations are needed to capture and treat process gases where fugitive emissions are significant.

The following table shows that fugitive or uncaptured emissions are important issues:

	Dust emission kg/a	
	Before additional secondary gas collection (1992)	**After additional secondary gas collection (1996)**
Anode production t/a	220000	325000
Fugitive emissions		
Total Smelter	66490	32200
Smelter roofline	56160	17020
Primary smelter stack emissions		
Smelter/acid plant	7990	7600
Stack-secondary hoods	2547	2116

Comparison of abated and fugitive dust loads at a primary copper smelter

Many processes use sealed cooling and process water systems but there is still the potential to discharge heavy metals to water. The methods to reduce water use and wastewater generation and to treat process waters are reviewed in Chapter 2.

The production of residues is also a significant factor in this industry, but the residues often have recoverable metal quantities and it is common practice to use residues on-site or in other installations to recover metals. Many slags that are produced are inert, non-leachable and are used in many civil engineering works. Other slags, such as salt slag, can be treated to recover other components for use in other industries, but the industry needs to ensure that these recovery operations are operated to a high environmental standard.

5. Key BAT Conclusions

The exchange of information during the preparation of the BREF for non-ferrous metal production has allowed conclusions on BAT to be reached for the production and associated processes. The sections in each of the chapters that describe BAT should therefore be referred to for a complete understanding of BAT and the associated processes and emissions. The key findings are summarised below.

- **Up-stream Activities**

Process management, supervision and the control of the process and abatement systems are very important factors. Good training practices and operator instruction and motivation are also important especially to prevent environmental pollution. Good techniques for raw material handling can prevent fugitive emissions. Other important techniques include:

- Consideration of the environmental implications of a new process or raw material at the earliest stages of the project with reviews at regular intervals thereafter.
- Design of the process to accept the anticipated range of raw material. Severe problems can result for example if gas volumes are too high or if the energy use of the material is higher than anticipated. The design stage is the most cost-effective time to introduce improvements in overall environmental performance.
- Use of an audit trail of the design and decision-making process to show how various processes and abatement options were considered.
- Planning of commissioning procedures for new or modified plant.

The following table summarises the techniques for raw material storage and handling on the basis of type and characteristics of the material.

Raw material	Metal group	Method for handling	Method for storage	Comments
Concentrates:	All - if dust forming	Enclosed conveyors or pneumatic	Enclosed building	Prevention of water contamination.
	All - if non dust forming	Covered conveyors	Covered store	
Fine grained material (e.g. metal powder)	Refractory metals	Enclosed conveyors or pneumatic Covered conveyors	Closed drum, bins and hoppers	Prevention of water contamination and fugitive air emissions
Secondary raw materials:	All - Large items	Mechanical loader	Open	Prevention of water contamination or reactions with water. Oily drainage from swarf
	All - Small items	Charge skips	Covered bays	
	All - Fine material	Enclosed or agglomerated	Enclosed if dusty	
Fluxes:	All - if dust forming	Enclosed conveyors or pneumatic	Enclosed building	Prevention of water contamination.
	All - if non dust forming	Covered conveyors	Covered store	
Solid fuel & coke:	All	Covered conveyors If not dust forming	Covered store If not dust forming	
Liquid fuels and LPG	All	Overhead pipeline	Certified storage Bunded areas.	Back venting of delivery lines
Process gases:	All	Overhead pipeline Reduced pressure pipeline (Chlorine, CO)	Certified storage	Pressure loss monitoring, Alarms for toxic gases.
Solvents	Cu, Ni, Zn group, PM, Carbon	Overhead pipeline Manual	Drums, tanks	Back venting of delivery lines.
Products – Cathodes, wire-rod, billets, ingots, cakes etc.	All	Depends on conditions.	Open concrete area or covered storage.	Appropriate drainage system.
Process residues for recovery.	All	Depends on conditions.	Open, covered or enclosed depending on dust formation and reaction with water.	Appropriate drainage system.
Wastes for disposal. (e.g. furnace linings)	All	Depends on conditions.	Open covered or enclosed bays or sealed (drums) depending on the material.	Appropriate drainage system.

Summary of raw material and handling techniques

Furnace design, the use of suitable pre-treatment methods and process control were identified as important features of BAT.

The use of raw material blending to optimise the process prevents inappropriate material being used and maximises process efficiency. Sampling and analysis of feed materials and the segregation of some materials are important factors in this technique.

Good design, maintenance and monitoring are important for all process and abatement stages. Sampling and monitoring of emissions to the environment should be carried out according to national or international standard methods. Important parameters that can be used for the control of process or abatement should be monitored. Continuous monitoring of key parameters should be carried out if practical.

- **Process control**

Process control techniques that are designed to measure and maintain optimum parameters such as temperature, pressure, gas components and other critical process parameters etc are considered to be BAT.

Sampling and analysis of raw materials to control plant conditions. Good mixing of different feed materials should be achieved to get optimum conversion efficiency and reduce emissions and rejects.

The use of feed weighing and metering systems, the use of microprocessors to control material feed-rate, critical process and combustion conditions and gas additions allow process operation to be optimised. Several parameters can be measured to allow this and alarms provided for critical parameters, which include:

- On-line monitoring of temperature, furnace pressure (or depression) and gas volume or flow.
- Monitoring of gaseous components (O_2, SO_2, CO, dust, NO_x etc).
- On-line monitoring of vibration to detect blockages and possible equipment failure.
- On-line monitoring of the current and voltage of electrolytic processes.
- On-line monitoring of emissions to control critical process parameters.
- Monitoring and control of the temperature of melting furnaces to prevent the production of metal and metal oxide fume by overheating.

Operators, engineers and others should be continuously trained and assessed in the use of operating instructions, the use of the modern control techniques and the significance of alarms and the actions to be taken when alarms are given.

Optimisation of levels of supervision to take advantage of the above and to maintain operator responsibility.

- **Gas collection and abatement**

The fume collection systems used should exploit furnace or reactor sealing systems and be designed to maintain a reduced pressure that avoids leaks and fugitive emissions. Systems that maintain furnace sealing or hood deployment should be used. Examples are: through electrode additions of material; additions via tuyeres or lances and the use of robust rotary valves on feed systems. Secondary fume collection is expensive and consumes a lot of energy, but is needed in the case of some furnaces. The system used should be an intelligent system capable of targeting the fume extraction to the source and duration of any fume.

Overall for dust and associated metal removal, fabric filters (after heat recovery or gas cooling) can provide the best performance provided that modern wear resistant fabrics are used, the particles are suitable and continuous monitoring is used to detect failure. Modern filter fabrics (e.g. membrane filter) offer significant improvements in performance, reliability and life and therefore offer cost savings in the medium term. They can be used in existing installations and can be fitted during maintenance. They feature bag burst detection systems and on-line cleaning methods.

For sticky or abrasive dusts, wet electrostatic precipitators or scrubbers can be effective provided that they are properly designed for the application.

Gas treatment for the smelting or incineration stage should include a sulphur dioxide removal stage and/or after-burning if this is considered necessary to avoid local, regional or long-range air quality problems or if dioxins may be present.

There may be variations in the raw materials that influence the range of components or the physical state of some components such as the size and physical properties of the dust produced. These should be assessed locally.

- **Prevention and the destruction of dioxins**

The presence of dioxins or their formation during a process needs to be considered for many of the pyro-metallurgical processes used to produce non-ferrous metals. Particular instances are reported in the metal-specific chapters and in these cases the following techniques are considered to be BAT for the prevention of the formation of dioxins and the destruction of any that are present. These techniques may be used in combination. Some non-ferrous metals are reported to catalyse de-novo synthesis and it is sometimes necessary to have a clean gas prior to further abatement.

- Quality control of scrap inputs depending on the process used. The use of the correct feed material for the particular furnace or process. Selection and sorting to prevent the addition of material that is contaminated with organic matter or precursors can reduce the potential for dioxin formation.
- The use of correctly designed and operated afterburners and rapid quenching of the hot gases to < 250°C.
- The use of optimum combustion conditions. The use of oxygen injection in the upper part of a furnace to ensure complete combustion of furnace gases if necessary to achieve this.
- Absorption onto activated carbon in a fixed bed or moving bed reactor or by injection into the gas stream, and removal as filter dust.
- Very high efficiency dust removal for example, ceramic filters, high efficiency fabric filters or the gas cleaning train prior to a sulphuric acid plant.
- The use of a catalytic oxidation stage or fabric filters that incorporate a catalytic coating.
- The treatment of collected dusts in high temperature furnaces to destroy dioxins and to recover metals.

The emission concentrations that are associated with the above techniques range from <0.1 to 0.5 ng/Nm^3 TEQ depending on the feed, the smelting or melting process and the techniques or combination of techniques that are used for dioxin removal.

- **Metallurgical Processes**

The range of raw materials available to the various installations is wide and means that there is a need to include a variety of metallurgical production processes in the BAT sections of the majority of the metal groups. In many instances the process choice is governed by the raw materials, so the type of furnace has only a minor effect on BAT, provided that the furnace has been designed for the raw materials used and energy recovery is used where practicable.

There are exceptions. For example, the use of multiple point feeding of alumina to centre worked prebake cells was identified as BAT for primary aluminium, as was the use of sealed furnaces in the production of some ferro-alloys to allow collection of high calorific value gas.

For primary copper the reverberatory furnace is not considered to be BAT. The other major influences are the blending of the raw materials, process control, management and the collection of fume. The hierarchy in the choice of a new or changed process was identified as:

- Thermal or mechanical pre-treatment of secondary material to minimise organic contamination of the feed.
- The use of sealed furnaces or other process units to prevent fugitive emissions, allow heat recovery and allow the collection of process gases for other use (e.g. CO as a fuel and SO_2 as sulphuric acid) or for abatement.
- The use of semi-sealed furnaces where sealed furnaces are not available.
- The minimisation of material transfers between processes.
- Where such transfers are unavoidable, the use of launders in preference to ladles for molten materials.
- In some cases the restriction of techniques to those that avoid molten material transfers may prevent the recovery of some secondary materials that would then enter the waste stream. In these cases the use of secondary or tertiary fume collection is appropriate so that these materials can be recovered.
- Hooding and ductwork design to capture fume arising from hot metal, matte or slag transfers and tapping.
- Furnace or reactor enclosures may be required to prevent release of fume losses into the atmosphere.
- Where primary extraction and enclosure are likely to be ineffective, then the furnace can be fully closed and ventilation air drawn off by extraction fans to a suitable treatment and discharge system.
- The maximum use of the energy content of sulphidic concentrates.

- **Emissions to Air**

Emissions to air arise from the storage, handling, pre-treatment, pyro-metallurgical and hydrometallurgical stages. Transfer of materials is particularly important. Data provided has confirmed that the significance of fugitive emissions in many processes is very high and that fugitive emissions can be much greater than those that are captured and abated. In these cases it is possible to reduce environmental impact by following the hierarchy of gas collection techniques from material storage and handling, reactors or furnaces and from material transfer points. Potential fugitive emissions must be considered at all stages of process design and development. The hierarchy of gas collection from all of the process stages is:

- Process optimisation and minimisation of emissions;
- Sealed reactors and furnaces;
- Targeted fume collection;

Roofline collection of fume is very energy consuming and should be a last resort.

The potential sources of emissions to air are summarised in the following table, which also gives a review of prevention and treatment methods. Emissions to air are reported on the basis of collected emissions. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. Standard conditions are used: 273 K, 101.3 kPa, measured oxygen content and dry gas with no dilution of the gases.

Sulphur capture is an important requirement when sulphidic ores or concentrates are roasted or smelted. The sulphur dioxide produced by the process is collected and can be recovered as sulphur, gypsum (if no cross-media effects) or sulphur dioxide or can be converted to sulphuric acid. The process choice depends on the existence of local markets for sulphur dioxide. The production of sulphuric acid in a double contact sulphuric acid plant with a minimum of four passes, or in a single contact plant with gypsum production from the tail gas and using a modern catalyst, are considered to be BAT. Plant configuration will depend on the concentration of sulphur dioxide produced in the roasting or smelting stage.

Process stage	Component in off-gas	Treatment method
Materials handling and storage.	Dust and metals.	Correct storage, handling and transfer. Dust collection and fabric filter if necessary.
Grinding, drying.	Dust and metals.	Process operation. Gas collection and fabric filter.
Sintering/roasting Smelting Converting Fire refining	VOCs, dioxins.	Afterburner, adsorbent or activated carbon addition.
	Dust and metal compounds.	Gas collection, gas cleaning in fabric filter, heat recovery.
	Carbon monoxide	Afterburner if necessary
	Sulphur dioxide	sulphuric acid plant (for sulphidic ores) or scrubber
Slag treatment.	Dust and metals.	Gas collection, cooling and fabric filter.
	Sulphur dioxide.	Scrubber.
	Carbon monoxide.	Afterburner
Leaching and chemical refining.	Chlorine.	Gas collection and re-use, wet chemical scrubber.
Carbonyl refining.	Carbon monoxide. Hydrogen.	Sealed process, recovery and re-use. Afterburner and dust removal in fabric filter for tail gas.
Solvent extraction.	VOC. (depends on the solvent used and should be determined locally to assess the possible hazard).	Containment, gas collection, solvent recovery. Carbon adsorption if necessary.
Thermal refining.	Dust and metals.	Gas collection and fabric filter.
	Sulphur dioxide.	Scrubber if necessary.
Molten salt electrolysis	Fluoride, chlorine, PFCs	Process operation. Gas collection, scrubber (alumina) and fabric filter.
Electrode baking, graphitisation	Dust, metals, SO_2, Fluoride, PAHs, tars	Gas collection, condenser and EP, afterburner or alumina scrubber and fabric filter. Scrubber if necessary for SO_2.
Metal powder production	Dust and metals	Gas collection and fabric filter.
Powder production	Dust, Ammonia	Gas collection and recovery. Acid medium scrubber.
High temperature reduction	Hydrogen.	Sealed process, re-use.
Electro-winning.	Chlorine. Acid mist.	Gas collection and re-use. Wet scrubber. De-mister.
Melting and casting.	Dust and metals.	Gas collection and fabric filter.
	VOCs, dioxins (organic feed)	Afterburner (Carbon injection)

Note. Dust arrestment using a fabric filter may require the removal of hot particles to prevent fires. Hot electrostatic precipitators would be used in a gas cleaning system prior to a sulphuric acid plant or for wet gases.

Summary of sources and treatment/abatement options

A summary of the emission levels associated with abatement systems that are considered to be BAT for the non-ferrous metal processes is shown in the following table. More details are given in the BAT conclusions in the metal-specific chapters.

Abatement Technique	**Associated Range**	**Comment**
Fabric filter	Dust 1 - 5 mg/Nm^3 Metals - dependent on dust composition	Depends on characteristics of dust.
Carbon or Bio filter	Total organic C < 20 mg/Nm^3	Phenol < 0.1 mg/Nm^3
Afterburner (including temperature quench for dioxin removal)	Total organic C < 5 - 15 mg/Nm^3 Dioxin < 0.1 - 0.5 ng/Nm^3 TEQ PAH (OSPAR 11) < 200 µgCNm^3 HCN < 2 mg/Nm^3	Designed for gas volume. Other techniques are available to reduce dioxins further by carbon/lime injection, catalytic reactors/filters.
Optimised combustion conditions	Total organic C < 5 - 50 mg/Nm^3	
Wet EP Ceramic filter	Dust < 5 mg/Nm^3	Depends on characteristics e.g. dust, moisture or high temperature
Wet or semi-dry alkaline scrubber	SO_2 < 50 - 200 mg/Nm^3 Tar < 10 mg/Nm^3 Chlorine < 2 mg/Nm^3	
Alumina scrubber	Dust 1 - 5 mg/Nm^3 Hydrocarbon < 2 mg/Nm^3 PAH (OSPAR 11) < 200 µgC/Nm^3	
Chlorine recovery	Chlorine < 5 mg/Nm^3.	Chlorine is re-used. Possible accidental fugitive releases.
Oxidising scrubber	NO_x < 100 mg/Nm^3	From use of nitric acid - recovery followed by removal of traces.
Low NO_x burner.	< 100 mg/Nm^3	Higher values are associated with oxygen enrichment to reduce energy use. In these cases gas volume and mass emission are reduced.
Oxy-fuel burner.	< 100 - 300 mg/Nm^3	
Sulphuric acid plant	> 99.7% conversion (double contact)	Including mercury scrubber using Boliden/Norzink process or thiosulphate scrubber Hg < 1 ppm in acid produced
	> 99.1% conversion (single contact)	
Cooler, EP, lime/carbon adsorption and fabric filter	PAH (OSPAR 11) < 200 µgC/Nm^3 Hydrocarbons (volatile) < 20 mgC/Nm^3 Hydrocarbons (condensed) < 2 mgC/Nm^3	
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period and standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas without dilution of the gases with air. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used. For some components, the variation in raw gas concentration during batch processes may affect the performance of the abatement system.		

Emissions to air associated with the use of BAT

Several specific reagents are used in chemical treatment of solutions of metals or in various metallurgical processes. Some of the compounds, sources and treatment methods of gases produced from the use of these reagents are given below:

Process/Reagent Used	Component in off-gas	Treatment Method
Use of arsenic or antimony oxide. (refining of Zn/Pb)	Arsine/stibine	Permanganate scrubbing
Pitch etc	Tars and PAH	Afterburner, condenser and EP or dry absorber.
Solvents, VOCs	VOC, Odour	Containment, condensation. Activated carbon, bio-filter
Sulphuric acid (+ sulphur in fuel or raw material)	Sulphur dioxide	Wet or semi-dry scrubber system. Sulphuric acid plant.
Aqua Regia	NOCl, NO_x	Caustic scrubber system
Chlorine, HCl	Cl_2	Caustic scrubber system
Nitric acid	NO_x	Oxidise and absorb, recycle, scrubber system
Na or KCN	HCN	Oxidise with hydrogen peroxide or hypochlorite
Ammonia	NH_3	Recovery, scrubber system
Ammonium chloride	Aerosol	Recovery by sublimation, scrubber system
Hydrazine	N_2H_4 (possible carcinogen)	Scrubber or activated carbon
Sodium borohydride	Hydrogen (explosion hazard)	Avoid if possible in PGM processing (especially Os, Ru)
Formic acid	Formaldehyde	Caustic scrubber system
Sodium chlorate/HCl	Cl_2 oxides (explosion hazard)	Control of process end point

Overview of chemical treatment methods for some gaseous components

- **Emissions to water**

Emissions to water arise from a number of sources and a variety of minimisation and treatment options are applicable depending on the source and the components present. In general the wastewaters can contain soluble and non-soluble metal compounds, oil and organic material. The following table summarises the potential wastewaters, the metals produced, minimisation and treatment methods.

Source of wastewater	Associated process	Minimisation methods	Treatment Methods
Process water	Alumina production, Lead-acid battery breaking. Pickling.	Return to process as far as possible.	Neutralisation and precipitation. Electrolysis.
Indirect cooling water	Furnace cooling for most metals. Electrolyte cooling for Zn	Use of sealed or air cooling system. System monitoring to detect leaks.	Settlement.
Direct cooling water	Al, Cu, Zn castings. Carbon electrodes.	Settlement Closed cooling system.	Settlement. Precipitation if needed.
Slag granulation	Cu, Ni, Pb, Zn, precious metals, ferro alloys		Settlement. Precipitation if needed.
Electrolysis	Cu, Ni, Zn	Sealed system. Electro-winning of electrolyte bleed.	Neutralisation and precipitation.
Hydro-metallurgy (blow-down)	Zn, Cd	Sealed system.	Settlement. Precipitation if needed.
Abatement system (blow-down)	Wet scrubbers. Wet EPs and scrubbers for acid plants.	Re-use of weak acid streams if possible.	Settlement. Precipitation if needed.
Surface water	All	Good raw materials storage and prevention of fugitive emissions	Settlement. Precipitation if needed. Filtration.

Overview of BAT for wastewater streams

Wastewater treatment systems can maximise the removal of metals using sedimentation and possibly filtration. The reagents used for precipitation may be hydroxide, sulphide or a combination of both, depending on the mix of metals present. It is also practicable in many cases to re-use treated water.

	Main components [mg/l]					
	Cu	**Pb**	**As**	**Ni**	**Cd**	**Zn**
Process water	<0.1	<0.05	<0.01	<0.1	<0.05	<0.15
Note: The associated emissions to water are based on a qualified random sample or a 24-hour composite sample. The extent of wastewater treatment depends on the source and the metals contained in the wastewater.						

Example of emissions to water associated with the use of BAT

- **Process Residues**

Process residues are produced at various stages of the process and are highly dependent on the constituents of the raw materials. Ores and concentrates contain quantities of metals other than the prime target metal. Processes are designed to obtain a pure target metal and to recover other valuable metals as well.

These other metals tend to concentrate in the residues from the process and in turn these residues form the raw material for other metal recovery processes. The following table gives an overview of some process residues and the options available to deal with them.

Source of the residues	Associated Metals	Residue	Options for dealing with them
Raw materials handling etc.	All metals	Dust, sweepings	Feed for the main process
Smelting furnace	All metals	Slag	Construction material after slag treatment. Abrasive industry Parts of slag may be used as refractory material e.g. slag from the production of chromium metal
	Ferro-alloys	Rich slag	Raw material for other ferro-alloy processes
Converting furnace	Cu	Slag	Recycle to smelter
Refining furnaces	Cu	Slag	Recycle to smelter
	Pb	Skimmings	Recovery of other valuable metals
	Precious metals (PMs)	Skimmings and slag	Internal recycle
Slag treatment	Cu and Ni	Cleaned slag	Construction material. Matte produced
Melting furnace	All metals	Skimmings Slag and salt slag.	Return to process after treatment. Metal recovery, recovery of salt and other material
Electro-refining	Cu	Electrolyte bleed Anode remnants Anode slime	Recovery of Ni. Return to converter Recovery of precious metals
Electro-winning	Zn, Ni, Co, PMs	Spent electrolyte	Re-use in leaching process
Fused salt electrolysis	Al	Spent Pot Lining Excess bath Anode stubs	Carburant or disposal Sale as electrolyte Recovery
	Na and Li	Cell material	Scrap iron after cleaning
Distillation	Hg	Residues (Hollines)	Re-use as process feed
	Zn, Cd	Residues	Return to process
Leaching	Zn	Ferrite residues	Safe disposal, re-use of liquor
	Cu	Residues	Safe disposal
	Ni/Co	Cu/Fe residues	Recovery, disposal
Sulphuric acid plant		Catalyst	Regeneration
		Acid sludges	Safe disposal
		Weak acid	Leaching, disposal
Furnace linings	All metals	Refractory	Use as slagging agent, disposal
Milling, Grinding	Carbon	Carbon and graphite dusts	Use as raw material in other processes
Pickling	Cu, Ti	Spent acid	Recovery
Dry abatement systems	Most – using fabric filters or EPs	Filter dust	Return to process Recovery of other metals
Wet abatement systems	Most – using scrubbers or wet EPs	Filter sludge	Return to process or recovery of other metals (e.g. Hg). Disposal
Wastewater treatment sludge	Most	Hydroxide or sulphide sludges.	Safe disposal, re-use Re-use
Digestion	Alumina	Red mud	Safe disposal, re-use of liquor

Overview of residues and available options for dealing with them

Filter dusts can be recycled within the same plant or used for the recovery of other metals at other non-ferrous metal installations, by a third party or for other applications.

Residues and slags can be treated to recover valuable metals and render the residues suitable for other uses e.g. as construction material. Some components can be converted into saleable products.

Residues from water treatment may contain valuable metals and can be recycled in some cases.

The regulator and operator should satisfy themselves that the recovery of residues by a third party is carried out to high environmental standards and does not cause negative cross-media effects.

- **Toxic Compounds**

Specific toxicity of some compounds that may be emitted (and their environmental impact or consequences) varies from group to group. Some metals have toxic compounds that may be emitted from the processes and so need to be reduced.

- **Energy recovery**

Energy recovery before or after abatement is applicable in the majority of cases but local circumstances are important, for example, where there is no outlet for the recovered energy. The BAT conclusions for energy recovery are:

- Production of steam and electricity from the heat raised in waste heat boilers.
- The use of the heat of reaction to smelt or roast concentrates or melt scrap metals in a converter.
- The use of hot process gases to dry feed materials.
- Pre-heating of a furnace charge using the energy content of furnace gases or hot gases from another source.
- The use of recuperative burners or the pre-heating of combustion air.
- The use as a fuel gas of CO produced.
- The heating of leach liquors from hot process gases or liquors.
- The use of plastic contents in some raw materials as a fuel, provided that good quality plastic cannot be recovered and VOCs and dioxins are not emitted.
- The use of low-mass refractories where practicable.

6. Degree of Consensus and Recommendations for Future Work

This BREF has met a high level of support from the TWG and participants at the 7th meeting of the Information Exchange Forum. Critical remarks have mainly related to information gaps and presentational aspects (calls for more BAT associated emission and consumption levels to be included in the Executive Summary).

It is recommended that this document be revised in 4 years time. The areas where additional efforts should be made to establish a sound basis of information include, above all, fugitive emissions and also specific emission and consumption data, process residues, wastewater and aspects related to small and medium-sized companies. Chapter 13 contains further recommendations.

PREFACE

1. Status of this document

Unless otherwise stated, references to “the Directive” in this document means the Council Directive 96/61/EC on integrated pollution prevention and control. This document forms part of a series presenting the results of an exchange of information between EU Member States and industries concerned on best available techniques (BAT), associated monitoring and developments in them. It is published by the European Commission pursuant to Article 16(2) of the Directive and must therefore be taken into account in accordance with Annex IV of the Directive when determining "best available techniques".

2. Relevant legal obligations of the IPPC Directive and the definition of BAT

In order to help the reader understand the legal context in which this document has been drafted, some of the most relevant provisions of the IPPC Directive, including the definition of the term “best available techniques”, are described in this preface. This description is inevitably incomplete and is given for information only. It has no legal value and does not in any way alter or prejudice the actual provisions of the Directive.

The purpose of the Directive is to achieve integrated prevention and control of pollution arising from the activities listed in its Annex I, leading to a high level of protection of the environment as a whole. The legal basis of the Directive relates to environmental protection. Its implementation should also take account of other Community objectives such as the competitiveness of the Community’s industry thereby contributing to sustainable development.

More specifically, it provides for a permitting system for certain categories of industrial installations requiring both operators and regulators to take an integrated, overall look at the polluting and consuming potential of the installation. The overall aim of such an integrated approach must be to improve the management and control of industrial processes so as to ensure a high level of protection for the environment as a whole. Central to this approach is the general principle given in Article 3 that operators should take all appropriate preventative measures against pollution, in particular through the application of best available techniques enabling them to improve their environmental performance.

The term “best available techniques” is defined in Article 2(11) of the Directive as “the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole.” Article 2(11) goes on to clarify further this definition as follows:

“techniques” includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;

“available” techniques are those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator;

“best” means most effective in achieving a high general level of protection of the environment as a whole.

Furthermore, Annex IV of the Directive contains a list of “considerations to be taken into account generally or in specific cases when determining best available techniques ... bearing in mind the likely costs and benefits of a measure and the principles of precaution and prevention”.

These considerations include the information published by the Commission pursuant to Article 16(2).

Competent authorities responsible for issuing permits are required to take account of the general principles set out in Article 3 when determining the conditions of the permit. These conditions must include emission limit values, supplemented or replaced where appropriate by equivalent parameters or technical measures. According to Article 9(4) of the Directive, these emission limit values, equivalent parameters and technical measures must, without prejudice to compliance with environmental quality standards, be based on the best available techniques, without prescribing the use of any technique or specific technology, but taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In all circumstances, the conditions of the permit must include provisions on the minimisation of long-distance or transboundary pollution and must ensure a high level of protection for the environment as a whole.

Member States have the obligation, according to Article 11 of the Directive, to ensure that competent authorities follow or are informed of developments in best available techniques.

3. Objective of this Document

Article 16(2) of the Directive requires the Commission to organise "an exchange of information between Member States and the industries concerned on best available techniques, associated monitoring and developments in them", and to publish the results of the exchange.

The purpose of the information exchange is given in recital 25 of the Directive, which states that "the development and exchange of information at Community level about best available techniques will help to redress the technological imbalances in the Community, will promote the world-wide dissemination of limit values and techniques used in the Community and will help the Member States in the efficient implementation of this Directive."

The Commission (Environment DG) established an information exchange forum (IEF) to assist the work under Article 16(2) and a number of technical working groups have been established under the umbrella of the IEF. Both IEF and the technical working groups include representation from Member States and industry as required in Article 16(2).

The aim of this series of documents is to reflect accurately the exchange of information which has taken place as required by Article 16(2) and to provide reference information for the permitting authority to take into account when determining permit conditions. By providing relevant information concerning best available techniques, these documents should act as valuable tools to drive environmental performance.

4. Information Sources

This document represents a summary of information collected from a number of sources, including in particular the expertise of the groups established to assist the Commission in its work, and verified by the Commission services. All contributions are gratefully acknowledged.

5. How to understand and use this document

The information provided in this document is intended to be used as an input to the determination of BAT in specific cases. When determining BAT and setting BAT based permit conditions, account should always be taken of the overall goal to achieve a high level of protection for the environment as a whole.
The rest of this section describes the type of information that is provided in each section of the document.

Chapter 1 provides general information on the industrial sector concerned. Chapter 2 provides information on the common industrial processes, abatement systems and general techniques that are used across the sector. Chapters 3 to 12 give the applied processes, current emission and consumption levels, techniques to consider in the determination of BAT, the techniques that are considered to be BAT and emerging techniques for the metal groups that represented by these chapters.

For each of the chapters 3 to 12, data is provided for the group of metals in that chapter according to the following sections: -

Section 1 describes the applied processes and techniques used for the particular group of metals.

Section 2 provides data and information concerning current emission and consumption levels reflecting the situation in existing installations at the time of writing.

Section 3 describes in more detail the emission reduction and other techniques that are considered to be most relevant for determining BAT and BAT based permit conditions. This information includes the consumption and emission levels considered achievable by using the technique, some idea of the costs and the cross-media issues associated with the technique, and the extent to which the technique is applicable to the range of installations requiring IPPC permits, for example new, existing, large or small installations. Techniques that are generally seen as obsolete are not included.

Section 4 presents the techniques and the emission and consumption levels that are considered to be compatible with BAT in a general sense. The purpose is thus to provide general indications regarding the emission and consumption levels that can be considered as an appropriate reference point to assist in the determination of BAT-based permit conditions or for the establishment of general binding rules under Article 9(8). It should be stressed, however, that this document does not propose emission limit values. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also needs to be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and levels presented in the BAT sections will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account by permitting authorities.

Since the best available techniques change over time, this document will be reviewed and updated as appropriate. All comments and suggestions should be made to the European IPPC Bureau at the Institute for Prospective Technological Studies at the following address:

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Best Available Technique Reference Document on the Non Ferrous Metals Production Process

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Glossary of Terms

Associated emissions to air are given as daily averages based on continuous monitoring and standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas without dilution of the gases with air. In cases where continuous monitoring is not practicable the value will be the average over the sampling period.

Emissions are quoted as the daily average unless stated to the contrary.

Values for the emission of total carbon to air does not include carbon monoxide (CO).

Associated emissions to water are based on a qualified random sample or a 24-hour composite sample.

ppm is parts per million. Concentrations of metals or other substances in water or wastewater are given as a total of soluble and insoluble material.

ppb is parts per billion

An afterburner is - A specifically designed additional combustion unit with burner system (not necessarily used all of the time) that provides time, temperature and turbulence with sufficient oxygen to oxidise organic compounds to carbon dioxide. Units can be designed to use the energy content of the raw gas to provide most of the heat input required and are more energy efficient.

BAT is Best Available Techniques according to Article 2 (11) of the Directive.

B(a)P is benzo(a)pyrene and is used as an indicator of PAH content.

Blast furnace is a vertical furnace using tuyeres to blast heated or cold air into the furnace burden to smelt the contents. (also known as a hearth shaft furnace, a water jacket furnace and a lead shaft furnace).

CWPB is a centre worked pre-baked anode cell.

DEVS4 - Leaching test according to German DIN 38 414.

Dioxins means polychlorinated di-benzo para dioxins and polychlorinated di-benzo para furans (PCDD and PCDF).

I-TEQ is the PCDD/F toxicity equivalent.

EU is the European Union

EFTA is the European Free Trade Area

EP means an Electrostatic Precipitator.

Fugitive emissions are un-captured or diffuse emissions.

GWP is global warming potential.

Irony material (Al, Cu) is material that includes discrete iron components.

"If necessary" - means if a pollutant is present and has an environmental impact.

Launder – A channel used to convey molten metal or slag.

Liquation is a refining technique that involves heating a molten metal to temperature where the solubility of impurities decreases so that they can be separated.

n.a. means not available.

n.d. means not detectable.

PFC means poly fluorinated hydrocarbon.

Recuperation is the recovery of heat. In this sector, it can be the use of process heat to pre-heat raw material, fuel or combustion air. Recuperative burners are designed to circulate hot gases within the burner system to achieve this.

PB is pre-baked anode.

SPL is spent pot lining.

Semis are semi finished products such as rod, wire, extrusions, ingots etc that are used as an input for the production of other finished products.

Shaft furnace is a vertical furnace used to melt metal.

SWPB is a side worked pre-baked anode cell.

Tapping is the opening of a furnace outlet to remove molten metal or slag.

VSS is vertical stud Soderberg anode cell.

Units

µg	Microgram	kg	Kilogram	Nm^3	Normal cubic metre (NTP) 273 K (0° C) 101.3 kPa (1 atmosphere)
€	Euro				
a	Year	kWh	Kilowatt hour	ng	Nanogram
cm	Centimetre	l	Litre	ppm	Parts per million
Cts (US)	Cents (United States)	lb	Pounds weight (avoirdupois)	Rpm	Revolutions (rotations) per minute
d	Day	m^3	Cubic metre	t	Tonne
DM	Deutsche Mark	mg	Milligram	Wt.-%	Weight-percent
g	Gram	mm	Millimetre	°C	Degree Celsius
GJ	Gigajoule	MJ	Megajoule	K	Absolute temperature - Kelvin
h	Hour	MWh	Megawatt hour		

Chemical Symbols

Ag	Silver	HCl	Hydrogen chloride	Pb	Lead
Al	Aluminium	HF	Hydrogen fluoride	PbO	Lead oxide
Al_2O_3	Aluminium oxide	Hf	Hafnium	S	Sulphur
As	Arsenic	Hg	Mercury	SO_2	Sulphur dioxide
Au	Gold	Ir	Iridium	SO_3	Sulphur trioxide
B	Boron	H_2SO_4	Sulphuric acid	Se	Selenium
Be	Beryllium	K	Potassium	Sn	Tin
Bi	Bismuth	K_2O	Potassium oxide	Sr	Strontium
C	Carbon	Li	Lithium	Sb	Antimony
Ca	Calcium	Mg	Magnesium	Si	Silicon
CaO	Calcium oxide, lime	MgO	Magnesium oxide, Magnesia	SiO_2	Silica, silicon oxide
Co	Cobalt	Mn	Manganese	Ta	Tantalum
Cd	Cadmium	MnO	Manganous oxide	Ti	Titanium
Cl	Chlorine	Mo	Molybdenum	Tl	Tellurium
Cr	Chromium	Na	Sodium	Re	Rhenium
Cs	Caesium	Nb	Niobium (columbium)	Rh	Rhodium
Cu	Copper	NO_2	Nitrogen dioxide	Ru	Ruthenium
F	Fluorine	Ni	Nickel	V	Vanadium
Fe	Iron	NO_x	Sum of all nitrogen oxides	W	Tungsten
FeO	Iron oxide	Os	Osmium	Zn	Zinc
Ga	Gallium	Pd	Palladium	ZnO	Zinc oxide
Ge	Germanium	Pt	Platinum	Zr	Zirconium

PMs are precious metals: - Ag, Au and PGMs

PGMs are platinum group metals: - Ir, Os, Pd, Pt, Rh, Ru

1 GENERAL INFORMATION

1.1 Processes covered in the scope of the work

There are many similarities between primary and secondary production of non-ferrous metals and in some cases it is impossible to distinguish between the techniques used. Secondary production of non-ferrous metals includes the production of metal from secondary raw materials (including scrap) and the re-melting and alloying processes. This BREF document covers the techniques for the production of both primary and secondary non-ferrous metals.

The production of carbon and graphite anodes (Section 6.8 of Annex I of the IPPC-Directive) is included because of the production of anodes at some aluminium smelters as an integral part of the production process.

The production of 42 non-ferrous metals and the production of ferro alloys were identified in countries who are obliged to implement IPPC. 10 groups of metals with similar production methods were identified. The study gathered data on the basis of these groups and this document is structured on this basis.

The Groups are:

- **Cu and its alloys, Sn and Be**
- **Al and its alloys**
- **Zn, Pb, Cd, Sb and Bi**
- **Precious Metals**
- **Mercury**
- **Refractory Metals e.g. Cr, W, V, Ta, Nb, Re, Mo.**
- **Ferro alloys e.g. FeCr, FeSi, FeMn, SiMn, FeTi, FeMo, FeV, FeB.**
- **Alkali Alkaline Earth Metals Na, K, Li, Sr, Ca, Mg and Ti**
- **Ni and Co**
- **Carbon and graphite electrodes**

The production of radioactive metals is excluded from the work. The production of components such as semi-conductors is also excluded.

Installations under 2.1 of Annex I, of the directive – sintering and roasting are covered by this document. Roasting and sintering operations are covered in two areas: - a) those which are part of the 2.5a) process to produce the metal, - b) where roasting and sintering are carried out independently, for example the roasting of molybdenum sulphide.

There are interfaces with the Chemicals Sector but there are specific issues and differences that must be taken into account when these processes are associated with metal production, or when metal compounds are produced as by-products of the production of metal. The following processes are included in the scope of this work: -

The production of sulphur products such as elemental sulphur, sulphur dioxide and sulphuric acid when associated with the production of a non-ferrous metal. In the case of sulphuric acid, it is produced from the sulphur dioxide in gases emitted from various stages of the process. The gas concentration, temperature and trace contaminants influence process design and the choice of catalyst.

- The production of zinc oxide from fume during the production of other metals,
- The production of nickel compounds from liquors produced during the production of a metal,

- The production of CaSi and Si which takes place in the same furnace as the production of ferro-silicon,

- The production of aluminium oxide from bauxite prior to the production of primary aluminium. This is a pre-treatment stage, which could be carried out at the mine or at the smelter. It is an integral part of the production of the metal when performed at the smelter and is included in the BREF.

Rolling, drawing and pressing of non-ferrous metals, when directly integrated with the production of metal would be covered by a permit and are therefore included by this document. Foundry processes are not included in this work and will be covered elsewhere.

1.2 Industry Overview

The European non-ferrous Metals Industry has an economic and strategic importance greater than employment, capital and turnover statistics indicate. For example high purity copper is essential for electricity generation and distribution and small amounts of nickel improve the corrosion resistance of steel.

Non-ferrous metals and their alloys therefore lie at the heart of modern life and many high technology developments, particularly in the computing, electronic, telecommunications and transport industries are dependent upon them.

1.2.1 Non-ferrous metals and alloys

All the non-ferrous metals considered in this document and listed in 1.1 above have there own individual properties and applications. In several cases however, e.g. copper and aluminium, alloys are used in more applications than pure metals because they can be designed to have specific strength, toughness, etc., to meet the requirements of particular applications.

Metals are inherently recyclable and can be recycled time after time without losing any of their properties. They thus make a significant contribution to sustainable development. It is normally not possible to distinguish between refined metal that has been produced from primary or secondary raw materials and that produced from secondary raw materials (i.e. scrap etc.).

1.2.2 Scope of the industry

The output of the industry is derived from a variety of primary and secondary raw materials. Primary raw materials are derived from ores that are mined and then further treated before they are metallurgically processed to produce crude metal. The treatment of ores is carried out close to the mines as, increasingly, is metal production. Secondary raw materials are indigenous scrap and residues.

In Europe, ore deposits containing metals in viable concentrations have been progressively depleted and few indigenous sources remain. Most concentrates are thus imported into Europe from a variety of sources worldwide.

The output of the industry is either refined metal or what is known as semi manufactures, i.e. metal and metal alloy cast ingots or wrought shapes, extruded shapes, foil, strip, rod etc.

For this BREF Document the non-ferrous foundries that produce cast metal products have not been included but are covered by the Smitheries and Foundries BREF Document. The collection, sorting and supply of secondary raw materials for the industry lies within the metals recycling industry, which again is not considered in this BREF.

Although an apparent contradiction in terms, the production of ferro-alloys, which are mainly used as master alloys in the iron and steel industry, is considered part of the non-ferrous metals industry. Their alloying elements, i.e. refractory metals, chromium, silicon, manganese and nickel are all non-ferrous metals.

The precious metals sector is also considered part of the non-ferrous metals industry for the purposes of this document.

1.2.3 Structure of the industry

The structure of the industry varies metal by metal. There are no companies that produce all, or even a majority of, non-ferrous metals although there are a few pan European companies producing several metals, e.g. copper, lead, zinc, cadmium etc.

The size of the companies producing metals and metal alloys in Europe varies from a few employing more than 5000 people and a large number having between 50 and 200 employees.

Ownership varies between pan European and national metals groups, industrial holdings groups, stand-alone public companies and private companies.

1.1.4 Economics of the industry

The key statistics of the European Non-Ferrous Metals Industry as defined for the purpose of this document are:

Output	18 - 20 million tonnes
Sales	40 - 45 billion €
Employees	more than 200000

Many refined non-ferrous metals are international commodities. The major metals (aluminium, copper, lead, nickel, tin and zinc) are traded on one of two futures markets, the London Metal Exchange and Comex in New York. The collectively named ‘minor’ metals have no central market place; price levels are imposed by either producers or by merchants trading in the free markets. In most applications non-ferrous metals are in competition with other materials, notably ceramics, plastics and other ferrous and non-ferrous metals.

The profitability of each metal or metals group, and thus the economic viability of the industry varies, both absolutely and on a short term basis, depending upon the current metal price and a wide range of other economic factors.

The general economic rule applies however, i.e. that the nearer a material or product approaches global market conditions and international commodity status the lower is the return on the capital invested.

There are thus severe constraints on the availability of capital for non-productive expenditure on environmental protection improvements. These are generally a part of overall process development and improvement. Investments in environmental and process improvements in general need to be competitive in a global environment as the European industry is in competition with similar plants in other developed and developing countries.

1.2.5 Environmental performance

There has been a steady, and in some cases a very significant, improvement in the environmental performance and energy efficiency of the industry over the last twenty five years since the adoption of Directive 84/360/EEC ‘On the Control of Pollution from Industrial Plants’. The requirement to use Best Available Techniques to minimise pollution is well understood by the industry in most Member States.

The recycling performance of the industry is unmatched by any other industry.

1.3 Copper and its' Alloys

1.3.1 General

Copper has been used for many centuries; it has a very high thermal and electrical conductivity and is relatively corrosion resistant. Used copper can be recycled without loss of quality. These properties mean that copper is used in diverse sectors such as electrical engineering, automobiles, construction, plumbing, machinery, shipbuilding, aircraft, and precision instruments. Copper is frequently alloyed with Zn, Sn, Ni, Al and other metals to make a range of brasses and bronzes [tm 36, Panorama 1997].

Copper production is based on grade A copper cathodes i.e. 99.95% Cu. The grade A designation comes from the London Metal Exchange vocabulary for cathodes and refers to a British Standard. This has been replaced recently by a European CEN Standard - EN 1978, where the quality is designated as Cu CATH1 or in the new European alphanumeric system CR001A.

The maximum tolerable impurities in% are as follows: -

- Ag 0.0025 - As 0.0005 - Bi 0.00020 - Fe 0.0010 - Pb 0.0005 - S 0.0015 - Sb 0.0004 - Se 0.00020
- Te 0.00020 with As+Cd+Cr+Mn+P+Sb 0.0015
- Bi+Se+Te 0.0003
- Se+Te 0.0003
- Ag+As+Bi+Cd+Co+Cr+Fe+Mn+Ni+P+Pb+S+Sb+Se+Si+Sn+Te+Zn 0.0065

1.3.2 Sources of materials

Refined copper is produced from primary and secondary raw materials by a relatively small number of copper refineries; their product is copper cathode. This is melted, alloyed and further processed to produce rods, profiles, wires, sheets, strips, tubes, etc. This step may be integrated with the refinery but is frequently carried out at another site.

About 55% of the feed supplies to the copper refineries are purchased on the international market in the form of copper concentrates, blister, anodes or scrap. The remaining 45% come from domestic copper concentrates as well as domestic copper bearing residue or scrap.

The EU possesses few primary copper resources, but its copper metallurgical activities are highly significant. Sizeable copper mine production can only be found in Portugal (start-up of mining at Neves Corvo in 1989, 106500 tonnes of copper in 1997) and in Sweden (86600 tonnes). With about 239000 tonnes of copper extracted from domestic ores in 1997, the EU accounts for around 2% of the total worldwide copper mine output.

Refining and semis manufacturing capabilities have developed in line with the requirements of its large consumption, using imported primary raw materials and domestic as well as imported scrap. Access to primary supplies has become increasingly difficult over the past few years, as copper mining countries have developed their own refining facilities close to their mines, thereby reducing raw materials availability on the international market.

Recycling constitutes an important component of the raw material supplies to the copper refining and manufacturing facilities. Altogether, secondary raw materials account for about 45% of the use of copper and it's alloys in Europe, either by refineries as the whole or part of their feed or by the semis manufacturers directly.

The quality of secondary raw materials varies greatly and many sources of these materials are not suitable for direct use by the Semis manufacturers. The scrap industry is relied upon to provide graded material of adequate cleanliness for the Industry and although there are agreed specifications for scrap, wide variations are encountered. Additional treatment or abatement systems may be needed.

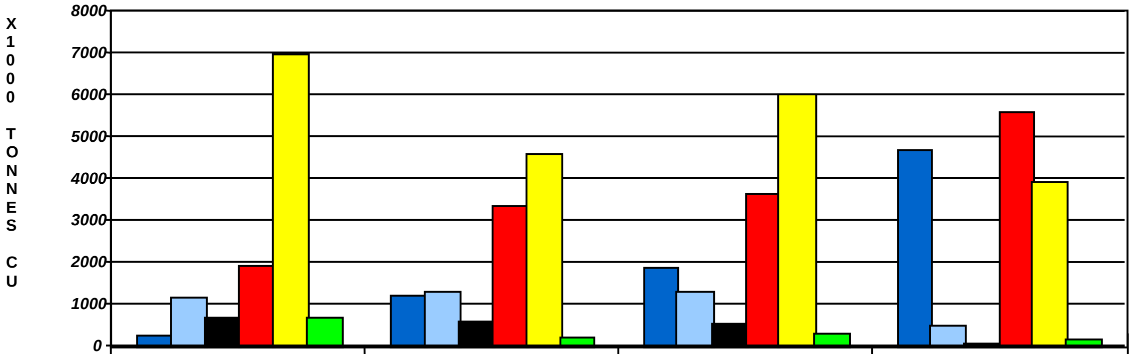
1.3.3 Production and consumption

Annual production of copper cathode at the time of writing is 959000 tonnes from primary sources and 896000 tonnes from secondary sources. Beryllium is not produced in EU and is not thought to be present in sufficient amounts in scrap to present any environmental issues.

Three of the secondary smelters and nearly all of the primary smelters have increased their production output. This significant increase in production capacity has been made simultaneously with environmental improvements. Computer scrap and printed circuit boards are becoming more common secondary sources even though the copper content is low. The scrap is pre-treated by both the scrap industry and by some smelters. This provides an outlet for these materials.

Recycling is at a high level as copper can be reprocessed without loss of its intrinsic properties and many secondary materials are available. EU copper refining activity has been able to grow primarily by securing raw materials on the international market and making use of copper or brass scrap and residues generated by consumers and processors.

EU copper semis manufacturers have an output that is three times that of EU refinery output. They use the international market to secure adequate volumes of supplies of copper and brass, together with alloying materials (mainly zinc, tin and nickel). This part of the industry is a net exporter of about 500000 tonnes per year.



	MINE	SMELTER	REFINERY	SEMIS
🟦 EU	239	1168	1854	4700
🟦 NON EU EUROPE	1135	1310	1271	500
⬛ AFRICA	642	562	531	20
🟥 ASIA	1884	3330	3630	5600
🟨 AMERICA	6952	4586	6000	3900
🟩 OCEANIA	672	208	271	150

Figure 1.1: Worldwide copper production in 1997

Country	Mine production	Primary cathode(Anode)	Secondary cathode (anode)	Semis Production
Austria			77	58
Belgium		203 (35)	183 (126)	392
Denmark				
Finland	9	116 (171)		120
France		6	29	684
Germany		296	378	1406
Greece				81
Ireland				
Italy		6	80	990
Luxembourg				
Netherlands				
Portugal	108			
Spain	37	229 (+61)	63 (+28)	268
Sweden	87	95	34	206
U K		9	58	483
Iceland				
Norway	7*	33		
Switzerland				70

Notes:

* Current ore production will cease in 2000.

Table 1.1: E U (and EAA) Production of copper and it's alloys in 000's tonnes in 1997
Ore production in Europe accounts for ~30% of primary feed

1.3.4 Production sites

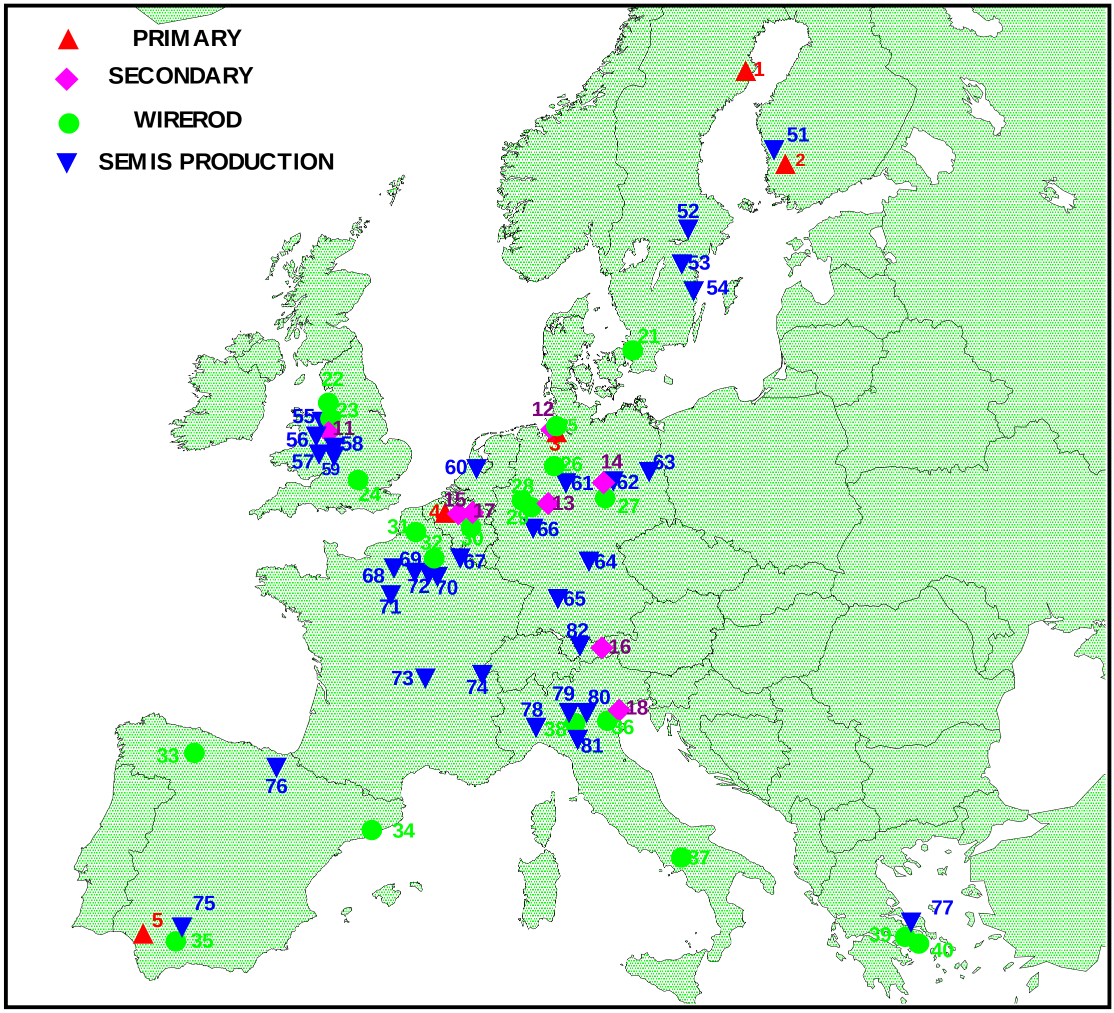
There are ten major refineries in the EU. Five use primary and secondary raw materials and the others use secondary raw materials only. It is estimated that the copper refining industry employed more than 7500 people in 1997. Three companies have capacities of over 250000 tonnes refined copper cathode per year capacity: Atlantic Copper (E), Union Minière (B) and Norddeutsche Affinerie (D). Four others, MKM Hettstedt (D), Hüttenwerke Kayser (D), Boliden (SW) and Outokumpu (FIN), each produce more than 100000 tonnes per year. Production capacity at the other facilities in Italy, Spain, Austria, the United Kingdom and Belgium range between 35000 and 100000 tonnes of copper cathode per year.

There are many more companies in the Semis manufacturing industry. They use refined copper and high quality secondary raw materials as feed materials. About 100 companies are involved throughout the EU, employing some 40000 people. The industry can suffer from over-capacity and is vulnerable to cyclical movements in demand. EU copper demand follows the slow growth pattern of a mature market.

The electrical wire-rod sector accounts for around half of semis production. Some 20 companies, employing around 3000 people, are involved in this sector. A significant part of this activity is attached to the cable sector as an integrated upstream input source (Alcatel, Pirelli, BICC etc.) whilst another part is attached to the refinery sector as integrated downstream output (Deutsche Giessdraht, Norddeutsche Affinerie, Union Minière, Atlantic Copper etc.).

There are many more companies in the other copper semis manufacturing industry, producing copper and copper alloys rods, bars, wires, sections, tubes, plates, sheet and strip: about 80 companies are involved throughout the EU, employing some 35000 people. The industry is however dominated by three large groups: KME-Europa Metal (D), with major manufacturing activities in France, Germany, Italy and Spain; Outokumpu (FIN) in Finland, Sweden, Netherlands and Spain; and Wieland Werke (D) in Germany and UK. Other major independent companies include Boliden (S), with plants in Sweden, Netherlands, Belgium and the UK, Carlo Gnutti (I), and IMI (UK).

There has been considerable rationalisation of and subsequent investment in the copper industry in Europe over the past two decades. This has been in response to the creation of the single market in the EU and economic pressures, such as increased energy costs, the need for substantial investment in pollution abatement and frequent changes in exchange rates.



PRIMARY
1 Boliden, Rönnskär
2 Outokumpu, Harjavalta
3 Norddeutsche Affinerie, Hamburg
4 Union Miniere, Olen
5 Atlantic Copper, Huelva

SECONDARY
11 IMI Refiners, Walsall
12 Norddeutsche Affinerie, Hamburg
13 Hüttenwerke Kayser, Lünen
14 MKM, Hettstedt
15 Metallo-Chimique, Beerse
16 Montanwerke Brixlegg
17 Union Miniere, Hoboken
18 Enirisorse, Porto Marghera

WIREROD
21 Electrokoppar, Helsingborg
22 BICC, Prescott
23 RODCO, Skelmersdale
24 BICC, Enfield
25 Norddeutsche Affinerie, Hamburg
26 Lacroix & Kress, Bramsche
27 MKM, Mansfeld
28 Deutsche Giessdraht, Emmerich
29 Kemper, Duisburg
30 Union Miniere, Olen
31 Alcatel, Lens
32 Alcatel, Chauny
33 SIA, Santa Barbara
34 Lacambra, Barcelona
35 Metalcable (Atl.Copper), Cordoba
36 Cavi Rivest, Padova
37 Metalrame, Avelino
38 Colata Continua, Pizzighetone
39 Halcor, Inofita
40 Fulgor, Athens

SEMIS (with foundry)
51 Outokumpu, Pori
52 Outokumpu, Vasteras
53 Outokumpu, Finspang
54 Boliden, Gusum
55 IMI Copper Tubes, Kirkby
56 Boliden MKM, Walsall
57 Wednesbury, Bilston
58 Delta Extr., W.Bromwich
59 B. Mason, Birmingham
60 HME, Drunen
61 KME, Osnabruck
62 MKM, Hettstedt
63 KME, Berlin
64 Diehl, Rothenbach
65 Wieland Werke, Ulm
66 Sundwiger, Hemel
67 Trefimetaux, Givet
68 Trefimetaux, Boisthorel
69 Trefimetaux, Serifontaine
70 Griset, Villers Saint Paul
71 Lego, La Ferté Bernard
72 CLAL-MSX, Bornel
73 Trefimetaux, Pt deCheruy
74 Bonmartin, Domene
75 Locsa, Cordoba
76 Outokumpu, Zaratamo
77 Halcor, Athens
78 Europa Metalli, Serravalle
79 Carlo Gnutti, Chiari
80 Eredi Gnutti, Brescia
81 Europa Metalli, Fornaci di Barga
82 Buntmetall, Amstetten

Figure 1.2: European Production Sites

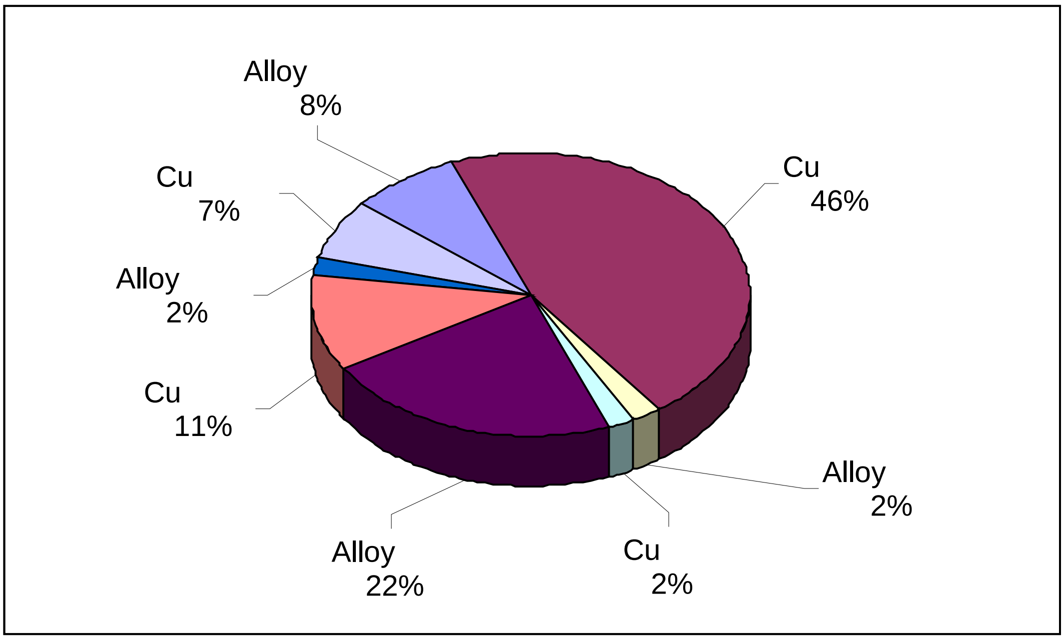


Figure 1.3: Copper Semis Production 1995. Total for 1995 = 4700000 tonnes

1.3.5 Environmental issues

Historically the major environmental problem associated with the production of copper from primary sources was the emission of sulphur dioxide to air from the roasting and smelting of sulphide concentrates. This problem has been effectively solved by the EU smelters who now achieve on average 98.9% fixation of the sulphur and produce sulphuric acid and liquid sulphur dioxide.

The main environmental issues associated with the production of secondary copper are also related to the off gases from the various furnaces in use. These gases are cleaned in fabric filters and so can reduce the emissions of dust and metal compounds such as lead. There is also the potential for the formation of dioxins due to the presence of small amounts of chlorine in the secondary raw materials and the destruction of dioxins is an issue that is being pursued.

Fugitive or uncaptured emissions is also an issue that becoming increasingly important for both primary and secondary production. Careful plant design and process operation is needed to capture process gases.

The control of emissions to air and discharges to water from the production of copper wire-rod and copper and copper alloy semis is well developed. The control of the emissions of carbon monoxide from shaft furnaces especially those operating under reducing conditions is achieved by burner optimisation.

Recycling constitutes an important component of the raw material supplies of the copper refining and manufacturing facilities. Copper can be recovered from the major part of its applications and returned to the production process without loss of quality in recycling. Having very limited access to domestic primary sources of copper, the EU industry has traditionally given much attention to so-called "surface mines", relying to a large extent on scrap feed to reduce the large deficit of its copper raw materials trade balance.
Almost 100% of new or process copper scrap is recycled and according to some studies it has been estimated that 95% of old copper scrap that becomes available is also recycled.

Overall, secondary raw materials account for the production of about 45% of EU copper but in some cases, such as brass rods, the product is made entirely from recycled copper and brass, with only a small input of primary zinc.

The EU copper industry has developed advanced technologies and made considerable investments so as to be able to process a wide range of copper scrap, including complex, low-grade residues, and to comply at the same time with increasingly stringent environmental constraints.

The ability of the industry to increase this high recycling rate depends on a number of complex factors.

1.4 Aluminium

1.4.1 General

Aluminium [tm 36, Panorama 1997] is a material with a large range of applications, in the transportation, construction and packaging industries, the electricity sector, in all high voltage electricity distribution systems, household appliances, and the mechanical and agricultural sectors. It is light, has good electrical conductivity and forms a surface oxide layer when exposed to air that prevents further corrosion. Aluminium is highly reactive particularly in the form of powder and is used in alumino-thermic reactions to produce a variety of other metals.

The aluminium industry is the youngest and largest of the non-ferrous metal industries, aluminium smelting only began about a century ago. The EU aluminium industry directly represents a workforce of about 200000 people and its annual turnover is in the order of 25 billion €. Total production of un-wrought metal amounted to 3.9 million tonnes in 1997. About 43% of this output is accounted for by the processing of recycled scrap, which has been constantly increasing.

1.4.2 Sources of materials

Primary aluminium is produced from bauxite that is converted into alumina. 100 tonnes of bauxite produces 40 - 50 tonnes of alumina (aluminium oxide) which then produces 20 - 25 tonnes of aluminium. Most of the bauxite is mined outside Europe but there are several alumina production facilities within Europe.

The secondary industry is dependent on sources of scrap. Scrap can be termed “New Scrap” that is generated during the production and fabrication of wrought and cast products or “Old Scrap” that is recovered from articles at the end of their useful life. The recycling rate of “New Scrap is 100% of the amount produced. The supply of raw materials to the EU primary and secondary industry is largely met by domestic alumina production and scrap recycling. The total metal output however, falls short of the processing industry needs and at present it meets only 55% of the EU demand.

1.4.3 Production and consumption

The European aluminium industry features mining and alumina production, primary and secondary smelting and metal processing into semi-finished products (e.g. bars, profiles, wires, sheets, foils, tubes, pipes) or speciality products (e.g. powders, special alloys).

Area	Production	Consumption
Europe	3216	5603
USA	3603	5390
Russia	2907	509
Canada	2327	642
China	1776	2013
Australia	1495	362
Brazil	1189	479
Venezuela	643	193

Table 1.2: Primary aluminium production by country 1997 (thousand tonnes)

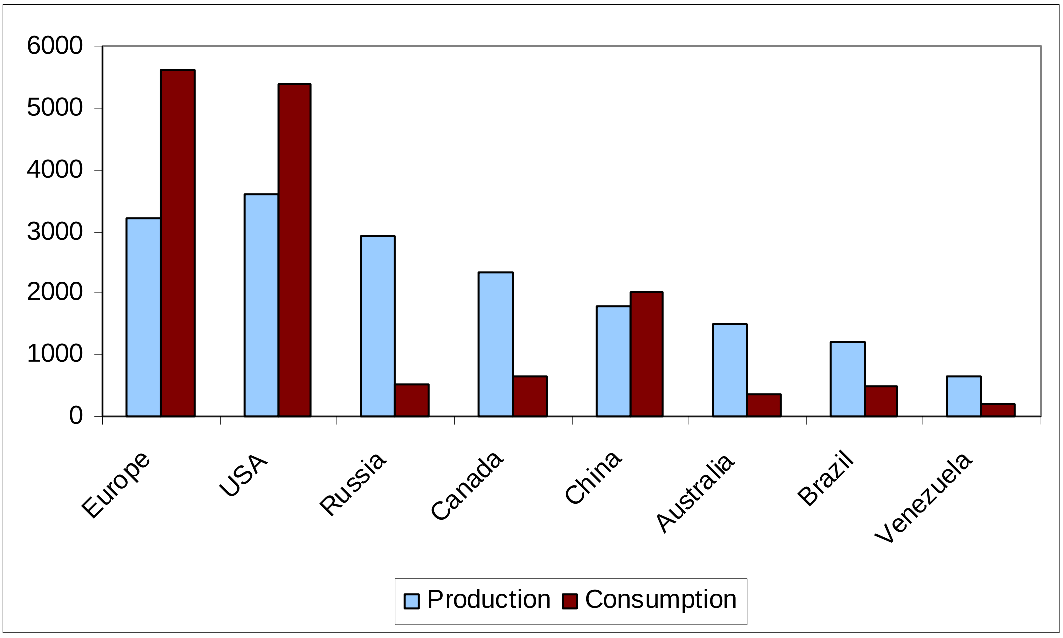


Figure 1.4: Primary aluminium production by country 1997 (thousand tonnes)

Many of these activities are integrated, but a number of EU manufacturers focus their activity on one particular segment only, such as recycling and secondary smelting or semis fabrication.

The EU accounted for 10% of the total world production in 1997. Production of aluminium from secondary raw materials in the EU is one of the highest in the world at about 1.7 million tonnes in 1997. It represented 23% of the Western world output from recycled materials.

1.4.4 Production sites

At the beginning of 1998, twenty-two primary aluminium smelters were operating in the EU, and a further 8 in the EEA. The number of producer companies is, in fact, much smaller: the major ones are Aluminium Pechiney (F), VAW aluminium (D), Alcoa Spain (E), Alcoa Italy (I), Hoogovens (NL), British Alcan (UK), Hydro (N) and Alusuisse (CH). Some of these companies operate plants in different European countries or have subsidiaries or branches in other parts of the world, or are part of international corporations.

The number of companies involved in secondary aluminium production is very much larger. There are about 200 companies whose annual production of secondary aluminium is more than 1000 tonnes per year [tm 116, Alfed 1998]. There is a good integration of the rolling activity with the production processes but the extrusion industry is much less integrated, with about 200 production sites scattered on the EU territory.

Country	**Bauxite Production** in 1000's of tonnes	**Alumina Production** in 1000's of tonnes	**Primary Aluminium** in 1000's of tonnes	**Secondary Aluminium** in 1000's of tonnes	**Semis Production** in 1000's of tonnes
Austria				98	189
Belgium					353
Denmark				14	18
Finland				33	35
France		600	399	233	741
Germany		750	572	433	1797
Greece	2211	640	133	10	213
Ireland		1250			
Italy		880	188	443	862
Luxembourg					
Netherlands			232	150	200
Portugal				3	
Spain		1110	360	154	330
Sweden			98	26	131
U K		120	248	257	507
Iceland			123		
Norway			919	59	250
Switzerland			27	6	131
Europe Total	2211	5350	3216	1803	5757

Table 1.3: European aluminium production in 1997

1.4.5 Environmental issues

The main environmental issues for primary aluminium are the production of poly fluorinated hydrocarbons and fluorides during electrolysis, the production of solid waste from the cells and the production of solid waste during the production of alumina. Similarly for the production of secondary aluminium there are potential emissions of dust and dioxins from poorly operated furnaces and poor combustion and the production of solid wastes (salt slag, spent furnace linings, dross and filter dust). The industry has made progress to reduce these emissions. They have been reduced over the last fifteen years by a factor of between four to ten, depending on the type of emission and the process used.

The main cost of producing primary aluminium is electricity and production tends to concentrate where low cost electricity is available, this influences the distribution of sites. The European aluminium industry has made considerable efforts to reduce its electricity consumption, bringing it down from 17 kWh per kg produced in 1980 to 15 kWh per kg in 1998. The production and refining of secondary aluminium is much less energy demanding and consumes less than 5% of the energy needed to produce primary aluminium.

There are many initiatives involved in improving the return of scrap aluminium and the industry is an active player in this area. The recycling of used beverage cans (UBCs) is an example of this. Collected material is recycled in a closed loop to produce more beverage cans to the same alloy specification. Much attention is paid by the secondary industry to producing the correct alloy composition and pre-sorting of scrap types is important. An example of this is the segregation of extrusion scrap to preserve the particular alloy.

1.5 Zinc, Lead and Cadmium

1.5.1 Zinc

1.5.1.1 General

Zinc [tm 36, Panorama 1997; tm 120, TU Aachen 1998] has the third highest usage of non-ferrous metal, behind aluminium and copper. It has a relatively low melting point and is used in the production of a number of alloys such as brass. It can easily applied to the surface of other metals such as steel (galvanising) and when it is used as a metal coating, zinc corrodes preferentially as a sacrificial coating. Zinc is also used in the pharmaceutical, nutrient, construction, battery and chemical industries.

Commercial use of zinc	World-wide 1975 [%]	World-wide 1984 [%]	World-wide 2005 [%]	Europe 1995 [%]
Galvanising	38.0	48.5	54.8	43
Brass	19.8	17.6	16.6	23
Die casting	18.3	14.3	10.5	13
Semi-finished products	8.5	7.3	6.4	12
Chemicals	12.7	9.6	8.0	8
Others	2.8	2.7	3.7	1

Table 1.4: World and European uses of zinc.

Zinc is supplied to the market in various qualities, the highest quality is special high grade (SHG) or Z1 which contains 99.995% zinc while the lowest quality good ordinary brand (GOB) or Z5 is about 98% pure. Extrusion products such as bars, rods and wires (mainly brass); rolling products such as sheets and strips; casting alloys; and powders and chemical compounds, such as oxides are produced.

Grade Classification	Colour code	Nominal Zinc content	1 Pb max.	2 Cd* max.	3 Fe max.	4 Sn max.	5 Cu max.	6 Al max.	Total of 1 to 6 max.
Z1	white	99.995	0.003	0.003	0.002	0.001	0.001	0.001	0.005
Z2	yellow	99.99	0.005	0.005	0.003	0.001	0.002	-	0.01
Z3	green	99.95	0.03	0.01	0.02	0.001	0.002	-	0.05
Z4	blue	99.5	0.45	0.01	0.05	-	-	-	0.5
Z5	black	98.5	1.4	0.01	0.05	-	-	-	1.5
Notes: *For a period of five years after the date of ratification of this standard the max. Cd contents of grades Z3, Z4 and Z5 shall be 0.020, 0.050 and 0.050 respectively									

Table 1.5: Primary zinc grades

Grade	Nominal Zinc content	1 Pb max.	2 Cd* max.	3 Fe max.	4 Sn max.	5 Cu max.	6 Al max.	Total of 1 to 6 max.	Remarks
ZS1	98.5	1.4	0.05	0.05	*)	-	-	1.5 **)	Grades made mainly by recycling of scrap and used products
ZS2	98	1.6	0.07	0.12	*)	-	-	2.0 **)	
Z3S	97.75	1.7	0.09	0.17	-	-	-	2.25	
ZSA	98.5	1.3	0.02	0.05	-	-	-	1.5	Grade made mainly from Zn containing residues, ashes

Notes:
*) Sn max 0.3% for brass making, 0.7% for galvanising. When present at these levels the actual Zn content may be lower than the nominal Zn content.
**) Excluding Sn when present at the levels given in *)

Table 1.6: Secondary zinc grades

End-uses include a wide range of applications, the most important being steel protection against rust for the automobile, appliance and building industries. Zinc alloys (e.g. brass, bronze, die casting alloys) and zinc semis are respectively the second and third major consumption areas with applications also in the building, appliance and car industries.

1.5.1.2 Sources of materials

The metal is produced from a range of zinc concentrates by pyrometallurgical or hydrometallurgical processes. Some concentrates contain high proportions of lead and these metals are also recovered. Zinc is also associated with cadmium and the concentrates are a source of this metal.

EU concentrates used to meet more than 45% of the EU refinery requirements 10 years ago but they now account for less than 25% of these. The deficit is filled in by increased imports, as mine production capacity is currently increasing in North America, Australia and some South American countries.

Secondary raw materials such as galvanising residues (ashes, skimmings, sludges etc), flue dust from steel plants and brass processing and die-casting scrap are also sources of zinc. Metal production from secondary sources accounted for more than 8% of the total EU refined zinc output in 1994. The recycling of zinc and zinc containing products is a key issue for the industry.

1.5.1.3 Production and consumption

The EU mine output is essentially accounted for by Ireland and Spain and was 383000 tonnes of zinc concentrates in 1994. This was a fall from 397000 tonnes in 1993, as a result of the exhaustion of reserves and the lower ore grades at some mining operations. Metal production stepped back below the 1.8 million tonnes mark which it had overstepped in 1992, while consumption of refined zinc increased from 1640000 tonnes to 1770000 tonnes, accounting for 30% of the demand for zinc in the market economy countries.

Country	**Production in 1992** (in 1000's of tonnes)	**Production in 1993** (in 1000's of tonnes)	**Production in 1994** (in 1000's of tonnes)
Canada	1325	1004	1008
Australia	1014	1007	928
Peru	626	668	682
USA	551	513	601
European Union	500	411	383

Table 1.7: Production of zinc concentrates
[tm 36, Panorama 1997]

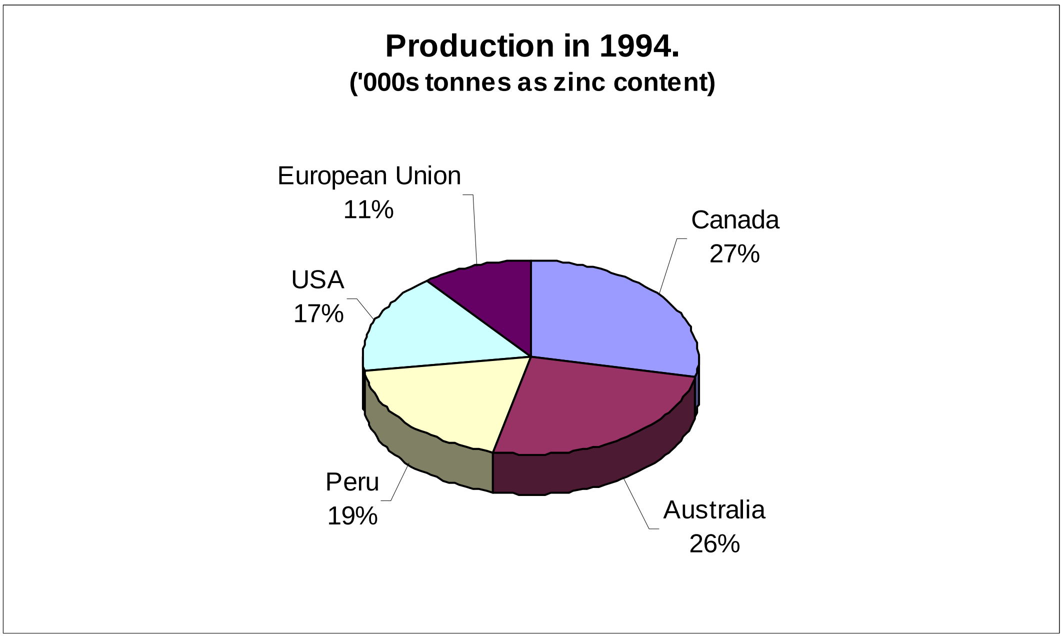


Figure 1.5: World production of zinc from concentrates in 1994

The EU stands as the world leader in zinc production, far ahead of Canada and Japan, which rank second and third respectively. In 1994, the EU output was recorded at 1749000 tonnes metal, accounting for nearly 33% of the market economy countries' total of 5376000 tonnes. The EU is also the major consumer area for zinc among the market economy countries. The 1770000 tonnes zinc consumed in 1994 was 49% above the second largest consumer market, (USA) and 145% above the third (Japan).

Country	Production in 1992 (in 1000's of tonnes)	Production in 1993 (in 1000's of tonnes)	Production in 1994 (in 1000's of tonnes)
European Union	1844	1819	1749
Canada	672	662	693
Japan	729	696	666
USA	400	382	356
Australia	333	317	318
CIS		431	390

Table 1.8: Production of refined zinc

1.5.1.4 Production sites

Zinc is produced by roast-leach-electro-winning processes and by the Imperial Smelting Furnace – distillation process. The following tables show the location and capacities of the sites in EU.

Country	Company	Location	Process	Capacity [t/a]
Belgium	Union Minière	Balen-Wezel	E	200000
Germany	Ruhr-Zink MIM Hüttenwerke Duisburg Metaleurop Weser Zink	Datteln Duisburg-Wanheim Nordenham	E ISF-RT E	96000 100000 130000
Spain	Asturiana de Zinc Española del Zinc	Sun Juan de Nieva Cartagena	E E	320000 60000
France	Union Minière France Metaleurop	Auby Noyelles Godault	E ISF-RT	220000 100000
Finland	Outokumpu Zinc Oy	Kokkola	E	175000
Italy	Enirisorse Pertusola Sud	Porte Vesme (Sardegna) Porte Vesme (Sardegna) Crotone (Calabria)	ISF-RT E E	75000 100000 80000
Netherlands	Budelco (Pasminco)	Budel-Dorplein	E	210000
Norway	Norzink		E	140000
UK	Britannia Zinc (MIM Holdings)	Avonmouth	ISF-RT	105000

Notes:
E = electrolytic plant;
ISF= imperial smelting furnace;
RT = fire refining. Source: industry statistics

Table 1.9: Top European producers in terms of annual capacity, 1994

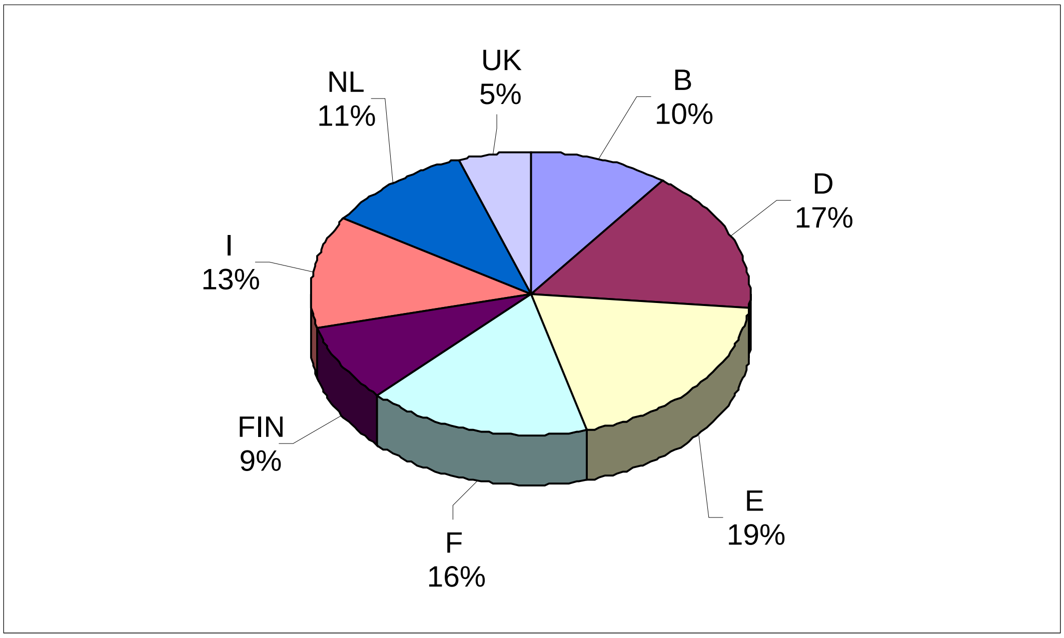


Figure 1.6: Production of zinc metal in EU (1994)

1.5.1.5 Environmental issues

Historically the major environmental problem associated with the production of zinc from primary sources was the emission of sulphur dioxide to air from the roasting and smelting of sulphide concentrates. This problem has been effectively solved by the EU smelters who now achieve a high fixation of the sulphur and produce sulphuric acid and liquid sulphur dioxide.

The leaching of calcine and other material produces liquor that contains iron. The removal of iron results in the production of significant quantities of solid waste that contains a variety of metals. The disposal of this waste requires a very high standard of containment and monitoring.

Fugitive emissions from roasting and calcining are also very important and need to be considered for all of the process stages. The fugitive emissions of acid mists from the electro-winning of zinc is a particular example of this.

Zinc and zinc containing products can be recycled largely. Estimates based on historical consumption and product life cycles indicate that a recovery rate of 80% of recoverable zinc has been reached. The recycling system of zinc is far advanced, not only as zinc metal but also in several different forms.

1.5.2 Lead

1.5.2.1 General

Lead [tm 36, Panorama 1997] is the most abundant heavy metal in the earth's crust and has been used for many centuries. It is found in pure sulphide ores or nowadays more in mixed ores where it is associated with zinc and small amounts of silver and copper. Lead is a soft metal, it has a low melting point and is resistant to corrosion. These properties give it great functional value, both in its pure form and in as alloys or compounds.
Lead is classified in terms of the composition of the product, the following table shows the chemical composition of lead according to the new European Standard.

Grade Designation	Pb min.	1 Bi max.	2 Ag max.	3 Cu max.	4 Zn Max.	5 Ni max.	6 Cd max.	7 Sb max.	8 Sn max.	9 As max.	Total of 1 to 9 max.
PB 990	99.990	0.010	0.0015	0.0005	0.0002	0.0002	0.0002	0.0005	0.0005	0.0005	0.010
PB 985	99.985	0.015	0.0025	0.0010	0.0002	0.0005	0.0002	0.0005	0.0005	0.0005	0.015
PB 970	99.970	0.030	0.0050	0.0030	0.0005	0.0010	0.0010	0.0010	0.0010	0.0010	0.030
PB 940	99.940	0.060	0.0080	0.0050	0.0005	0.0020	0.0020	0.0010	0.0010	0.0010	0.060

Notes:
The German standard DIN 1719 is the basis for the new European Standard EN 12659,

Table 1.10: Lead grades

There have been major changes in the pattern of use of lead. The battery industry creates up to 70% of the demand and is fairly stable but other uses for lead which include pigments and compounds, protection against radiation, rolled and extruded products for the building industry, cable sheathing, shots and gasoline additives are in decline.

Commercial use	1973 %	1983 %	1993 %	1994 %
Batteries	38	48	56	59
Chemicals	24	27	22	22
Semi-finished products. and casting	17	17	16	16
Cables	15	5	2.5	2.0
Alloys	2	3	1.1	0.8
Others	4	-	1.6	0.2

Table 1.11: Uses of lead Worldwide

1.5.2.2 Sources of materials

Refined lead is derived from primary material in the form of lead ores and concentrates, and secondary material in the form of scrap and residue. Primary production requires the smelting of lead-bearing ores to produce lead bullion that is then refined. The economics of primary lead ore production is linked to the silver and zinc contents of the ore bodies. Lead metal production requires the sulphur content of the ores to be treated to produce sulphuric acid. Most primary lead smelters have a complex refining process associated with them and associated processes to recover the silver content as an Ag-Au alloy. Primary refining is therefore linked to the economics of mining lead-zinc ore-bodies. The zinc and silver content of the ores are the principal profit makers.

The EU possesses few lead mine resources but lead production is a large and important industry. During the last 10 years, EU consumption and production have experienced only modest growth, resulting in a decrease in the EU's share in world markets.

The secondary refining industry now supplies more than 50% of lead consumed. Lead acid accumulators in cars are the main source of scrap for secondary refining. The industry makes positive steps to encourage recycling of these batteries, this proportion is increasing as the world car population increases and the return rate of old batteries increases. Secondary production may also require refining facilities if the secondary raw materials contain unwanted compounds.

1.5.2.3 Production and consumption

EU lead production is high, ranking first among the market economy countries with 1398000 tonnes in 1994, of which 52% was from secondary feed materials. The industry is responding to ecological concern by recovering ever increasing amounts of lead so that primary production is steadily declining.

The EU is the largest lead producing area worldwide, ahead of the United States. In 1994, these two regions together accounted for 59% of the market economy countries' total refined production of 4.5 million tonnes. The United Kingdom, Germany, France and Italy are the major producers and, on average, 49% of their output is based on secondary feed supplies. The EU average of 52% is in this respect significantly lower than the US average of 72%, which is the highest world-wide, but it remains well above that in any other market economy country.

The EU ranks second to the United States in terms of consumption, accounting for 28% of the market economy countries lead consumption in 1994, whilst the US share is close to 30%. The four major producing member states of the EU are also the major consuming market.

1.5.2.4 Production sites

Within the EU there are 7 primary smelters/refiners whose production capacity ranges in size from 40000 tonnes per year to 245000 tonnes per year. The primary refineries are mostly multinational, and are spread throughout the United Kingdom (Britannia refined metals), France (Metaleurop), Germany (Ecobat, Metaleurop), Belgium (Union Minière) and Italy (Enirisorse). All plants smelt lead or lead/zinc concentrates before refining lead bullion and also refine crude bullion from other sources to recover precious metals. Britannia refined metals also refines crude lead bullion imported from its parent company MIM in Australia. With the exception of Union Minière, all of these primary refiners are involved in secondary recycling/refining as well.

The secondary industry is characterised by a large number of smaller refineries, many of which are independent. There are approximately thirty secondary smelters/refiners in the EU producing from 5000 to 65000 tonnes per year. They recycle and refine scrap generated in their local area. The number of these refineries is decreasing as the large multinational companies, and the major battery manufacturing groups as well, acquire the smaller secondary facilities or set up their own new recycling operations.

Country	Lead blast furnace annual capacity * t/a	Direct smelting annual capacity * t/a	Secondary rotary furnaces annual capacity t/a	Total lead refining capacity t/a
Austria			32000	32000
Belgium	115000		20000	175000
France	110000		162000	299000
Germany	35000	220000	130000	507000
Greece			12000	12000
Italy		90000	125000	235000
Netherlands			20000	20000
Spain	14000		62000	76000
Sweden	50000	65000		155000
United Kingdom		40000 (200000 t/a refining capacity)	107000	307000

Notes:
* Primary and/or secondary raw materials.

Table 1.12: Annual capacities for European lead processes

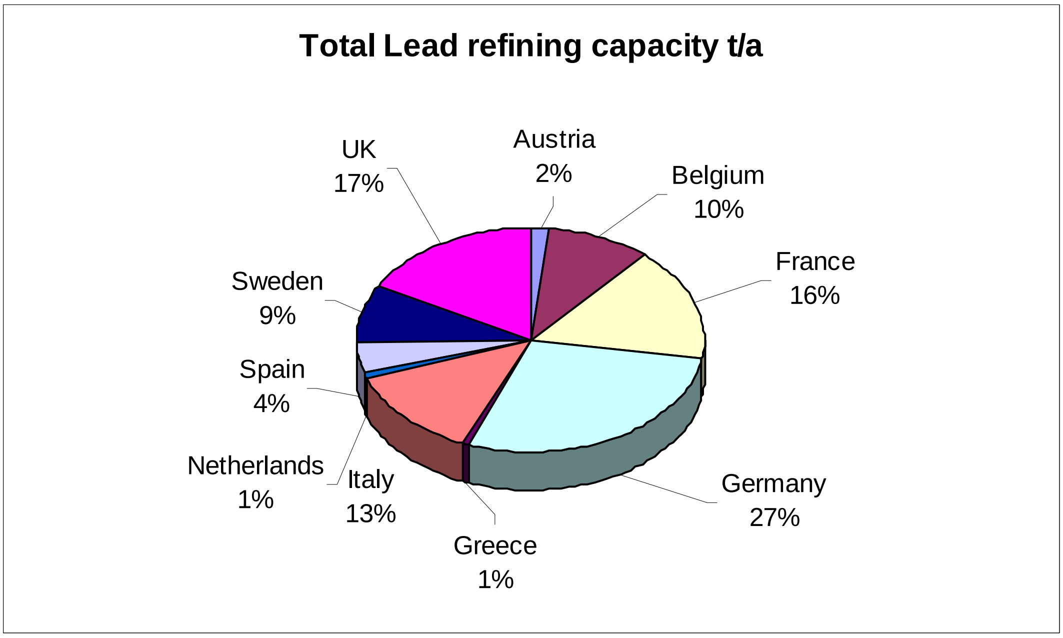


Figure 1.7: European lead refining capacity

1.5.2.5 Environmental issues

Historically the major environmental problem associated with the production of lead from primary sources was the emission of sulphur dioxide to air from the roasting and smelting of sulphide concentrates. This problem has been effectively solved by the EU smelters who now achieve a high fixation of the sulphur and produce sulphuric acid and liquid sulphur dioxide. The main environmental issues associated with the production of secondary lead are also related to the off gases from the various furnaces in use. These gases are cleaned in fabric filters and so can reduce the emissions of dust and metal compounds. There is also the potential for the formation of dioxins due to the presence of small amounts of chlorine in the secondary raw materials and the destruction of dioxins is an issue that is being pursued.

Lead is of great environmental concern and many lead compounds are classified as toxic. General policy is normally to restrict emissions to the lowest practicable levels given the state of technology, and recycling is normally conducted whenever appropriate and economic. Most control measures are concerned principally with human exposure (humans are most affected by lead exposure) although there are certain instances in which animals can be exposed to environmental lead.

Environmental legislation will require investment to reduce lead in air emissions. In recent years several new technologies have been developed and implemented which offer more efficient methods of smelting lead concentrates. These processes have also reduced emissions to the environment. Existing processes have been improved by using up to date control and abatement systems.

Batteries, which created 52% of lead consumption in the EU in 1994, are recycled with more than 90% efficiency.

Regulations affecting lead fall into three main categories: occupational exposure, emissions (ambient air quality) and controls on food water and products. Occupational exposure is addressed under EU directive 82/605/EEC of July 28, 1992 on the protection of workers from risks related to exposure to metallic lead and its ionic compounds at work. This directive sets limitson the level of lead in air in the workplace and on certain biological indicators which reflect the level of exposure of individual workers. The limit values are complemented by rules on the protection of the workforce providing for the use of protective clothing, respirators, washing facilities or specifying rules on eating, drinking, smoking, etc.

Lead in the general atmosphere is limited under directive 82/844/EEC of December 3, 1982, which sets a limit for levels of lead in air throughout the EU. These limit values are currently being revised. Levels of lead in water are also controlled in a number of directives relating to water depending on its type and use e.g., water intended for human consumption, water for bathing, fishing waters, etc.

1.5.3 Cadmium

1.5.3.1 General

Cadmium belongs to the zinc subgroup of the periodic table and was discovered by Strohmeyer in 1817 during an investigation into $ZnCO_3$. It is associated with zinc in minerals at a ratio of 1 : 200 Cd to Zn. It is physically similar to zinc but is more dense softer and can be polished. Unlike zinc it is also resistant to alkalis. Cadmium is also a good absorber of neutrons and is therefore often used in nuclear reactors.

In its compounds it has an oxidation state of 2^+. Cadmium is widely distributed Worldwide with a content between 0.1 and 1 ppm in the topsoil.

1.5.3.2 Source of materials

There are only a few cadmium-minerals, such as Greenockite (CdS) or Otavite ($CdCO_3$) and as CdO. None of these minerals is industrially important. Zinc minerals, which contain cadmium as an isomorphic component at concentrations of about 0.2% have economic significance for cadmium recovery. In addition, lead- and Cu-ores may contain small amounts of cadmium.

1.5.3.3 Production and consumption

Unlike other heavy metals, cadmium has been refined and utilised only relatively recently; production and use have risen only during the last 40 - 50 years. The main uses today are: -

- electroplated cadmium coatings,
- nickel-cadmium batteries,
- some pigments and stabilisers for plastics,
- alloys for solders, in fire protection, for control rods in nuclear reactors, for electrical conductors.

Small amounts are used for solar cells.

Since 1970 the cadmium-production of the Western World remained fairly constant between 12000 and 16000 t/a. The World production has been around 20000 t/a. The use of cadmium in various applications has varied since 1970 and has been affected by technical, economic and environmental factors. This has influenced the metal prices. Metal prices in the Seventies reached 3 US $/lb, and in the eighties varied between 1.1 and 6.9 US $/lb. Since that time the cadmium-price fell to 1 US $/lb and even went as low as 0.45 US $/lb, which is equivalent to the zinc-price level.

Main producer and user countries are shown in the following table.

Country	Production t/a	Use t/a
Canada	2832	107
Japan	2357	6527
Belgium	1579	2017
PR China	1300	600
United States	1238	1701
Germany	1145	750
Finland	600	-
France	205	1276

Table 1.13: Main cadmium producers and users in 1996

Cadmium is recovered: -

- From pyro-metallurgical Pb-Cu recovery in the flue dust from the smelting operation.
- From pyro-metallurgical Pb-Zn recovery in the flue dust from the sinter/roast operation and from crude zinc.

Flue dusts are generally leached with H_2SO_4 to separate the cadmium which is afterwards precipitated as $CdCO_3$ or reduced to cadmium sponge with more than 90% cadmium. The sponge may be either smelted under NaOH, or vacuum distilled, or dissolved and electrolysed to produce cadmium of high purity
[$\geq$ 99.99% cadmium].

Crude zinc may be distilled in New Jersey columns to produce pure zinc and a Cd-Zn-alloy with more than 60% cadmium. The Cd/Zn alloy from the New Jersey distillation operation has to be distilled twice, before pure cadmium is produced.

Recycling takes place, but only very few companies take part. Mainly used batteries are recycled to recover cadmium and Ni.

1.5.3.4 Environmental issues

The status of cadmium compounds has a significant impact on the assessment of emissions and nickel is listed in the Directive 76/464 Dangerous Substances Directive for Water in List II. A technical working group under Directive 96/62/EC Air Quality Assessment and Management is developing an environmental air quality standard for cadmium. These factors need to be taken into account.

Cadmium has been ubiquitously distributed in the natural environment for millions of years. Industrial production has affected the total distribution only insignificantly, but in some restricted areas environmental problems have been developed. A typical zinc production process can produce 600tonnes per year of cadmium. Cadmium production is closely controlled to prevent fugitive emissions and remove dust to a very high standard.

More than 90% of the non-smoker intake of cadmium is reported to be by food. Consequently cadmium contamination of cultivated soil has to be lowered and controlled. Limiting emission values for cadmium to air are < 0.2 mg/Nm^3 and for water < 0.2 mg/l.

The critical effect of cadmium is renal tubular dysfunction. The tubular damage is irreversible, so prevention is more important than diagnosis. The long biological half-life of cadmium can lead to a continuous increase in renal levels over many years and so past exposure is often more important than present exposure.

In many applications, cadmium alloys are essential and cannot be substituted with other materials. Similarly the use of cadmium in rechargeable batteries can also be an environmental benefit.

1.6 Precious Metals

1.6.1 General

Precious metals [tm 36, Panorama 1997] include such well-known metals as gold and silver as well as the six platinum group metals: platinum, palladium, rhodium, iridium, ruthenium and osmium. They are termed precious metals because of their rarity and corrosion resistance.

The EU has the largest refining and fabricating capacity for precious metals in the world, even though its actual mineral resources of such metals are very limited. The recycling of precious metals from scrap and industrial residues has always been an important raw material source for the EU industry.

Consumption of gold in the EU is mainly for jewellery, with smaller amounts used in electronics and other industrial and decorative applications. The principal users of silver are the photographic and jewellery industries. The platinum group metals are used extensively as catalysts and the imposition of strict emissions limits on vehicles sold in the EU has stimulated demand for their use in catalytic converters.

1.6.2 Sources of materials

Mines in all parts of the world consign large quantities of precious metals, in crude ore or by-product forms, to the EU refineries. Refineries with significant precious metal capacities are found in Belgium, Germany, Sweden, Finland and the United Kingdom. These typically recover precious metals from lead and zinc, copper or nickel ores, as well as low-grade scrap materials of all kinds, and they supply the pure metals in bars or plates, grain or sponge.

There are small deposits of precious metal ores in Europe, the following table shows the primary resources in 1997. These resource account for approximately 4.5% of world primary silver, 1.1% of world primary gold and 0.08% of world primary PGM. Deposits of gold are being developed in Greece and their contribution will be significant in coming years.

Country	Silver t/a	Gold t/a	PGM t/a
Finland	11.0	1.0	0.1
France	0.1	5.7	
Greece	1.2		
Ireland	0.4		
Italy	0.3		
Portugal	1.1		
Spain	6.2	5.4	
Sweden	8.8	6.3	

Table 1.14: Precious metal - primary resources 1997

Europe has a number of companies who specialise in the collection, pre-processing and trading of scrap and secondary materials before the actual assay and refining stages take place. Typical items are discarded printed circuit boards, obsolete computers, old photographic film, X-ray plates and solutions, spent electro-plating baths etc.

1.6.3 Production and consumption

The cost of recovery and recycling is more than justified by the high intrinsic value of the precious metals contained in these scrap and residues. It is not just the economic aspects that encourage the recycling of precious metals but also the environmental issues where stricter limits on the tolerable metal content of waste materials sent for dumping are being set.

The refining of gold, silver and the platinum group metals in the EU takes place either at the specialist precious metal refining and fabricating companies or at base metal refineries. Total precious metal refining capacity of the EU firms is the largest in the world.

Country	Silver t/a	Gold t/a	PGM t/a
Austria	190	70	1
Belgium	2440	60	45
France	1520	135	12
Germany	2700	193	92
Italy	1050	115	15
Luxembourg			
Netherlands	130	15	1
Spain	830	30	5
Sweden	250	15	1
U K	2320	300	100
Switzerland	620	565	14
Other EU Countries	50	10	5

Table 1.15: Annual capacity of European refineries (tonnes)

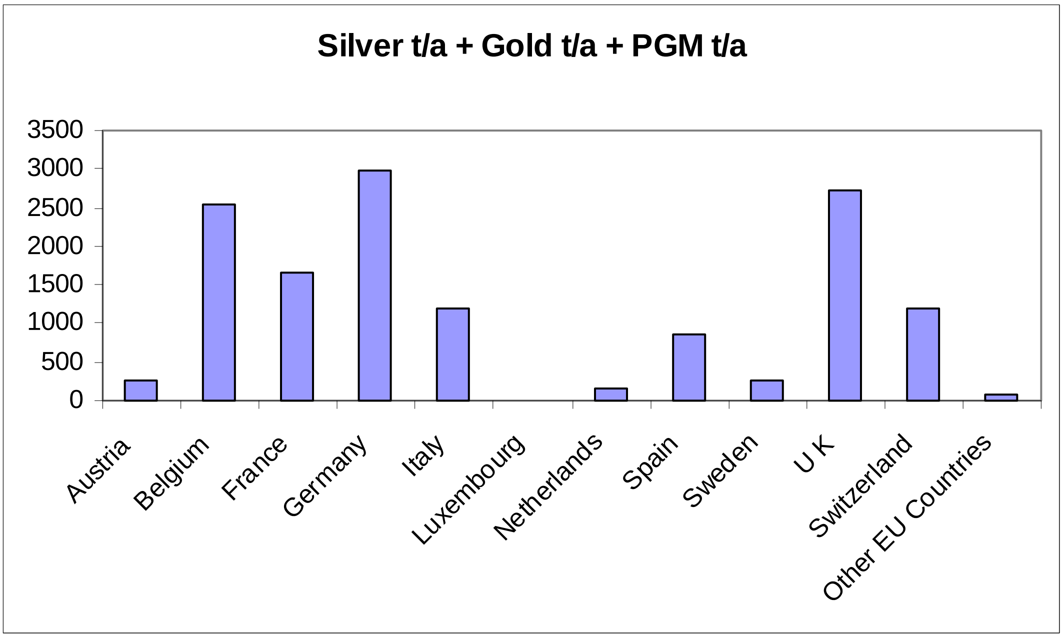


Figure 1.8: Total European precious metal refining capacity

The refinery capacity is approximately double the amount actually processed so that a rapid turn round of processed metal can be maintained.

Most of the precious metals are fairly easily fabricated either as pure metals or as alloys. Gold in particular is usually turned into specific alloys for jewellery or dental purposes in order to improve its wear-resistance or colour. Because of the high intrinsic value and the wide range of forms and alloys required, such metals are usually fabricated or processed in relatively small quantities compared with base metals. One of the few precious metal products manufactured in tonnage quantities is silver nitrate for the photographic industry.

European demand for precious metals is high. The jewellery trade has the highest consumption of gold and the photographic trade for silver. The highest consumption of platinum is in the production of auto catalysts. Other principal uses are in chemicals, dentistry and investment such as coinage. The demand in 1996 for precious metals is shown below.

	Silver t/a	**Gold t/a**	**PGM t/a**
Total European Demand	5710	881	85
Total World Demand	19600	2621	360

Table 1.16: Precious Metal Demand 1996

1.6.4 Production sites

The principal precious metals refiners and fabricators of the EU operate on an international scale and are world leaders in their field. Prominent names are Degussa and Heraeus in Germany and Johnson Matthey in the United Kingdom. The US precious metals firm, Engelhard Corporation, has been operating in the EU for a number of years and in late 1994 announced a joint venture with the French precious metals company CLAL.

Major EU base metal refiners with significant precious metal involvement include Union Minière in Belgium, Norddeutsche Affinerie in Germany, Outokumpu in Finland and Boliden in Sweden.

1.6.5 Environmental issues

The EU precious metal refineries form an advanced technology, high performance industry that is very strongly focused on research and development. The processes often use hazardous reagents such as HCl, HNO_3, Cl_2 and organic solvents. Advanced processing techniques are used to contain these materials and the small scale of production allows these techniques to be used effectively to minimise and abate potential emissions. This encompasses not merely new uses for the precious metals but also the discovery of techniques for economising the quantities of precious metals used in existing applications. The raw materials are subject to intensive sampling and assay and any process wastes are analysed to the same standard.

The recovery of these metals from secondary raw materials is particularly important and many of these materials are classified as wastes from other industries. There are delays in moving raw materials because of the Trans-boundary Shipment of waste legislation and this can be an obstacle to recycling.

1.7 Mercury

1.7.1 General

Mercury is the only metal that is liquid at room temperature and has the lowest fusion and boiling points of all metals. It also has a high electrical conductivity and these features are used in a variety of applications such as electrical switch-gear and battery production. Mercury forms alloys easily with a number of other metals and these are known as Amalgams, which are extensively used in dentistry. The major use of mercury is as a flowing cathode in the Chlor-Alkali process. This process exploits mercury's high conductivity and the formation of an amalgam with sodium.

Mercury is characterised by the toxicity of the metal and its' vapour and the extreme toxicity of some of its' compounds. The result is that mercury is being replaced by alternative materials in many of its' uses and so the demand and production of mercury has declined rapidly. There are implications in the future as it is likely that some existing inventories of mercury will come on the market or may even become wastes.

1.7.2 Sources of materials

Mercury appears in nature in the form of cinnabar (sulphide of mercury), which is associated with very hard gangues such as the quartzite and the basalts. It is also present in the form of other compounds such as oxides, sulphates, chlorides or selenides. These are rare and are always associated with the cinnabar and generally have a low relevance. There are exceptions such as livinstonite (HgSbS), which has been used in Mexico. The quality of primary ores varies considerably from 0.1% mercury to more than 3%.

Other sources of mercury are the ores and concentrates of other metals such as copper, lead and zinc etc. Mercury is produced from the purification of gases emitted during the production of these metals. Mercury is also recovered from secondary materials such as dental amalgam and batteries and it is also obtained from the refining of oil.

1.7.3 Production and consumption

The decomposition of the cinnabar is complete at temperatures of 600º C shown by the formula below. Mercury metal is condensed at room temperature. The heating can be carried out in either "Herreschoff", "Muffle" or rotating furnaces. The last two are not frequently used.

$$\mathbf{HgS + O_2 \rightarrow Hg + SO_2}$$

Source	Mercury content in the ore [%]	Production [t/a]
Almaden, Spain	> 3	390
Mc Dermitt, USA	0.5	
Nikitovska, Ukraine	0.1	

Table 1.17: Sources of mercury

In the case of rich ores, above 2% mercury, pre-treatment by crushing and grading is only required and the crushed ore can then be fed directly into the furnace. In the case of poor ores with 0.5% mercury, differential flotation is used to separate the silica rock to obtain concentrates with an average mercury content of 70%. For minerals below 0.1% of mercury, the ore is roasted after crushing. Furnaces of large capacity (1000 t/day) are used.

Mercury production from the production of other non-ferrous metals in Europe for 1997 is estimated at 350 tonnes. These processes generally produce mercury or calomel in the range 0.02 to 0.8 kg of mercury per tonne of metal produced depending on the mercury content of the concentrate.

The decline in mercury production can be seen in the European production for 1960, 1970 and 1980.

Year	**Production [t/a]**
1960	4250
1970	3700
1980	1100

Table 1.18: Production of mercury in Western Europe

1.7.4 Environmental issues

The toxicity of mercury and its compounds is a significant factor. Mercury in the environment can interact with various organic compounds to produce very toxic organo-mercury compounds. Current legislation is therefore imposing more stringent standards on the industry to prevent emissions, to curtail its' use in various processes and to remove mercury from the environment.

Mercury is a List 1 Substance under the 76/464 Directive on Pollution covered by the section Dangerous Substances Discharged to the Aquatic Environment of the Community. Directive 84/156 set EU wide discharge limit values for mercury.

1.8 Refractory Metals

1.8.1 General

The term refractory metals refers to a group of metals (in some cases rare earth metals) that can mostly be characterised by the same physical properties. These properties, are for the majority of refractory metals, a high melting point, high density, special electrical properties, inertness and in particular, the ability to confer in small additions to steel and other metals exceptional increases in physical performance. Selected physical properties of some refractory metals are shown below.

Metal	Symbol	Atomic Number	Atomic Mass	Melting Point [ºC]	Boiling Point [ºC]	Density [g/cm^3]
Chromium	Cr	24	51.99	1857	2672	7.19
Manganese	Mn	25	54.94	1220	2150	7.44
Tungsten	W	74	183.85	3410	5900	19.3
Vanadium	V	23	50.94	1929	3450	6.11
Molybdenum	Mo	42	95.94	2610	5560	10.22
Tantalum	Ta	73	180.95	2996	5425	16.65
Titanium	Ti	22	47.88	1725	3260	4.5
Niobium	Nb	41	92.90	2468	4927	8.57
Rhenium	Re	75	186.2	3180	5900	21.02
Hafnium	Hf	72	178.4	2230	4602	13.09
Zirconium	Zr	40	91.22	1857	3580	6.5

Table 1.19: Physical properties of refractory metals

Refractory metals and hardmetal powders are used for a wide range of industrial applications. Chromium metal is important in steel alloying and as a metal coating in the galvanic industry. Among a variety of other uses like steel alloying, manganese is the key component of certain widely used aluminium alloys and is used in oxide form in dry cell batteries [tm 174, T.S. Jones USGS 1997]. The largest use of tungsten is as cemented carbides, which are also called hardmetals. Cemented carbides are wear resistant materials used by the metalworking, mining and construction industry. Tungsten metal wires, electrodes, and /or contacts are used in lighting electronic, heating and welding applications [tm 175, K.S. Shedd USGS 1997]. Molybdenum finds significant usage as a refractory metal in numerous chemical applications, including catalysts, lubricants, and pigments[tm 176, J.W. Blossom USGS 1997]. Tantalum and its twin element niobium as used as tantalum and niobium powder and carbides. Tantalum powder is mainly used for the production of tantalum capacitors.

Niobium and columbium are synonymous names for the same element. Columbium was the first name given, and niobium was the name officially designated by the International Union of Pure and Applied Chemistry in 1950 [tm 172, L.D. Cunningham USGS 1997]. As a metal, titanium is well known for corrosion resistance and for its high strength-to-weight-ratio. However, approximately 95% of titanium is consumed in the form of titanium dioxide (TiO_2), a white pigment in paints, paper, and plastics [tm 177, J. Gambogi USGS 1997]. Rhenium is used in petroleum-reforming catalysts for the production of high-octane hydrocarbons, which are used in the production of lead free gasoline [tm 178, J.W. Blossom USGS 1997].

Zirconium is the 18th most abundant element in the Earth's crust with an average crystal abundance of 165 parts per million. Martin-Heinrich Klaroth discovered the element in 1789 by analysing zircon. Hafnium free zirconium is used as cladding for nuclear fuel rods. Commercial grade zirconium, unlike nuclear grade, contains hafnium and is used in the chemical process industries because of its excellent corrosion resistance. Hafnium is a bright silver, ductile, lustrous metallic element with a very high melting point. Hafnium metal was first produced in 19925 by Anton Edward van Arkel and Jan Hendrik de Boer by passing hafnium tetrachloride over a tungsten filament. Hafnium is used in nuclear control rods because of its high thermal neutron absorption cross section [tm 179, J.B. Hedrick USGS 1997]. Other applications of refractory metals include the use as mixing elements for the production of metal containing ceramics.

Due to their refractory nature the metals are sometimes processed in different ways from more common metals. The production generally requires hydrometallurgical methods for extraction and purification [tm 8, HMIP 1993] and hydrogen reduction and carburisation for the production of hardmetal powder and hardmetal carbides. The crude refractory metals and metal powders often need powder metallurgical techniques in order to produce finished or semi-finished products.

Processes for the manufacturing of refractory metals that includes the production of hardmetal powder and metal carbides will cover the metals chromium, manganese, tungsten, vanadium, molybdenum, titanium, tantalum, niobium, rhenium as well as the production of zirconium and hafnium.

1.8.2 Sources of materials

Refractory metals can be produced from a wide range of primary and secondary raw materials. Refractory metals are produced from primary raw materials by hydrometallurgical treatment of oxidic and sulphide ores and concentrates and further hydrogen reduction and carburisation in order to produce cemented carbides.

The production from secondary raw material is normally based on hardmetal scrap and residues from other production processes like spent catalysts. The fact that recycling plays an important role can be demonstrated by the point that about 30% of the world tungsten supply is produced from secondary raw materials. The tungsten processing industry is able to treat almost every kind of tungsten containing scrap and waste to recover tungsten and, if present, other valuable constituents.

The following table gives an overview about the most important primary and secondary raw materials that are used for the production of refractory metals. It provides also information about the mineral deposits within the European Union.

A number of other raw materials such as coke, coal, charcoal, silicon, aluminium, calcium and magnesium as reducing agents are also used. Different e.g. sulphuric acid chemicals are needed for leaching, purification, precipitation, ion exchange and electrolytic operations.

Metal	Primary raw material (Resources)				Secondary raw material
	Minerals	**Content**	**Other metals**	**Deposits within the EU**	
Chromium	Chromite	Cr < 50%	Fe, Mg, Al	Finland and Greece	• Chromium scrap
Manganese	Pyrolusite Braunite Manganite Psilomelane	Mn 63% Mn 66% Mn 62% Mn 45 - 60%	Si Ba	Greece [2] and Italy [2]	•
Tungsten	Wolframite Scheelite Ferberite Hübnerite	WO_3 76% WO_3 80% WO_3 76% WO_3 76%	Fe, Mn Ca Fe Mn	Austria, France, Portugal and UK	• Tungsten scrap (grinding wheel swarf and dust) • Hardmetal scrap
Vanadium	Titanomagnetite[3] Montroseite Corvusite Roscoelite	V 1.5% V 45% V 40% V < 14%	Fe, Al, Ti, Cr Fe Al, Si		• Boiler residues • Fly ashes from incinerators • Spent catalysts from the petrochemical and chemical industry • Waste salts from the production of alumina
Molybdenum	Molybdenite Wulfenite Powelite Ferrimolybdite Chalocpyrite[4]		Re Pb Ca, W Fe Cu		• Molybdenum containing spent catalysts from petroleum refining
Titanium	Rutile Ilmenite Leucoxene TiO_2 rich slag from ilmenite	TiO_2 94% TiO_2 < 70% TiO_2 80%			• Titanium scrap mostly from the production of semi-finished products • Titanium swarf
Tantalum	Tantalite Wodginite Microlite Columbite (Cassiterite)[5]	Ta_2O_5 42 - 84% Ta_2O_5 60 - 70% Ta_2O_5 1 - 40%	Fe, Mn, Nb Nb,Sn,Mn,Fe Na,Ca,Nb Fe,Mn,Nb		• Unoxidised metallic tantalum scrap • Tantalum anodes • Capacitors • Sintered pellets • Oxidised tantalum scrap related with other oxidised metals • Tantalum anodes coated with oxidised manganese
Niobium	Tantalite Columbite Microlite	Nb_2O_5 2 - 40% Nb_2O_5 40 - 75%	Fe, Mn, Ta Fe, Mn, Ta Na, Ca, Ta		• Hardmetal scrap
Rhenium	Molybdenite		Mo		• Platinum-rhenium catalysts used in the petroleum industry
Zirconium	Zircon [6]		Hf		
Hafnium	Zircon [6]		Zr		

Notes:

[1] The list contains not all possible raw materials, it only provides an overview of the most important material sources.

[2] The manganese deposits in Greece and Italy contain low-grade minerals and have been used only from time to time.

[3] The vanadium-bearing titanomagnetite deposits are of magmatogenic origin and occur in many parts of the world [tm 107, Ullmanns 1996]. From the titanomagnetite ore a vanadium slag can be produced, which is the first source to produce vanadium compounds.

[4] A copper-molybdenum sulphide concentrate which is used as a secondary ore.

[5] The production of tin from cassiterite ore led to a tantalum and niobium containing slag, which is a main raw material source of tantalum and niobium production

[6] Zirconium and Hafnium sometimes are by-products from heavy sand deposits, which always contain titanium and other rare earth metals.

Table 1.20: Primary and secondary raw materials for the production of refractory metals

1.8.3 Production and consumption

The World European refractory metal production and market is very sensitive to the political and economic situation of the raw material producing countries. The world consumption of primary tungsten for instance was strong in 1997 and remained well above world mine production. An estimated one-third of world supply was from tungsten mineral released from stockpiles in Russia and Kazakhstan The stockpile releases have maintained an oversupplied market and have kept the price of primary tungsten below the operating cost of most mines. As a result, many mines have closed, and world tungsten production capacity has fallen to around 75% of world consumption. Also China continues to be a strong competitor in case of increasing their refractory metal production. However, due to the advantageous properties of refractory metals and the growing understanding how to use refractory metals the production will increase at least on a long-term basis. Future consumption of tungsten cemented carbides for instance, the largest end-use sector is estimated to increase by more than 5% on the 1998 basis [tm 175, K. B. Shedd USGS 1997]. The world production of chromium metal is presented in the following table.

Country	Production capacity [t/a]
Brazil	500
China	4000
France	7000
Germany	1000
India	500
Japan	1000
Kazakhstan	1000
Russia	13000
United Kingdom	10000
USA	3000

Table 1.21: World chromium metal production capacity
[tm 173, J.F. Papp USGS 1997]

1.8.4 Production sites

The production of refractory metals in the European Union is based on a limited number of companies. Mainly two major companies for instance produce chromium metal. These are London and Scandinavian Metallurgical Co Limited who operate a new modern chromium plant built in 1997, and Delachaux in France who just reported the completion of its chromium metal plant in Valenciennes.

The following companies, Kennametal Hertel AG, Widia GmbH and HC Stark GmbH in Germany, Treibacher Industrie AG and Plansee AG in Austria, Sandvik and Seco Tools in Sweden and Eurotunstène Poudres in France [tm 182, ITIA 1999] are producing tungsten metal powder and carbides in Europe.

The companies mentioned above for the production of tungsten metal powder produce some other refractory metals. An overview of the worlds largest tantalum and niobium producing companies and their products is shown in table 1.22. Unfortunately there is no information on Chinese producers available and therefore missing in the table.

Country	Company	Products (N 1)
Austria	Treibacher Chemische Werke AG	Nb and Ta oxide/carbide, FeNb, NiNb.
Brazil	Cia. Brasileira de Metalurgia e Mineracao (CBNM	Nb oxide/metal, FeNb, NiNb.
	Cia. Industrial Fluminense (N 2)	Nb and Ta oxide.
	Mineracao Catalao de Goias S.A. (Catalao)	FeNb.
Canada	Cainbior Inc., and Teck Corp. (Niobec)	FeNb.
Estonia	Silmet	Nb oxide/metal.
Germany:	Gesellschaft Fur Elektrometallurgie mbH (GFE) (N 2) H.C. Stark GmbH & Co. KG	FeNb, NiNb. Nb and Ta oxide/metal/carbide, K-salt, FeNb,_NiNb, Ta capacitor powder.
Japan	Mitsui Mining & Smelting Co.	Nb and Ta oxide/metal/carbide.
	Showa Cabot Supermetals (N 3)	Ta capacitor powder.
	H.C. Stark-V Tech Ltd. (N 4)	Ta capacitor powder.
Kazakstan	Ulba Metallurgical	Ta oxide/metal.
	Irtysh Chemical & Metallurgical Works	Nb oxide/metal.
Russia	Solikamsk Magnesium Works	Nb and Ta oxide.
Thailand	H.C. Starck (Thailand) Co. Ltd. (N 4)	K-salt, Ta metal.
United States	Cabot Corp.	Nb and Ta oxide/metal, K-Salt, FeNb, NiNb,
		Ta capacitor powder.
	H.C. Starck Inc. (N 5)	Nb and Ta metal, Ta capacitor powder.
	Kennametal, Inc.	Nb and Ta carbide.
	Reading Alloys, Inc.	FeNb, NiNb.
	Shieldalloy Metallurgical Corp. (N 2)	FeNb, NiNb.
	Wah Chang (N 6)	Nb oxide/metal, FeNb, NiNb.
	H.C. Starck-TTI, Inc. (N 4)	Ta capacitor powder.

Notes:
(N 1) Nb, niobium; Ta, tantalum; FeNb, ferroniobium; NiNb, nickel niobium; K-salt potassium fluotantalate; oxide, pentoxide.
(N 2) A wholly owned subsidiary of Metallurg Inc., New York-.
(N 3) A joint venture between Showa Denko and Cabot Corp.
(N 4) A subsidiary of H.C. Starck GmbH & Co. KG.
(N 5) Jointly owned by Bayer USA and H.C. Starck GmbH & Co. KG.
(N 6) A subsidiary of Allegheny Teledyne Inc.

Table 1.22: Principal world producers of niobium and tantalum producers
[tm 172, L.D. Cunnigham USGS 1997]

1.8.5 Environmental issues

The main environmental impact by producing refractory metals is metal containing dust and hardmetal powder as well as fume from the smelting processes for instance by producing chromium metal. Dust emissions occur from storage, handling of raw materials and products and the furnace operation, where both stack and fugitive emissions play an important role.

The use of hydrogen as a reducing agent contains the possible risk fire hazards. Hydrogen fluoride, which is used in several processes, is highly toxic and needs therefore to be handled very carefully to avoid any health problems for the plant staff. Another environmental impact of the production of hardmetals is the high radioactive level of some raw materials (e.g. Pyrochlore), and the toxicity of metal compounds such as cobalt and nickel.

Process residues and by-products are slag, metal containing sludge, filter dust and spent refractories. These materials are already recycled and reused to a large extent where it is possible. Due to the radioactive levels of several raw materials, residues of such metal processes might be radioactive.

Water emissions are produced from cooling, granulation and other process and site related effluents. An important issue is the wastewater that is generated by wet cleaning abatement systems.

The emissions to air, water and soil and therefore the environmental impact is relatively low compared with other sectors of the non-ferrous metal industry. This is due to the small quantities of refractory metals produced and the high value of these metals. This makes it very important to collect, filter and recycle as much as possible from an economic point of view. The treatment of small off-gas volumes is also less difficult because high performance bag filters for instance may advantageously be used.

1.9 Ferro-Alloys

1.9.1 General

Ferro-alloys are master alloys containing some iron and one or more non-ferrous metals as alloying elements. Ferro-alloys enable alloying elements such as chromium, silicon, manganese, vanadium, molybdenum etc. to be safely and economically introduced into metallurgical processes, thus giving certain desirable properties to the alloyed metal, for instance to increase the corrosion resistance, hardness or wear resistance.

Their importance grew with progress of steel metallurgy, which implied more diversified alloying elements, in better controlled quantities, in purer steel. The ferro-alloy industry became a key supplier to the steel industry.

The ferro-alloys are usually classified in two groups:

- Bulk ferro-alloys (ferro-chrome, ferro-silicon together with silicon-metal, ferro-manganese and silico-manganese), which are produced in large quantities in electric arc furnaces;
- Special ferro-alloys (ferro-titanium, ferro-vanadium, ferro-tungsten, ferro-niobium, ferro-molybdenum, ferro-boron and ternary/quaternary alloys) which are produced in smaller quantities, but with growing importance.

Bulk ferro-alloys are used exclusively in steel making and steel or iron foundries. The uses of special ferro-alloys are far more varied, and the proportion used in steel making has diminished over recent years in favour of those used in the aluminium and chemical industries, especially silicon products. The following figures presents the use of ferro-alloys, bulk and special ferro-alloys as a breakdown by sector for 1994.

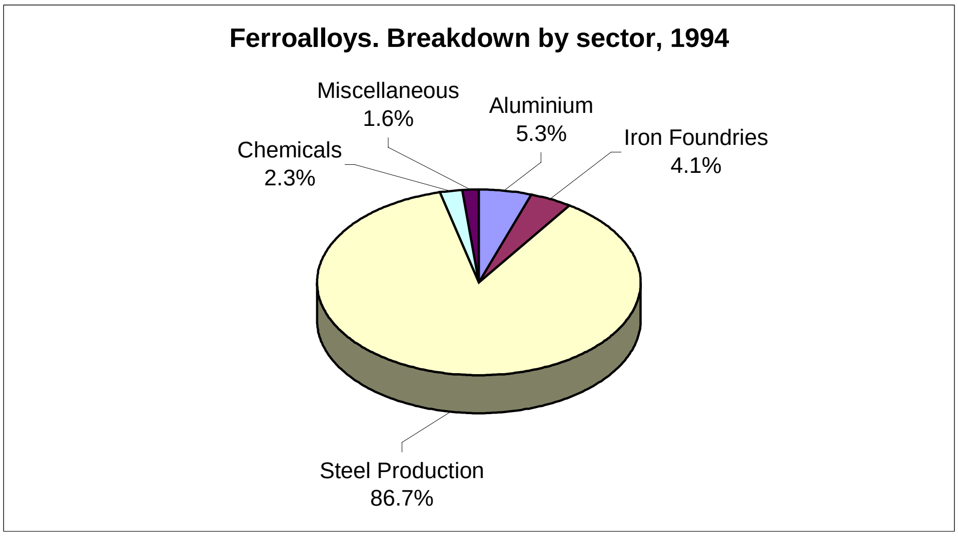
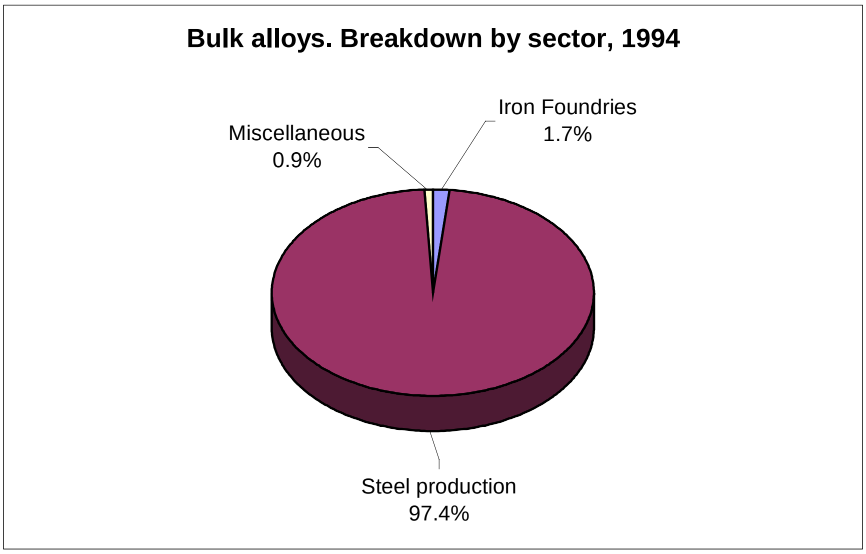


Figure 1.9: Use of ferro-alloys in different industrial sectors in 1994
[tm 36, Panorama 1997]



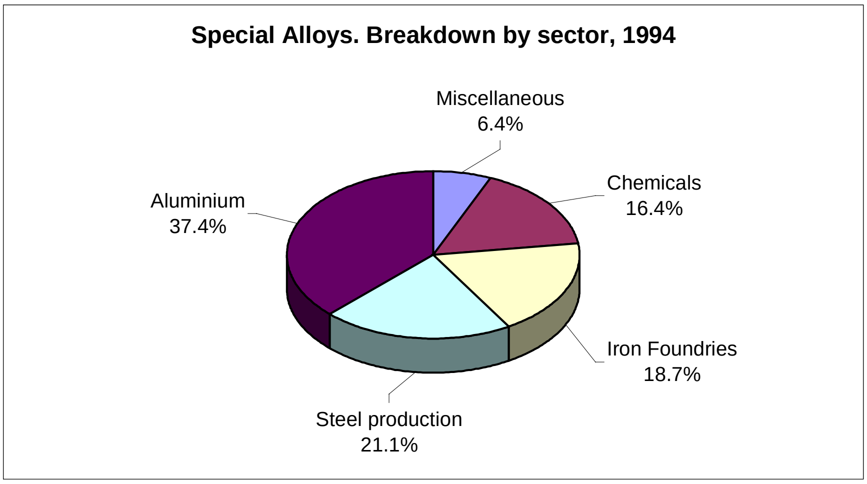


Figure 1.10: Use of bulk- and special ferro-alloys in different industrial sectors in 1994 [tm 36, Panorama 1997]

1.9.2 Sources of material

The raw materials (alloying elements) for the production of ferro-alloys are either mined for themselves (quartzite for silicon, chromite for chrome…) or by-products of another production (e.g. molybdenite from copper mining). Of course the two sources can exist simultaneously.

They can also be recovered from scrap, which is most often the case for the iron share of the composition, which comes from iron and steel scrap, but also for the alloying element itself, titanium for example. Residues from steel mills like electric arc furnace and converter filter dust, as well as shot blasting and grinding dust is an important secondary raw material with increasing significance. The main raw material sources and mineral deposits for the alloying elements are:

- Chromite that is concentrated in two big deposits, which are mainly located in South-Africa and Kazakhstan. Smaller deposits are found in other places in the world, and especially in Europe (Finland, Turkey, Albania, Greece);
- Raw material to produce ferro-silicon and silicon-metal is available everywhere in the world, although not all sources allow the production, under economic and quality conditions, of all the ranges of silicon alloys;

- Manganese containing ore is mainly found in South Africa, Ukraine, Gabon and Australia. Smaller occurrences are found in Brazil, India, Mexico and Burma. The quality (content of manganese and level/nature of the impurities) of the ore can influence greatly the economic of the ferro-alloy production;
- The special alloying elements are very often concentrated in few countries (molybdenum in North America, Chile and China; niobium in Brazil) and prices and availability are very sensitive to economic conditions.

1.9.3 Production and consumption

Over the last 15 to 20 years, the world pattern of the ferro-alloy market has deeply changed:

- The consumption of the developing countries has vastly increased with the development of their steel production;
- Their production has even more increased because they have taken a growing share of the traditional markets of the industrialised countries, where the steel production was stagnant or growing at a slow rate.
- The ferro-alloy industry is facing a growing proportion of imports, at first from the new industrialised countries and in recent years from the countries of East Europe and the CIS.

As a consequence, EU ferro-alloy production has been submitted to a difficult competition that results in a decreasing trend of the total amount of ferro-alloys produced. Although the last years showed some stabilisation, even a slightly increase of the production, the European industry remains very sensitive. The actual production rate of bulk ferro-alloys in the EU expressed in tonnes per year is shown in the graphic below and by the table on the next page. Information’s on the production figures are taken from [tm 180, M. Tenton USGS 1997] and have been supplied by the ferro-alloy expert group.

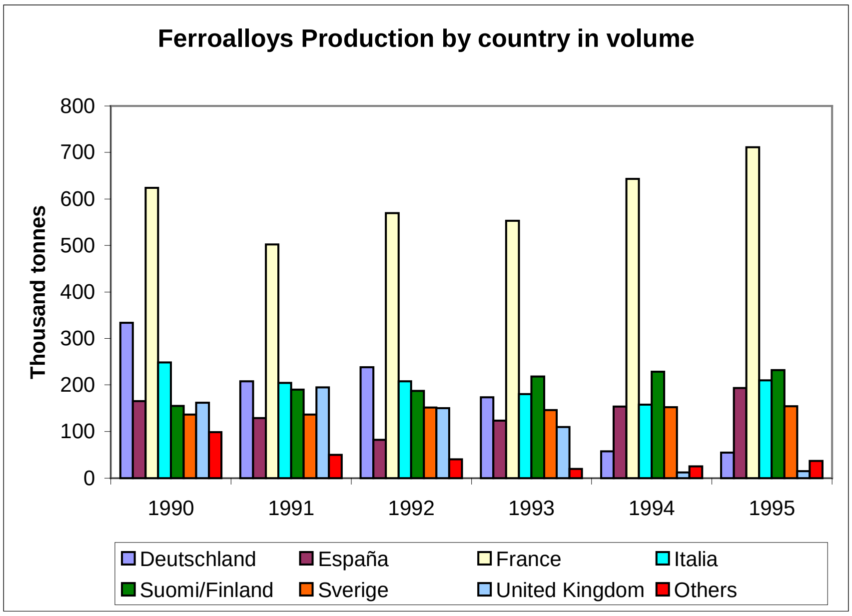


Figure 1.11: Production of bulk ferro-alloys in Europe
[tm 36, Panorama 1997]

The total European production of bulk ferro-alloys split into the different alloys and the furnaces where they are being produced is seen in the following table. The figures presented might not give the exact production capacities and should be seen more like an indication

Production	1993	1994	1995	1996	1997
Austria: Electric furnace:					
Ferronickel 1/	8000	5250	6200	5000	5000
Other e/	5900	5900	5900	5900	5900
Total	13900	11150	12100	10900	10900
Belgium: Electric furnace, ferromanganese e/	25000	25000	25000	25000	25000
Finland: Electric furnace, ferrochromium	218370	229000	232300	236100r/	236652 6/
France:					
Blast furnace, ferromanganese	300000	294000	384000 r/	337000 r/	326000
Electric furnace:					
Ferromanganese	57000	66200	46000 r/	65000 r/	60000
Ferrosilicon	84000	111000	108000	130000 r/e/	130000
Siliconmanganese e/ 2/	80000	66000 r/	71000 r/	61000 r/	66000
Silicon metal	59000	66000	71450 r/	73800 r/	74000
Other e/	29000	20000	20000	20000	20000
Total e/	609000	623000 r/	664000 r/	687000 r/	676000
Germany: e/					
Blast furnace, ferromanganese 3/	100000	--	--	--	--
Electric furnace:					
Ferrochromium	16400 6/	17283 6/	21665 r/6/	25303 r/6/	25856 6/
Ferromanganese 4/	20000	20000	20000	20000	20000
Ferrosilicon	20000	20000	20000	20000	20000
Silicon metal	500	500	500	500	500
Other 5/	30000	30000	30000	30000	30000
Total	187000	87800	92200 r/	95800 r/	96400
Greece					
Ferronickel	10930	16190	17170	17800	17610
Iceland: Electric furnace, ferrosilicon	67375	66003	71410	70520 r/	71000
Italy: Electric furnace: e/					
Ferrochromium	53504 6/	22650 6/	51017 6/	29915 6/	11295 6/
Ferromanganese	17000	16000	20216 r/6/	25143 r/6/	16000
Siliconmanganese	50000	40000	103961 r/6/	100353 r/6/	100000
Silicon metal	10000	--	10000 r/	14000 r/	15000
Other 6/	12000	12000	12000	10000	10000
Total	143000	90700	197000 r/	179000 r/	152000
Norway: Electric furnace:					
Ferrochromium	80000	120000	148000 r/	108900 r/	145124 6/
Ferromanganese	226018	248648	213000 r/	215000 r/	215000
Ferrosilicon	399559	452984	474875 r/	462423 r/	470000
Silicomanganese	218566	197328	210000 r/e/	210000 r/e/	210000
Silicon metal	81000	92000	101000	110000 e/	110000
Other e/ 2/	14000	14000	15000	15000	15000
Total e/	1020000	1120000	1160000 r/	1120000	1170000
Spain: Electric furnace: e/					
Ferrochromium	2390 6/	2300 6/	1320 6/	805 6/	490 6/
Ferromanganese	40000	35000	25000	30000 r/	35000
Ferrosilicon	30000	25000	30000	30000	30000
Silicomanganese	35000	35000	50000	70000 r/	100000
Silicon metal	5000	3000	5000	5000	15000
Other e/ 10/	5000	4000	5000	5000	5000
Total e/	117000	104000	116000	141000 r/	185000
Sweden: Electric furnace					
Ferrochromium	127543	134076	130170	138110	101842 6/
Ferrosilicon	20381	21392	21970	21287 r/	22000
Total	147924	155468	152140	159397 r/	124000
Switzerland: Electric furnace					
Ferrosilicon	3000	--	--	--	--
Silicon metal	2000	--	--	--	--
Total	5000	--	--	--	--
United Kingdom:					
Blast furnace, ferromanganese	45000	--	--	--	--
Electric furnace, other e/	10000	--	--	--	--
Total e/	55000				

Notes: e/ estimated; r/ revised; 1/ Reported figure; 2/ Includes silicospiegeleisen, if any. 3/ Includes spiegeleisen, if any; 4/ Includes silicomanganese, if any; 5/ Includes ferrochromiumsilicon and ferronickel, if any; 6/ Series excludes calcium-silicon.

Table 1.23: European production of bulk ferro-alloys in tonnes per year [tm 180, M. Tenton USGS 1997]

The total world production capacity of bulk ferro-alloys split into the different alloys and the furnaces where they are being produced is seen in the following table. The figures presented might not give the exact production capacities and should be seen more like an indication.

Furnace type, 1/2/ and alloy type 3/	1993	1994	1995	1996	1997 e/
Grand total:	15700000 r/	16300000 r/	17700000 r/	17900000 r/	17600000
Of which:					
Blast furnace:					
Ferromanganese 4/	1210000	1010000	874000 r/	927000 r/	871000
Spiegeleisen 5/	12000	10000	9500	9500	9500
Other 28/	225000	230000	230000	220000	220000
Total, blast furnace	1450000	1250000	1110000 r/	1160000 r/	1100000
Electric arc furnace:					
Ferrochromium 6/	3270000 r/	3530000 r/	4550000 r/	4010000 r/	4470000
Ferrochromiumsilicon	62500	89500	90700	52200	50000
Ferromanganese 7/ 8/	2320000	2770000 r/	2780000 r/	3050000 r/	2900000
Ferronickel	755000 r/	772000 r/	964000 r/	923000 r/	913000
Ferrosilicon	4010000 r/	3830000 r/	4070000 r/	4370000 r/	4130000
Silicomanganese 8/ 9/	2740000 r/	2850000 r/	3010000 r/	3110000 r/	3000000
Silicon metal	564000	559000	588000 r/	649000 r/	662000
Other 10/	575000 r/	635000 r/	589000 r/	589000 r/	383000
Total, electric furnace	14300000 r/	15000000	16600000 r/	16700000 r/	16500000

Notes:
(tonnes, gross weight). e/ Estimated. r/ Revised.
1/ Production of manganese ferroalloys, ferrosilicon, and silicon metal began in 1996 for Saudi Arabia, but data for actual production were not available.
2/ To the extent possible, ferroalloy production of each country has been separated according to the furnace type from which production is obtained; production derived from metallo-thermic operation is included with electric furnace production.
3/ To the extent possible, ferroalloy production of each country has been separated to show the following individual major types of ferroalloys: ferrochromium, ferrochromiumsilicon, ferromanganese, ferronickel, ferrosilicon, silicomanganese, silicon metal, and spiegeteisen. Ferroalloys other than those listed that have been identified specifically in sources, as well as those ferroalloys not identified specifically, but which definitely exclude those listed previously in this footnote, have been reported as "Other." Where one or more of the individual ferroalloys listed separately in this footnote have been inseparable from other ferroalloys owing to a nation's reporting system, deviations are indicated by individual footnotes.
4/ Spiegeleisen, if any, for Germany is included with blast furnace ferromanganese.
5 lncludes ferrophosphorus and data contained in "Blast furnace: Other."
6/ Ferrochromium includes ferrochromiumsilicon, if any, for Japan, South Africa, and the United States.
7/ Ferromanganese includes silicomanganese, if any, for countries carrying footnote 12 on "Ferromanganese" data line. 3 I/ U.S. production under "Other."
8/ Includes silicospiegeleisen, if any, for France.
9/ Includes calcium-silicon, ferromolybdenum, ferrovanadium, and data contained in "Electric furnace:
10/ Other for each country indicated.

Table 1.24: World production of bulk ferro-alloys
[tm 180, M. Tenton USGS 1997]

Due to the technical and metallurgical developments and changes in the iron and steel production also the consumption pattern of ferro-alloys has changed, especially in the industrialised countries:

- A stagnant carbon steel production is increasingly produced in electric arc furnaces from scrap, which allow recovery of the alloying elements, reducing the relative consumption of ferro-alloys;
- A more efficient carbon steel production (continuous casting, for example) and a more advanced metallurgy led to a significant drop of the specific consumption of manganese (from 7 kg/tonne of steel, to 5 kg/tonne in 20 years) and of ferro-silicon (from 5 kg/tonne of steel, to 3.5 kg/tonne in 20 years).
- A growing need for metallurgically sophisticated alloying elements (niobium, molybdenum), and for treatment elements (calcium), led to an increased consumption of special alloys;
- An increasing production of stainless steel led to a significant increase of the consumption of chromium alloys (mainly high carbon ferro-chrome).

All taken into account, Western Europe consumption, has been more or less stagnant, around 4.2 millions tonnes/year, and its production went down from 4 millions tonnes to 3 millions tonnes over the last 10 years.

1.9.4 Production sites

There are a number of companies producing different ferro-alloys in about 60 industrial production sites in Europe. The largest European ferro-alloy producing countries are Norway for the production of bulk ferro-alloys and France and Spain especially for the production of manganese- and silicon-alloys. Finland is a major producer of ferro-chrome from a local chrome ore mine. In Sweden mainly ferro-chrome and ferro-silicon is produced. Special ferro-alloys like ferro-molybdenum, ferro-vanadium and ferro-titanium are produced in the UK, in Belgium, Austria and Germany.

1.9.5 Environmental issues

Production of ferro-alloys generally involves the use of electric arc furnaces and reaction crucibles into which natural products (e.g. quartz, lime, various ores, wood etc.) with relatively fluctuating physical compositions are loaded. Due to this, the main environmental impact by producing ferro-alloys is the emission of dust and fume from the smelting processes. Dust emissions occur as well from storage, handling and the pre-treatment of raw materials where fugitive dust emissions play an important role. Depending on the raw material and the process used other emissions to air are SO_2, NOx, CO-gas CO_2, polycyclic aromatic hydrocarbon (PAH), VOCs, and volatile metals. The formation of dioxins in the combustion zone and in the cooling part of the off-gas treatment system (de-novo synthesis) may be possible.

Process residues and by-products with a significant amount is slag, filter dust and sludge and spent refractories. These materials are already recycled and reused to a large extent where it is possible. Rich slag, that means slag with a relatively high proportion of metal oxides, is used as raw material in other ferro-alloy productions. For instance rich slag from the production of ferro-manganese is one of the most important raw materials for the production of silico-manganese.

Water emissions are produced from cooling, granulation and other processes and site related effluents. The wastewater generated by a wet cleaning abatement system plays also an important role.

The ferro-alloys industry, whose basic tool is an electric arc furnace in which metal oxides are reduced by carbon, is a major consumer of energy and a producer of carbon dioxide (CO_2). It has therefore, always regarded reduction of energy consumption as a vital priority. The laws of thermodynamics, which govern the reactions used, limit the reduction of energy necessary for the smelting process. The reduction of the overall energy consumption is therefore in most cases only possible by using an efficient energy recovery system. The recovered energy can be transferred into electrical energy or used as heat for various purposes. CO-rich off-gas from closed furnaces can as well be used as secondary fuel or raw material for chemical processes. The recovery of energy reduces the use of other natural energy resources and therefore the impact of global warming.

1.10 Alkali and Alkaline Earth Metals

1.10.1 General

Alkali metals, which belong chemically to the first group of the periodic table of the elements includes metals such as lithium, sodium, potassium, as well as the extremely rare radioactive substance - francium. Alkali metals are characterised by their low melting point and density. They have a silvery-white colour and are softer than other metals. Alkali metals have only one single, highly mobile electron in the outermost shell. Due to this fact alkali metals are highly reactive especially with oxygen or water where they also can react violently by producing gaseous hydrogen and heat.

Alkaline-earth metals resemble alkali metals in several ways but they react less vigorously with water. Alkaline metals are elements in the second group of the periodic table. In order of their increasing atomic number and their metallurgical and technical importance, they are magnesium, calcium and strontium.

1.10.2 Sources of materials

Sodium as sodium compounds and metal are widely used in industry for manufacturing of chemicals and pharmaceuticals, in metallurgical processes and a variety of other everyday products. Sodium metal is commonly produced by the electrolysis of fused sodium chloride.

Lithium metal is produced in a very similar way to sodium metal. The production occurs by the electrolysis of a molten eutectic mixture of lithium chloride and potassium chloride at about 450 ºC in a Downs cell.

Potassium, which was discovered in 1807 by the English chemist Humphry Davy occurs in many silicate rocks and minerals, where the major commercial source is salt deposits. Potassium metal is silvery-white in colour and was the first metal to be isolated by electrolysis. On industrial scale potassium metal will only be produced by the reduction of potassium chloride with sodium metal.

Like potassium, Humphry Davy discovered magnesium as a metallic element in 1808. It is a silvery–white ductile chemically active metal that depends to the group of alkaline metals. Magnesium can be produced either by electrolysis of magnesium chloride based on raw material as dolomite and sea water, magnesite, carnalite or brines or from dolomite that will be reduced by ferro-silicon and/or aluminium in a thermal reduction process. Magnesium will also be recovered and produced as secondary magnesium from a wide range of magnesium containing residues and metallic magnesium scrap.

The majority of magnesium is used in aluminium alloying, while the fastest rate of growth is experienced in the use of magnesium alloys in die casting of parts for use wherever the light weight is of importance, e.g. in the automotive industry. Another large area of application is steel desulphurisation using magnesium powder The increasing use of secondary magnesium residues for steel desulphurisation is reducing the growth in the production of primary magnesium powder. The world use of magnesium metal in the different markets is shown below [tm 1,HMIP 1993]

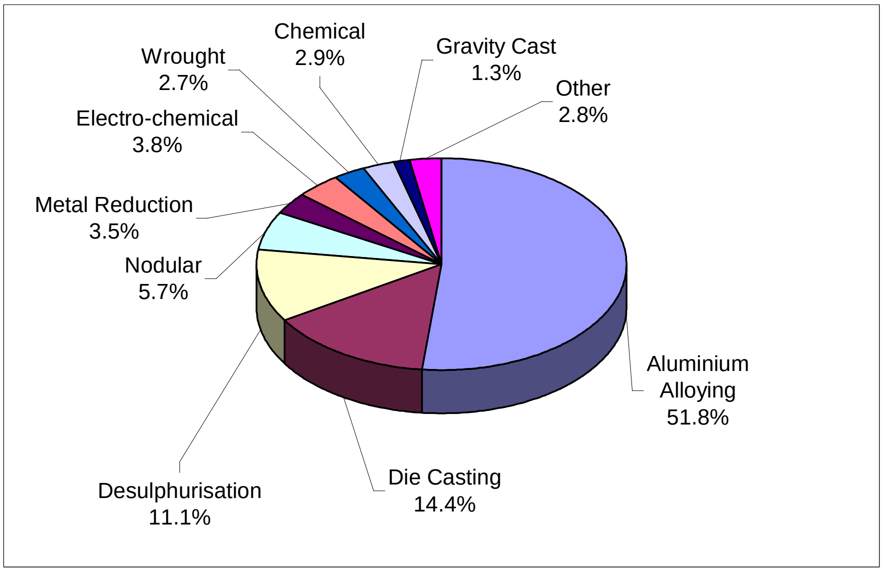


Figure 1.12: World use of magnesium metal

Calcium and strontium metal are used for a variety of purposes. Calcium as an alloying element improves the quality of steels especially the mechanical properties like formability, drawing and machinability. Because of its strong ability to form oxides and sulphites calcium is important in the production of ultraclean steel. Calcium metal may also be used for lead de-bismuthation. Strontium metal is needed in aluminium refining as well as for the rafination of steel slag.

1.10.3 Production and consumption

The production of alkali- and alkaline metals especially for the production of sodium, lithium, calcium and strontium metal is related to only a few companies. The world capacity for primary magnesium productions in the order of about 400000 tonnes per year, where the European production is about 57000 tonnes per year. The following tables gives an overview about the primary magnesium production capacity and the world wide produced amounts of primary and secondary magnesium by country [tm 189, D. Kramer, USGS 1997].

Continent and country	Capacity	Number of producers
North America:		
Canada	49000	2
United States	80000	2
Europe:		
France	17000	1
Kazakhstan (N 3)	10000	1
Norway	35000	1
Russia (N 3)	45000	2
Serbia and Montenegro	5000	1
Ukraine (N 3)	24000	1
Others		
China	~150000 - 200000	~200
India	900	1
Brazil	10000	1
Israel	27500	1
World total (N 1,2)	503400	~215

Notes:

N 1 Includes capacity at operating plants, as well as at plants on standby basis.

N-2 Data are rounded to three significant digits; may not add to totals shown.

N 3 Excluding magnesium production capacity that is used exclusively for titanium production.

Table 1.25: World primary magnesium production capacity by country

Country	1993	1994	1995	1996	1997 e/
Primary production:					
Brazil e/	9700	9700	9700	9000	9000
Canada e/	23000	28900	48100	54000	57700
China e/	11800	24000	93600	73100 r/	92000
France	10982	12280	14450	14000 e/	12000
Israel	-	--	-	-	8000
Japan	7471	3412	-	--	--3/
Kazakstan e/	2000	- 3/	9000 r/	9000 r/	8972 3/
Norway	27300	27635	28000 e/	28000 r/ e/	28000
Russia e/ 4/	30000	35400	37500	35000	39500
Serbia and Montenegro	- e/	-	2560	2500 e/	2500
Ukraine e/	14900	12000	10000 r/	10000 r/	10000
United States	132000	128000	142000	133000	125000 3/
Total	269000	282000	395000 r/	368000 r/	392000
Secondary production:					
Brazil e/	1600	1600	1600	1600	1600
Japan	13215	19009	11767	21243 r/	22797 3/
USSR e/ 5/	6000	5000	6000	6000	n.a.
United Kingdom e/ 6/	1000	1000	1000	1000	1000
United States	58900	62100	65100	70200 r/	80200 3/
Total	80700	88700	85500	100000 r/	106000

Notes:
1/ World totals and estimated data are rounded to three significant digits; may not add to totals shown.
2/ Table includes data available through July 22, 1998.
3/ Reported figure.
4/ Includes secondary.
5/ Dissolved in December. 1991; however, information is inadequate to formulate reliable estimates for individual countries of the former USSR.
6/ Includes alloys.
r/ revised
e/ estimated

Table 1.26: Produced amounts of primary and secondary magnesium in tonnes per year

1.10.4 Production sites

There are only a few production sites of sodium, lithium and potassium within the European Union. Sodium metal is produced by Associated Octel, a company located in the United Kingdom and a company who operates a sodium production in France. For the production of primary magnesium there are two companies in Europe. Hydro magnesium (NHM) operates an electrolytic magnesium plant in Porsgrunn, Norway, based on dolomite and seawater as raw material. Pechiney Électrométallurgie (PEM) operates a thermal reduction plant in Marignac in France, based on the Magnetherme process being a Pechiney developed process. There are some mostly smaller companies within the European Union producing secondary magnesium. In the European Union only one plant each produces calcium and strontium metal. Both plants are operated by Pechiney Électrométallurgie (PEM) in its factory at La Roche de Rame in France.

1.10.5 Environmental issues

The main environmental input by producing alkali and alkaline metals are air and water emissions. The generation of air emissions is due to dusty nature of some processes and unit operations that are used in the alkali and alkaline metal production. For instance unloading, crushing and calcining of raw materials are related to the generation of dust. Another main environmental issue is the emission of chlorine and chlorine related compounds like chlorinated hydrocarbons and dioxins. Chlorinated hydrocarbons and dioxin are mainly emitted in the chlorination process that is used in the electrolysis of magnesium. These pollutants need to be removed from the off-gas, which can be done by using a wet-cleaning system. This consequently results in pollulated washing water that itself needs an efficient wastewater treatment. Emissions to water are also be produced be washing the filter cake from a sodium process. To prevent the magnesium metal from re-oxidation by the surrounding air, sulphur-hexafluoride (SF_6) is used in the casting equipment, where it is also emitted to the atmosphere.

1.11 Nickel and Cobalt

1.11.1 Nickel

1.11.1.1 General

Nickel [tm 36, Panorama 1997; tm 94, Nickel Expert Group 1998] is a silver white metal with typical metallic properties. Although it was only discovered as a metal in 1751 its alloys have been used for several centuries e.g. the Chinese had been making "white copper" which resembled silver in appearance. Between 1870 - 1880, nickel's use in alloy steels was demonstrated and electrolytic nickel plating was successfully developed.

The great importance of nickel lies in its ability, when alloyed with other elements, to increase a metal's strength, toughness and corrosion resistance over a wide temperature range. Nickel is therefore an extremely important commercial element. Given these beneficial properties, nickel is used in a wide variety of products. Most primary nickel is used in alloys; the most important of which is stainless steel. Other uses include electroplating, foundries, catalysts, batteries, coinage, and other miscellaneous applications. Nickel is found in transportation products, electronic equipment, chemicals, construction materials, petroleum products, aerospace equipment, durable consumer goods, paints and ceramics. Nickel is a vital metal to industrialised societies.

Chemically, nickel resembles iron and cobalt, as well as copper. Nickel can form several compounds e.g. sulphate, chloride, oxide, and hydroxide. One property of nickel is its ability to react directly with carbon monoxide to form a binary carbonyl complex that is volatile at ambient temperatures. At moderate temperatures nickel is corrosion resistant against air, seawater, and non-oxidising acids. Another property of nickel is its corrosion resistance to alkalis. In contrast, nickel is attacked by aqueous ammonia solutions.

1.11.1.2 Sources of materials

Nickel is a naturally occurring element that exists in nature mainly in the form of sulphide, oxide, and silicate minerals. The deposits are of two main types: -

- Nickel sulphides often occur together with economically recoverable amounts of copper, cobalt, gold, silver, platinum group metals and several other metals. The most important occurrences are in Africa, Australia, Canada and Siberia.

- Nickel laterites are products of weathering of ultra-basic rocks that originally contained very small amounts of nickel. Over time impurities were washed out of the deposits and nickel is present as a complex oxide of silicon, iron and magnesium. Cobalt and iron are commonly associated with nickel, but laterites do not contain other valuable constituents. The most important occurrences are in the tropical areas in Southeast Asia, Australia, South-America, Caribbean Ocean and the Balkans area especially Greece, which is the only source of nickel ore in Europe at the time of writing.

The complex metallurgy of nickel is reflected in the wide range of extraction and refining processes in operation. Every plant presents a unique set of process features and environmental issues. The nickel content of sulphide ores usually can be concentrated several times by relatively economical ore dressing techniques before the concentrate is smelted and refined to nickel products.

Laterite ores, in contrast, are amenable to only limited benefication by physical methods e.g. magnetic or heavy media techniques, and therefore almost the entire volume of ore must go directly to metallurgical plants. Thus, laterite processing tends to be more cost intensive, but mining costs are usually much lower than for sulphide ores.

These differences, plus the availability of by-product value, can have an important influence on the viability of a specific deposit and whether refined metal or ferro-nickel is produced from it.

1.11.1.3 Production and consumption

Nickel products can be divided into three groups based in the Industry classification that is recognised internationally:

Class I - Refined nickel, nickel content 99% or more. The group includes electrolytic nickel, pellets, briquettes, granules, rondelles and powder/flakes.

Class II - Charge nickel, nickel content less than 99%. The group includes ferro-nickel, nickel oxide sinter and utility nickel.

Class III - Chemicals - nickel oxides, sulphate, chloride, carbonate, acetate and hydroxide, etc

The world production of nickel remained below 1000 tonnes per year until 1876; currently it is approximately 1 million tonnes per year. The world's primary nickel production in 1996 was approx. 950000 tonnes and the production capacity approx. 1200000 tonnes. In Europe the production capacity is approximately 200000 tonnes and the consumption is approximately 330000 tonnes therefore Ni is imported.

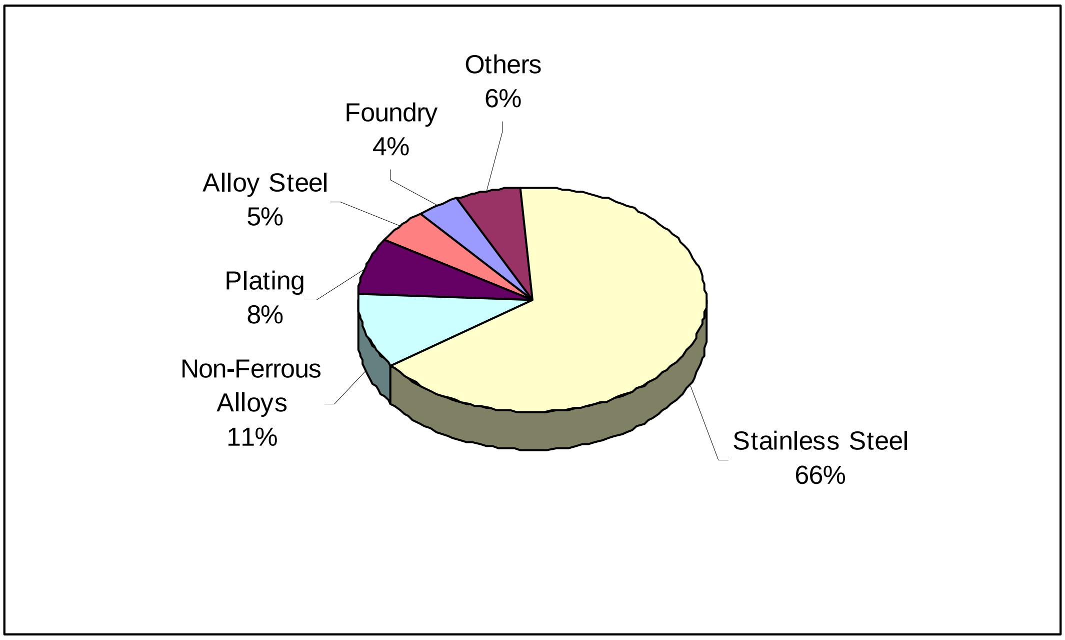


Figure 1.13: Western World uses of Ni in 1996

Western World nickel consumption increased by an average of 6.5% per annum from 1945 to 1974. Consumption dropped sharply in 1975, and the demand for nickel remained flat for the next ten years. Western-world nickel consumption increased respectively in 1987. The new recovery of nickel demand started in 1993 growing about 15% in 1995 in is continuing today. The world's nickel consumption in 1996 was approx. 940000 tonnes and demand is expected to remain strong.

1.11.1.4 Production sites

Nickel is produced in Europe at the following sites.

Producer	Source of Raw Material	Production Capacity t/a Ni	By Products
Outokumpu, Finland	Finland, Norway and Australia	36000	Cu, Co Sulphuric Acid
Eramet, France	New Caledonia	16000	Cobalt Chloride, Ferric Chloride.
Falconbridge, Norway	Canada & Botswana	85000	Cu, Co, Sulphuric Acid
INCO, UK	Canada	41000 (Ni powder and pellets)	Nickel Sulphate
Treibacher, Austria	Secondary	4000	FeNi is produced
Larco, Greece	Greece	20000	FeNi is produced
Total		202000	

Table 1.27: Nickel production sites

The actual production in total from the above sites was 167900 tonnes for 1996 compared to 144800 tonnes for 1994.

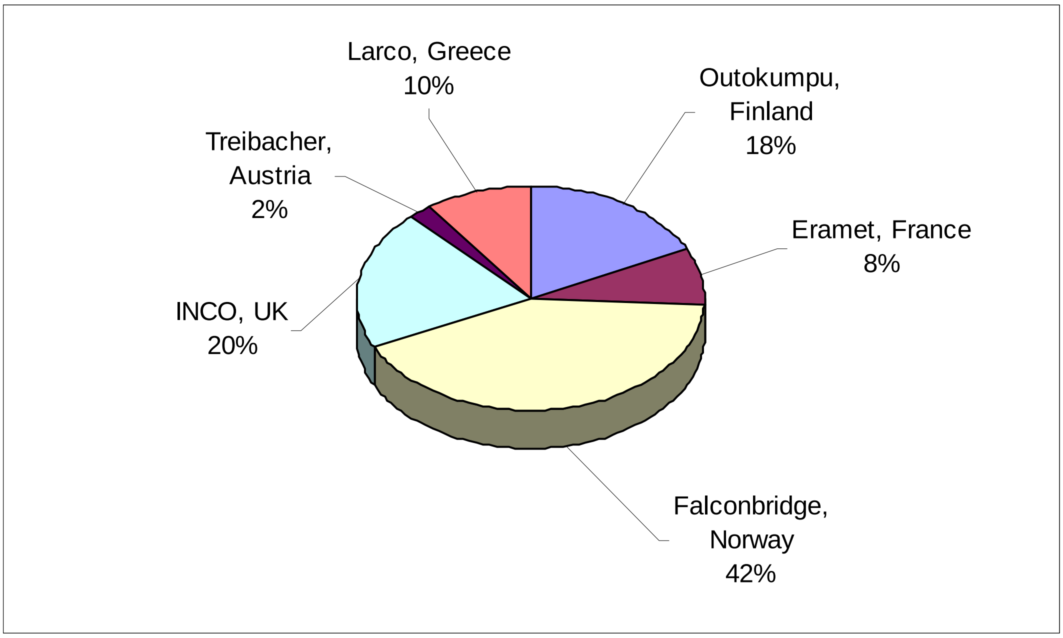


Figure 1.14: European nickel production

1.11.1.5 Environmental issues

The emission of sulphur dioxide to air from the roasting and smelting of sulphide concentrates is a potentially serious environmental issue. This problem has been effectively solved by the EU smelters who now achieve on average 98.9% fixation of the sulphur and produce sulphuric acid and liquid sulphur dioxide. Fugitive emissions of dust, metals and solvents are also an issue and need to be prevented and controlled. The use of chlorine in some processes is coupled with robust leak prevention measures and alarms.

The main environmental issues associated with the production of secondary nickel are also related to the off gases from the various furnaces in use. These gases are cleaned in fabric filters and so can reduce the emissions of dust and metal compounds such as lead. There is also the potential for the formation of dioxins due to the presence of small amounts of chlorine in the secondary raw materials and the destruction of dioxins is an issue that is being pursued.

The status of some nickel compounds has a significant impact on the assessment of emissions and nickel is listed in the Directive 76/464 Dangerous Substances Directive for Water in List II. A technical working group under Directive 96/62/EC Air Quality Assessment and Management is developing an environmental air quality standard for nickel. On the other hand, nickel has shown to be an essential element in certain micro-organisms, animals, and plants.

Nickel is a sustainable commodity. Stainless steel and other nickel bearing alloys are the primary sources of secondary nickel. It is estimated that around 80 per cent of the nickel is recycled from new and old stainless steel scrap and returns to that end use. Other nickel bearing materials such as precipitates and residues are recycled to primary production.

In many applications, nickel alloys are essential and cannot be substituted with other materials. The use of nickel in applications where its properties of strength, corrosion resistance, high conductivity, magnetic characteristics, and catalytic properties are exploited is seen as a positive environmental benefit. Similarly the use of nickel in rechargeable batteries is also of environmental benefit.

1.11.2 Cobalt

1.11.2.1 General

Cobalt [tm 36, Panorama 1997; tm 94, Nickel Expert Group 1998] is a silver white metal with typical metallic properties, it was first isolated in 1735. Pure metallic cobalt has few applications, but its use as an alloying element for heat or wear resistant applications and as a source of chemicals makes it a strategically important metal.

Although very little cobalt metal was used until the 20th century, its ores have been used for thousands of years as blue colouring agents for glass and pottery e.g. on Egyptian pottery around 2600 BC and on Chinese pottery around 700 AD for instance. The use of cobalt as metal dates from 1907 when E. Haynes patented a series of cobalt-chromium alloys named Stellites that were the forerunners of modern super alloys. Its ability to enhance the properties of permanent magnets was shown in 1930.

Cobalt is used in alloys including super alloys for aircraft engines, magnetic alloys for powerful permanent magnets, hard metal alloys for cutting tool materials, cemented carbides, wear- or corrosion resistant alloys, and electro-deposited alloys to provide wear and corrosion resistant metal coatings. Its use in rechargeable batteries has been a fast growing application over the last few years.

Cobalt chemicals are used in rechargeable batteries; as pigments in the glass, ceramics and paint industries; as catalysts in the petroleum industry; as paint dryers; and as trace metal additives for agricultural and medical use.

1.11.2.2 Sources of materials

From the beginning of the 20th century the world's main supply of cobalt moved from Europe to Africa, Australia, Russia and Canada. Production today is around 30000 t/a.
Cobalt is produced mainly as a by-product of the mining and processing of copper and nickel ores. Silver, gold, lead and zinc ores may also contain considerable amounts of cobalt, their processing does not always lead to recovery. The sources of ores are: -

- the copper-cobalt deposits in Congo and Zambia
- the nickel sulphide ore bodies in Australia, Canada, Finland and Russia
- the nickel oxide ore bodies in Cuba, New Caledonia, Australia and Russia.

Recovery from secondary sources can occur through introduction of the recycled material at an appropriate stage in a primary refining or transformation process, depending on its technical and economical capabilities. Additional or pre-treatment steps may be necessary. The final products can be cathodes, powders, oxides, salts or solutions.

1.11.2.3 Production and consumption

Primary cobalt always occurs associated with other metals, particularly copper and nickel, and these usually are predominant. Depending on the feed material several processes have been developed which can involve pyrometallurgical as well as hydrometallurgical steps. These steps produce either: -

- a cobalt-rich solution in integrated plants
- a cobalt-rich sulphide, hydroxide or carbonate if further refining is done elsewhere
- a cobalt-rich alloy.

Further refining is hydrometallurgical, although the final stage, the production of a commercial product, can be a high temperature process; especially when the product is a powder and the refining activity integrated in the transformation process. Worldwide production capacity is approximately 30000 tonnes.

Cobalt is used for variety purposes and these are shown in the following table.

Uses	Breakdown of the total cobalt production
Alloys	34%
Ceramics	12%
Hard metal	11%
Magnets	10%
Catalysis	8%
Cutting tools	6%
Batteries	6%
Magnetic tapes	4%
Others	9%

Table 1.28: Breakdown of the total cobalt production to the different sectors of use

Demand for cobalt in the western world is around 25000 t/year, Europe accounts for approximately 25% of this. The use of cobalt in batteries is a growth area and this requires cobalt metal, oxide or hydroxide powder, the morphology of the powder is an important factor.

1.11.2.4 Production sites

Cobalt and cobalt compounds are mainly produced at the same sites that produce nickel. The sites are shown in table 1.27 (under nickel). Additionally Union Miniere in Belgium also produces cobalt.

The Worldwide production is shown in the following figure.

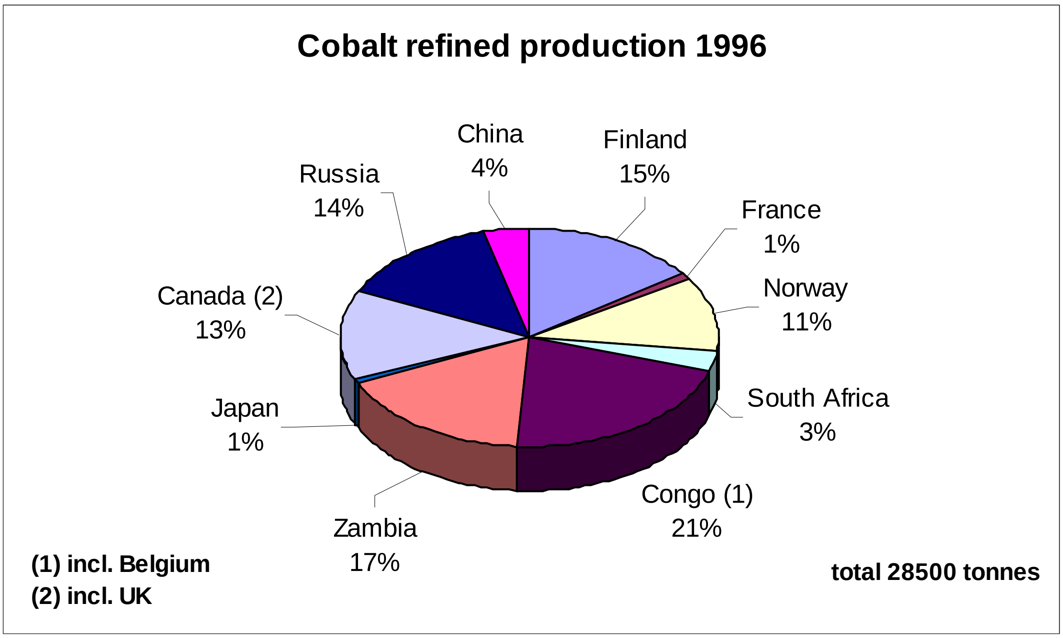


Figure 1.15: Worldwide cobalt production

1.11.2.5 Environmental issues

The status of some cobalt compounds has a significant impact on the assessment of emissions and cobalt is listed in the Directive 76/464 Dangerous Substances Directive for Water in List II. There are potential dust and metals emissions from grinding operations, and to a lesser extent from the hydrometallurgical operations; chlorine in electro-winning and VOC's in solvent extraction; metals in the effluents of hydrometallurgical purification and recovery operations; solid waste from purification and effluent treatment. The industry uses a variety of techniques to recover and produce cobalt depending on the raw materials and end products mix essentially, and the actual occurrence and significance of these issues is therefore site specific.

The use of cobalt in rechargeable batteries is an environmental benefit.

1.12 Carbon and Graphite

1.12.1 General

There is a vast range of carbon and graphite products that are in use at the time of writing. They range from large electrodes to small bushes and bearings. Other specialist products such as carbon fibres and carbon composites are also made for high technology industries that require the very high strength and low weight of these materials.

Carbon exists in three forms, diamonds, graphite and amorphous carbon. The difference between the allotropes is essentially the structure of the carbon atoms and the structure determines the properties of the resulting material. Carbon and graphite products are applied in multiple applications because they can be designed to have specific strength, toughness, electrical and mechanical properties and especially highly purity and chemical resistance under oxygen free conditions etc., to meet the requirements of particular applications [tm 207, TGI 1999].

Carbon and graphite materials are mainly applied for the conduction of electrical power (cathodes and graphite electrodes) and as chemical reducing agent in the aluminium industry (anodes).

Carbon and graphite products can basically divided into for product groups.

• Green mix and paste	Mainly used in the aluminium-, ferro alloys- and for blast furnaces in the steel industry.
• Anodes	Mostly used in the aluminium industry as reducing chemical agent.
• Carbon and graphite	Mostly used for recycling of steel in the arc steel furnace and as cathodes as not consumed electrode in the aluminium industry.
• Speciality carbon & graphite	A wide range of products ranging from very high purity to very high mechanical strength and thermal resistance

The application of carbon specialities can roughly divided into

- high purity carbon and graphite
- highly mechanical and thermal applications
- engineered products like carbon and graphite fibres,
- graphite foils and process equipment

Carbon or graphite anodes and furnace linings are produced for a variety of ferrous and non-ferrous metal production processes and are consumed during the production of the metals. More than 2000 other products of varying sizes, shapes and properties are produced for other applications. Carbon and high purity graphite materials are essential for the production of semi-conductors and microchips, graphite electrodes for the recycling of steel scrap and highly chemical resistant carbon and graphite are used for the recovery of residuals and the treatment of pollutants.

1.12.2 Sources of materials

The production of carbon and graphite materials are mainly based on petroleum coke and coal and a highly annealed coke based on coal tar. Petroleum pitch and coal tar-pitch are used as a binder material, which is finally converted to inert solid carbon or graphite. Resin based binder systems are used, which are cured before application.

The quality of coke varies depending on the source but the most important factor is the sulphur content of the coke as this will be emitted as sulphur dioxide during manufacture or use. Normally petroleum based cokes of a low or medium sulphur content are used for the major product like paste, anodes and electrodes.

The properties of the raw materials have to be very constant and are controlled by physical and chemical tests. New raw materials are tested in production trials to check their suitability and to adjust the production parameters to the new material. The final quality of raw materials is only based on the performance and acceptance of the manufactured carbon and graphite product.

Other materials are used in the production of specialist carbons and include metal and metal powders and a variety of resins.

1.12.3 Production and consumption

Coke or carbon is usually bound with pitch (14 to 18% by weight) to produce a green paste. This paste then undergoes a number of shaping, baking, impregnation and graphitising stages to produce the final product. Green paste is also used directly for Søderberg electrodes. The baking process results in a loss in weight of ~ 5% of the mass of the material. Packing coke is used in certain furnaces and in these cases is consumed at the rate of ~14 kg/t of product.

Carbon and graphite are mostly consumed during their application and converted into carbon dioxide (i.e. anodes for aluminium and steel electrodes). Steel production consumes electrodes at the rate 1.5 to 3 kg per tonne of steel. Due to the significant reduction of the consumption rates in some industries, the quantities of carbon and graphite used for the production of aluminium and steel has been reduced.

The processing stage and size of the process varies according to the product. The aluminium industry is by far the largest user of carbon materials as pre-bake anodes, Søderberg paste and cathode blocks. Generally the specialist graphite products are smaller in scale than electrode producers. The following table shows the size of the various production areas.

Product type	Production t/a
Green mix for Søderberg electrodes or paste.	410000
Anodes for primary Al.	1380000
Electrodes.	420000
Speciality carbon and graphite.	25000

Table 1.29: Annual production of carbon and graphite in EU and Norway

1.12.4 Production sites

Carbon and graphite products are made at 88 sites in EU with an annual capacity of ~ 2 million tonnes.

Country	Green mix pate	Anodes	Electrodes, large shapes	Carbon & graphite specialities
Austria			15(1)	0.2(1)
Belgium			18(1)	
Denmark				
Finland				
France		214(1)	62(2)	16(3)
Germany		450(4)	117(3)	6.2(4)
Greece		77(1)		81
Ireland				
Italy		85(1)	89(2)	0.2(1)
Luxembourg				
Netherlands		479(2)		
Portugal				
Spain	81(1)	100(1)	52(2)	
Sweden	37(1)	13(1)	34	
UK	7(1)	148(3)	11(1)	2.2(1)
Iceland				
Norway	221(3)	162(2)		
Switzerland				
Notes: The number in brackets presents the number of producers in the EU				

Table 1.30: E U Production of carbon & graphite in 1000's of tonnes in 1998

The following figure shows the distribution of the Industry throughout Europe.

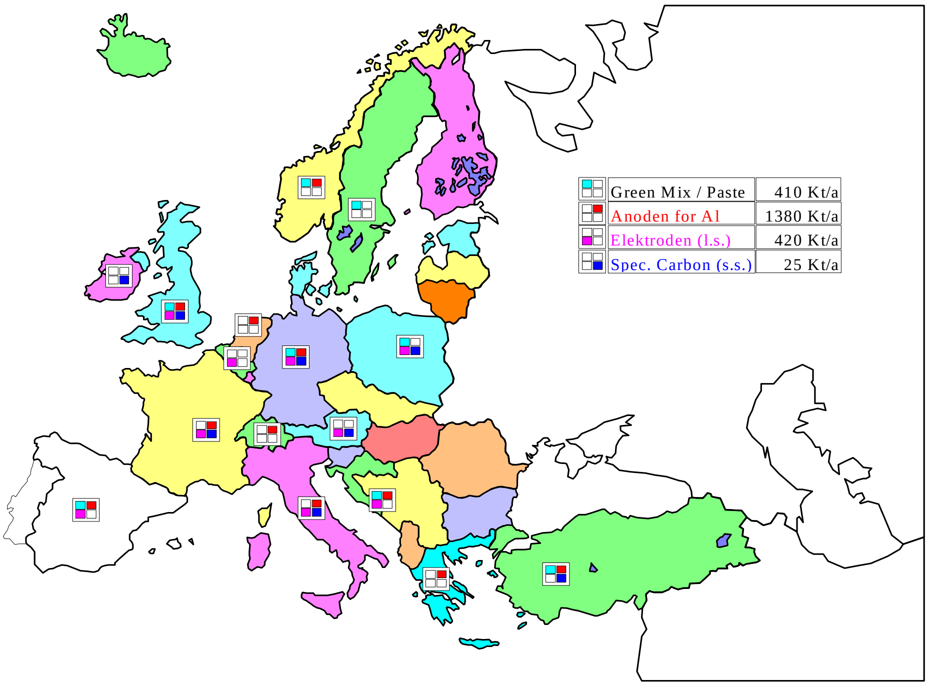


Figure 1.16: European production sites for carbon and graphite

There is a strong tendency to close on-site anode production and to switch to an off site supply. Some of the larger on-site producers with capacities up to 150000 t/a supply also smaller primary aluminium smelters with anodes. The biggest carbon producing plant in Europe and probably in the world is located in Netherlands with a production capacity of 340000 t/a and will be extended to 375000 t/a. Nevertheless the major quantities of anodes is still produced in numerous on-site units.

A few companies only produce cathodes due to the fact that there is a very high life time cycle demanded by the aluminium industry. The life cycle of a cathode block ranges from 6 to 10 years. The properties have to guarantee a very good performance in respect of lifetime, electrical resistance and abrasion.

1.12.5 Environmental issues

The main environmental impact of these processes is the impact of emissions to air of tars and PAHs, sulphur dioxide from coke and fuels and VOCs from impregnating agents. A variety of new abatement processes have been developed to destroy tars and PAHs using novel after-burning systems.

The main environmental issue for the production of carbon and graphite is the use of poly-aromatic, complex mixtures of binder and impregnation pitches.

The pitches release poly-nuclear hydrocarbon compounds while being carbonised. Benz(a)pyrene is used as an guideline substances to monitor the character of the emissions.

Emissions occur during the storage of pitch, mixing and shaping, while carbonising in the baking furnaces and during impregnation.

If cokes with increased sulphur content or sulphur additives are used during the production of carbon speciality products sulphur dioxide might be formed and released.

Dust or particulate emissions are potentially significant. Fine-grained materials are normally not used for paste, anode and electrode production, but are for other products.

The progress in the applied techniques to control the impact on the environment has been significant.

Water pollution is in general a minor issue of the carbon industry, production processes are dry and generally use contained cooling water systems. Exceptionally, surface water for cooling may be used where it is suitable due to local conditions.

Most successfully are the efforts of the carbon and graphite industry in recycling carbon materials (used and unused) and to open new fields of applications of these materials, replacing other natural sources.

2 COMMON PROCESSES AND EQUIPMENT

2.1 Organisation of the chapter

There are many processes, variations in equipment and techniques that are used for the production of non-ferrous metals. These processes and variations need to be treated in a logical manner to allow the information to be presented clearly. Many of the techniques and individual stages of the production processes are common for most of the non-ferrous metals produced and these common stages can be described together to avoid too much repetition. These common stages can be divided as follows: -

- Management, design and training;
- Receipt, storage and handling of raw materials;
- Pre-processing and pre-treatment of raw materials and transfer to production processes;
- Furnace types and process control techniques;
- Fume collection and abatement techniques;
- Water reuse and effluent treatment;
- Prevention, minimisation, recycling and treatment of process residues (including by-products and waste).

In addition the following common issues are covered in this chapter.-

- Emission measurement and use of emission data;
- Energy and waste heat recovery;
- Cross media issues;
- Noise and vibration;
- Odour;
- De-commissioning;

Techniques for reducing the environmental impact of an installation can be described in three categories: -

- management techniques: - relating to the systems and procedures for designing and operating a process and for training operators and other staff;
- process integrated techniques: - relating to the use of techniques to prevent or reduce emissions from activities such as storage, reaction, separation and purification;
- energy reduction and abatement techniques: - relating to end-of-pipe techniques to reduce emissions to air, water and land.

This chapter briefly describes the common techniques covering these three categories that are used in this sector. An indication is given where possible of the techniques that are able to prevent or reduce emissions to each environmental media. This chapter also indicates where these techniques can be used in the various process stages to improve existing processes. This theme is developed in the metal specific chapters that follow.

The **metallurgical production processes** for the 10 Groups identified by the Technical Working Group are covered in chapters 3 to 12 respectively. The techniques to consider in the determination of BAT in these chapters include more detailed process descriptions, examples and diagrams. They also provide more detail of how the integrated process operates and where the variations in the techniques described in Chapter 2 are used e.g. the way furnaces differ from the generic description. This approach has been used to minimise repetitive descriptions and to allow the transfer of information and techniques across the ten groups.

Best Available Techniques are not specified for all of the common processes described in this chapter but the various common processes and techniques will contribute to the Best Available

Techniques described in chapters 3 to 12. Additionally, the techniques described in this chapter are also suitable for reducing the overall emissions and will therefore influence the way existing plants are improved.

Chapter 2 should be used in conjunction with chapters 3 to 12 to give the complete production cycle e.g. chapters 2 and 3 will give the overall range for the production of copper and its alloys.

2.1.1 Installations that produce a number of metals or have associated processes on-site.

A significant number of installations produce a number of metals from different groups or may have associated processes integrated with them. Examples are the processing of bauxite at an aluminium smelter, the presence of an anode production plant at an aluminium smelter or the production of a range of different metals from complex raw materials in particular Cu, lead, zinc and precious metals.

The elements of Integrated Plants may be found in different parts of the BREF e.g. anode slime details in precious metals; prebaked anode details in Chapter 12 and other metals within their metal specific chapter. The chapter describing the main metal will contain some references to these processes e.g. anode slime production in Cu chapter and the presence of an anode plant in Al chapter. This section on integration will explain where these sections and cross-references are and will advise how a complex plant can be approached.

Materials produced in the same Installation	Chapters containing process and other details	Chapters containing overview	Comment
Alumina from bauxite in an Al smelter	Chapter 4 Aluminium	Chapter 4 Aluminium	Integrated with a few Installations
Prebaked anodes produced in an Al smelter	Chapter 12 Carbon & Graphite	Chapter 4 Aluminium	Factors of common abatement taken into account.
Lead, zinc, precious metals with the production of copper	Chapter 5 Lead, Zinc and Chapter 6 Precious Metals	Chapter 3 Copper (plus the main Cu detail)	Some duplication between Cu and the other chapters.
Nickel, cobalt and copper	Chapter 3 Cu and Chapter 11 Ni, Co	Chapter 11 Ni, Co	
Mercury during the production of other metals	Chapter 7 Mercury Chapter 2	Chapter 3 Cu Chapter 5 Pb, Zn	Mercury removal from smelter gases before acid plant.
FeCr, FeSi, FeMn etc	Chapter 9 Ferro Alloys	Chapter 9	Factors of common abatement taken into account. Energy recovery
Refractory metals	Chapter 8 Refractory metals	Chapter 8	
Ferro alloys and refractory metals	Chapters 8 and 9	Chapters 8 and 9	

Table 2.1: Processes that may form integrated installations

2.2 Emission measurement and use of emission data

This section is intended to ensure that the emissions reported in this document are measured in such a way that the results are representative, mutually comparable and clearly describe the relevant operating state of the plant. The methods and instruments used should be the relevant National or International Methods (e.g. European Committee for Standardisation [CEN]; ISO; VDI Richtlinien; Netherlands Emission Regulations - Ch4 [NER]; UK Guidance Notes: British Standards etc.). General principles are given below.

2.2.1 Measurement of emissions

The measurement of emissions is used to determine the substances in the clean gas or wastewater so that they can be reported, used to control the process or abatement plant or used to predict environmental impact. Fugitive (uncaptured) emissions can also be estimated using measurement. Prior to measurement plans can be made to take account of: -

- the mode of operation,
- the operating state of off-gas purification or effluent treatment plants,
- operating conditions in the plant (continuous, discontinuous, start-up and shut-down operations, load change) and
- the effect of thermodynamic interference factors.

These factors can then form the basis for the selection of operating conditions at which: the highest emissions may be recorded; the number and duration of the measurements chosen; the most appropriate method of measurement chosen; and the position of the measurement locations and points determined. For wastewater emissions these qualified random samples can be used or 24 hour composite samples based on flow proportional or time averaged samples taken.

For continuous operations, a minimum sample collection time or measurement time of half an hour (half-hour mean value) is usually necessary. If dust contents are low or if PCDD/PCDF are to be determined, longer measurement times and consequently, other reference times may be necessary because of the limitation of detection. Sampling or measuring should take place only during the operation of the process and dilution air should be excluded. For continuous operation when only slight fluctuations in the emission characteristics, 3 individual measurements can be performed at the highest emission level. If it is anticipated that the emission level will be very variable during continuous operation, more measurements can be carried out; the sampling and averaging time being limited to the emission phase.

For batch operation, the measurement time and the averaging time should be modified so that a sample or samples over the whole batch can be taken. These results can be used to calculate averages or to show where peaks occur during the cycle. Again sampling or measurements should only be made during periods of operation and dilution air should be excluded.

2.2.1.1 Sampling locations

The sampling points should meet the requirements of the relevant National Guidelines. The sampling points should normally: -

- be clearly marked,
- if possible, have a disturbance-free flow in the measurement section,
- have monitoring points that can be closed,
- have the required energy supplies,
- have sufficiently large working platforms, and
- ensure that the requirements for safety at work are met.

2.2.1.2 Components and parameters.

The most common components that are measured in the Non-ferrous Metals Sector include dust, metals, sulphur dioxide, total carbon (also VOC, tars and hydrocarbon), dioxins, oxides of carbon and nitrogen oxides. Acids such as HCl and HF are determined for some processes as are chlorides and fluorides. Specific determinands includes PFC and PAH for primary aluminium, PAH for carbon and graphite and some determinands that are specific to some of the reagents used for precious metals production. The components are reported in the Metal Specific chapters, methods of analysis are given in the relevant National and International Guidelines on monitoring and analysis.

The analysis of some parameters may be covered by methods established by other bodies for example OSPARCOM. In this particular case at the time of writing, several of the methods used in the sampling and measurement of emissions from the primary production of aluminium and the production of pre-bake anodes are defined by OSPARCOM or are subject to assessment. The measurement and determination of PAHs in particular is the subject of a review. The number of PAHs to be determined and the protocol for reporting some or all of them is not certain at the time of writing and the future recommendation from OSPARCOM may resolve this.

2.2.1.3 Reference conditions

For emissions to air, the following off-gas parameters should also be determined to convert the emission concentrations obtained to standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas: -

- the volumetric off-gas flow (in order to calculate the concentration and emission mass flow),
- the off-gas temperature,
- the water vapour content of the off-gas,
- the static pressure in the off-gas duct and
- the atmospheric pressure.

The production rate can also be reported so that the emissions can also be reported as specific emissions per tonne of metal. The specific gas volume m^3 per tonne of metal can also be calculated.

2.2.1.4 Continuous measurement

Continuous measurement of several components in gases or in wastewater is possible and in several cases accurate concentrations can be reported continuously or as mean values over agreed time periods (half hourly, daily etc). In these cases an analysis of the averages and the use of percentiles can allow a flexible method of demonstrating compliance with permit conditions and the averages can be easily and automatically assessed.

Methods are available to continuously measure: -

- Dust
- SO_2
- NO_x
- CO
- Fluorine and its compounds
- Chlorine and its compounds
- Total Carbon

Competent authorities may require continuous measurement depending on the mass flow of the pollutant. Conductivity, turbidity, pH and some ionic species can be continuously monitored for water.

Even in cases where absolute values may not be agreed as reliable the use of continuous monitoring can be used to give trends in emissions and as control parameters for the process or abatement plant and are therefore very important.

Some physical parameters can also be used to give an indication of the presence of certain components in the gas stream. For example the presence of an anode effect can indicate the production of PFCs in primary aluminium production and the temperature, oxygen and dust content of the gas can give an indication of the destruction of dioxins. pH can also be used to indicate the effective precipitation of metals.

2.2.2 Reporting emission data

Any measurement report and measurement protocol drawn up should conform to the relevant National and International Guidelines.

The report can contain:

- the objective,
- general information on the measurements,
- a description of the plant, its state and operating data,
- operating conditions during the measurement,
- information on the measurement planning,
- sampling locations,
- methods of measurement,
- tabular presentation of the individual measurements including temperatures, gas flow rates or volumes,
- evaluation of the results,
- consideration of errors,
- presentation of the quality assurance measures, and
- an abstract.

Present emission data in this document is normally reported as hourly or daily averages or as mass emissions per unit tonne of production, dilution of the gases or wastewater is not considered to be acceptable. Both methods of reporting are useful in defining the performance and impact of a process. Competent authorities normally use concentration units (mg/Nm^3 or mg/l) and/or specific emissions factors (g/t of metal) in their permits or in the data reported for emissions. The two forms of data can be linked provided data is available for the gas volumes of all of the process stages. This is not always the case and therefore in this document the emissions associated with the use of BAT are normally given as daily concentration averages based on continuous monitoring during the operating period. The standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas are used.

In cases where continuous monitoring is not practicable the value will be the average over the sampling period. Concentrations of metals or other substances in water or wastewater are given as a total of soluble and insoluble material. The emissions to water that have been reported or are associated with BAT are based on a qualified random sample or a 24-hour composite sample.

At the time of writing there has been insufficient reliable data reported to allow specific emissions associated with BAT to be reported in parallel with concentrations

2.2.2.1 Interrelationship between concentration and specific emissions.

Where information is available, an interrelationship can be provided to transform concentration units into specific emissions factors. Emission data in both forms is very useful for the regulator and operator. However when comparing or converting data in these forms, great care is needed to take account of fugitive (uncaptured emissions). Fugitive emissions can form the major portion of the total emissions, depending on the process.

In the following example a simple conversion of annually averaged emissions is used to show how to convert the concentration of the pollutant of concern (mg/Nm^3) into the specific volumetric loading (m^3/t of metal) and the specific emission factor (g/t of metal). For a complex site the total of all metals produced would be normally used to present the specific emissions.

a) Measured dust concentration on an annual basis, which is normally available as a range from continuous monitoring (mg/Nm^3)
b) Annual average dust concentration (mg/Nm^3)
c) Volumetric off-gas flow rate on a hourly basis (Nm^3/h)
d) Yearly operating time (h/a)

c × d = e

e) Annual off-gas volume (Nm^3/a)

b × e = f mg/a

f) Annual dust emission (kg of pollutant/a)

g) Annual production capacity (t of metal /a)

e ÷ g = h

h) Specific off-gas volume (Nm^3/t)

f ÷ g = i kg/t

i) Specific emission factor (kg/t of metal)

This calculation is based on the reliable knowledge of the following data:

- Dust concentration on an annual average basis (mg/Nm^3)
- Volumetric off-gas flow rate on a hourly basis (Nm^3/h)
- Yearly operating time (h/a)
- Annual production capacity (t of metal /a)

The above interrelationships are based on the knowledge of measured values for instance the range of annual dust concentrations and actual volumetric flow rate, which then need to be transferred into annual averages. The results of these calculations are only valid for captured emissions and are based on average values.

In the case of a new plant or a substantial change of an existing installation, the above interrelation may be based on theoretically calculated or estimated values. The data should take account of any uncertainties in measurement, for example the volume of the off-gases from any single process may vary with the composition of the concentrate. Reliance on the designed fan capacities can lead to errors in the estimates as variable speed fans are commonly used. This problem of volume measurement is also encountered in the estimation of uncaptured or fugitive emissions, the sampling and measurement of fugitive gases is also uncertain at the time of writing.

2.2.2.2 Uses of emission data

Where information is available, the calculation of the annual dust emissions (kg/a) and the specific emissions factors of a pollutant (g/t of metal produced) allows:-

- The magnitude of individual sources of emissions to air and water can be identified either within an installation or between installations.
- Fugitive emissions can be reported as mass emissions per unit of time or as Mass per tonne of metal produced. See section 2.7.
- The provision of a basis for setting priorities for the future environmental management of a plant or the application of a "bubble concept" for emissions to air or water over a complex site if this is desired.

The following table gives figures of annual dust emissions from some parts of a primary copper production process [tm 213, PRAM 1999] producing 170000 t/a blister copper.

System	Specific emission factor for dust [g/t of Cu]
Dryer	0.2
Roaster	1.5
Converter shaft filter	0.7
Pelletisation	0.1
Slag granulation	7.2
Anode caster	36.7
Hall ventilation	19.3

Table 2.2: Example of priority setting data

In this particular case the equation **[b × e =f]** allows the specific emission of dust to be calculated and leads to the conclusion that the anode caster and the hall ventilation are the largest single sources of dust emissions and can be given priority.

- The long term and long range effects of emissions can be determined by using dispersion modelling and other techniques.

The use of tall chimneys is used to improve the dispersion of gases and this can result in environmental impacts far beyond the installation. Components such as sulphur dioxide can have very long range, accumulative effects and in some cases "critical loads" for some species can be exceeded for some pollutants. Dispersion is therefore not a substitute for low emissions.

The use of concentrations based on defined parameters and methods of measurement allows many parameters to be monitored continuously. These parameters can be linked to the abatement system that is used. Concentration measurement allows:-

- Easy demonstration of compliance.

- Demonstration of "real time" performance.

- A high degree of abatement control and an early warning of equipment failure.

2.3 Management systems

Effective management is important in achieving good environmental performance. It is an important component of BAT and forms part of the definition of techniques given in Article 2 of the Directive.

The work undertaken in preparing this document has shown that there are many significant differences between the environmental performance of a process that is managed and operated well and an identical process that is managed and operated poorly. Management and communication systems are some of the most significant factors in this difference.

Achievement of a good performance requires commitment at all levels within a company staring at Board or policy level and include the site management, supervision and operators. The system needs to establish objectives, set targets and communicate instructions and results. Environmental management systems such as ISO14001 and EMAS or a quality management system such as ISO 9000 can assist by formalising the system.

Although they are not a requirement of the Directive, an installation should consider the benefits that can arise from adopting such a system. The techniques used can also improve economic performance by improving operating efficiency, reducing costs such as energy or disposal costs and improving metal yields. These techniques are therefore essential factors for a modern installation.

2.3.1 Management policy and commitment

An effective management system can include the following factors: -

- Identification of all health, safety and environmental impacts of activities, products and processes.
- A commitment to develop and implement the measures identified.
- The communication of the policy to employees and contractors to ensure that they are aware of the commitment and are involved in its delivery.
- The use of a clear structure for managing environmental issues that is fully integrated with the wider company and site decision- making systems.
- The environmental performance of the process is highly dependent on the attention and awareness of the process operator. Awareness of this and their role in the environmental performance is important.
- The overall environmental performance can be monitored on a regular basis and the results can form part of the management assessment process. Environmental performance indicators can be devised and disseminated to operators, feedback from operators can be obtained and used.
- Contingency plans can be prepared which identify the potential types of incident that can occur and provide clear guidance on how they will be managed and who is responsible. Procedures can be prepared to identify, respond to and learn from all complaints and incidents.
- Where new processes are being commissioned, or where existing processes are being re-commissioned after alterations, a commissioning plan can be prepared that clearly identifies the issues and the person(s) responsible for the environmental performance of the process during the commissioning period.

2.3.2 Design and maintenance

The Directive requires the achievement of “a high level of protection of the environment as a whole”. Design and maintenance have the main influence on fulfilling this requirement by assessing the effect of existing plant and any new or substantially changed processes on the degree of protection of air, water and land. This requirement can be achievedas follows: -

- The environmental implications (including noise) of a new or substantially modified process or raw material should be considered at the earliest stages of the project and should continue to be reviewed at regular intervals thereafter. This is the most cost-effective time to introduce improvements in overall environmental performance. An audit trail of the design and decision-making process is a useful method to show how various process and abatement options were considered. Commissioning issues should be planned for new or modified plant.
- Potential fugitive emissions should be considered at all stages.
- A programme of preventive maintenance should be used and be recorded. It should be coupled with diagnostic testing where appropriate.
- Local extraction systems should be examined regularly and defects or damage repaired promptly.
- All staff can be made aware of the role they can play by maintaining vigilance, for example, in relation to damage to hoods and duct work or plant failures. Appropriate procedures should be used to encourage staff involvement and respond to reports.
- An internal procedure should be used to authorise modifications and to undertake checks after modifications before a process starts up.

2.3.3 Training

- All staff should be aware of the implications to the environment of the process and their work activities.
- There should be a clear statement of the skills and competencies required for each job.
- Training given to staff involved in process operation should include the environmental implications of their work and the procedures for dealing with incidents.
- Records of the training given to process operation staff can be very useful in ensuring progressive and complete training.
- Training of other departments in the environmental issues and consequences that affect the installation can also be effective in preventing conflicts that affect environmental performance. For example finance and sales teams can have significant influences on environmental performance. For example full accounting measures can identify excess raw material usage and can identify true energy and disposal costs for process stages; unplanned deliveries and sales can lead to production short cuts and cause incidents.

2.4 Receipt, storage and handling of raw materials and residues

The main raw materials used by the production of non-ferrous metals are ores and concentrates, secondary raw materials, fuels (oil, gases and solid fuel) and process gases (such as oxygen, chlorine and inert gases). Other materials such as fluxes, additives and process chemicals (e.g. for abatement systems) are also used. This variety of materials possesses many handling and storage problems and the specific technique used depends on the physical and chemical properties of the material. The study identified that the following techniques are used.

2.4.1 Applied processes and techniques

2.4.1.1 Ores and concentrates

Ores and concentrates may be delivered to site by road, rail or ship. Dust collection and abatement systems are used extensively at these points.

Process control is becoming more important to improve conversion efficiency, reduce energy consumption and reduce emissions and is frequently based on effective sampling, analysis and recording of raw materials to establish optimum process operating conditions. This influences the choice of techniques for storage and handling.

The unloading, storage and distribution of solid material is carried out by similar techniques to those used for solid fuels. Generally more stringent containment methods are adopted for these materials as they are generally more reactive, have a smaller particle size and are more easily suspended in air or washed into water. Automatic quick sealing devices are commonly used. Fluxing and slagging agents are also received on site and are handled in a similar manner to ores and concentrates.

Ores or concentrates (if they form dust) and other dusty materials are usually stored in enclosed buildings. Closed, covered stockpiles and silos are also used. Open stockpiles are used for large, lumpy material but are usually formed on a hard impervious surface, such as concrete, to prevent material losses, land contamination and contamination of the ore. Some large materials are not stored on a hard surface as damage to surface can frequently occur and cause hidden problems. Bays are often used to segregate different grades of ore.

Ores and concentrates are normally used by large installations and therefore silos are not frequently used for primary storage but can be used for intermediate storage and the preparation of ore/flux blends. “Loss in weight” silo systems and belt weighers etc. are used to meter ores and fluxes to achieve effective optimum blends and improved process control.

Water sprays are frequently used to suppress dust but some operators require dry feed to the processes and are reticent about using water sprays. Alternative methods, such as using atomising sprays to give fine water mists, are used for dust suppression without over wetting the material. Some concentrates naturally contain sufficient water to prevent dust formation.

Sealing agents (such as molasses, lime or Poly Vinyl Acetate) can be used to prevent dust formation in windy conditions. Sealing can prevent oxidation of surface layers and subsequent leaching of material to ground or surface waters.

Unloading minerals may be a potential source of significant dust emissions. The main problem occurs when a rail car or other tipping vehicle discharges by gravity. The rate of discharge is not controlled and results in a high volume of displaced air and dust, which can overwhelm dust extraction systems. Enclosed delivery halls using automatic door closing are used.

Polycarbonate screens, which seal against the tipping car, are used. In this case, displaced air is passed to a sprung section and surge container to absorb the energy of the discharge; the increase in air volume is damped, allowing the extraction system to cope.

Material can be reclaimed by underfeed conveyor, grab crane or front-end loader, totally enclosed conveyors are used to transport dust forming material. Transfer by pneumatic, dense phase systems is also used. For dust forming materials extraction and filter systems may be used to deal with dust from static off-loading points and conveyor transfer points. In case of using open conveyors dust can be produced if the belt is running too fast (i. e. more than 3.5 m/s). When a front-end loader is used dust can be generated during the whole transport distance.

Solids may adhere to wheels and other parts of vehicles and will contaminate roadways both on and off site, the use of wheel and under-body washes (or other cleaning techniques if freezing temperatures are encountered) to decontaminate vehicles are frequently employed.

Road sweepers or other specialised equipment using a combination of water jets and vacuum collection are commonly used to keep internal roads clean.

Materials that contain components with a high environmental concern e.g. lead and cadmium are treated with the most effective of the measures reported.

2.4.1.2 Secondary raw materials

This industry is particularly active in recovering metal from a variety of sources and consequently uses a wide range of secondary raw materials. Scrap metal, skimmings, flue or filter dusts and drosses are used as sources of non-ferrous metals and these materials contain a number of metals or metal compounds. Secondary raw materials are also used in some primary processes.

The source of the secondary raw material may give information of the potential emissions due to the presence of acids, oils, organic contaminants (that can produce dioxins during melting processes), anions and components such as ammonia from the reaction of skimmings with moisture. This directly influences the potential emissions to air, water and land and any of the components of these materials can be emitted. Materials are checked (e.g. by inspection and sorting) for unforeseen impurities and contamination and this can be cost effective in maintaining a cleaner product and reducing emissions..

The physical state of the material also effects the storage and handling methods. These materials can be dusty, oily and range in size from fine dusts to entire components. These factors affect the delivery, handling and storage methods used. The techniques used for primary raw materials are used together with those below.

Secondary raw materials can be delivered to site as loose material, in tote bags or in drums. The physical state of the material dictates the delivery method and storage method used. The source of the material also has a significant impact and there are several methods available for grading material. Quality control and analysis of feed material is practised in most cases.

Large components and material such as swarf or grindings are stored on concrete areas that may be in the open, covered or inside buildings. Some large materials are not stored on a hard surface as damage to the surface can occur. The material is usually stored in segregated piles to keep different grades and alloy compositions separate.

Dusty materials and skimmings are also stored in segregated piles, which may be in the open, covered, or inside buildings. These materials can be pyrophoric or may react with moisture to form ammonia or other gases such as arsine or stibine, depending on the composition. The storage method therefore takes these factors into account. Cold dusty material can be coated with material such as molasses to form a dry crumb, which is not dust forming. The coating material does not affect pyrometallurgical processes.

Secondary raw materials may be contaminated with a variety of other materials such as oils, acids and organic matter which could be washed into drainage systems. The potential contamination of rain and other water by such contaminants is taken into account in the design of storage methods and the treatment of water run-off from these areas. Bunded areas, sealed floors and oil interceptors are used to prevent emissions to water.

Materials are handled by a variety of methods depending on storage. Grabs, conveyors and shovels are used. Secondary materials frequently need to be blended prior to processing or pre-treatment and intermediate storage is used.

Secondary materials that contain components with a high environmental concern e.g. lead, cadmium are treated with the most effective measures.

2.4.1.3 Fuels

The fuel may be used directly as a heat source, as a reducing agent or both. This needs to be identified for each installation. Fuels may be delivered to site by pipeline, road, rail or ship. The methods used for delivery are outside of the scope of this document but the use of road transport for frequent deliveries can give rise to noise and congestion.

Delivery and storage of fuel is usually controlled by the operator to prevent spillage and leaks, the techniques used include the following: -

a) Liquid fuels

Road and rail tankers are most commonly used for delivery. The site storage systems feature the use of vented or floating roof storage tanks, which are sited in sealed areas or bunds with sufficient capacity to contain the contents of the largest storage tank (or 10% of the total volume of individual tanks if it is greater). Efficient oil interceptors are used to prevent the discharge of oil in site run-off water.

Venting of gases from the storage tank back into the delivery tank is frequently practised unless floating roof storage tanks are used. Automatic resealing of connecting hoses is used when liquids and liquefied gases are delivered. Delivery connections are sited inside the bund.

Regular checks of the tank contents to identify leaks and safe volume for receipt is common practice. Alarms are used. Occasionally the use of inert atmospheres will be encountered.

Pipelines may also be used for liquid fuel delivery and may incorporate intermediate tank storage. Fuel distribution from the site storage tanks to the process is usually by overhead pipeline, by service trenches or less commonly by buried pipeline. Barriers are used for damage protection of overhead pipelines. The use of underground pipes hinders the prompt identification of fuel leaks that can cause contamination of the ground and sub surface water.

If there is a risk of ground water contamination the storage area should be impermeable and resistant to the material stored.

b) Gaseous fuels

Pipelines are the most common delivery system for gaseous fuels. Although LPG can be classed as a liquid, the same techniques are used. Process gases are dealt with later.

Some pyrometallurgical processes (i.e. the carbo-thermic production of ferro-alloys in closed submerged electric arc furnaces) produce a carbon monoxide rich off-gas as a by-product. The amount of CO varies largely depending on the metal and the production process. The off-gas can contain CO from lower amounts (low CV gas) up to 90% (high CV gas). The gas is cleaned (i. e. a cascade wet scrubber) and then distributed throughout the site as a secondary fuel or sold to neighbouring mills. Excess gas may be used for the production of electricity or flared-off.

The delivery of gases is often associated with pressure reduction equipment or occasionally compression equipment. In all cases the use of pressure and volume monitoring is frequently practised to identify leaks and gas monitors are sometimes used to monitor the workplace and in the vicinity of storage tanks.

Once again site distribution by overhead pipeline or pipelines in service trenches are common, damage protection methods are adopted.

c) Solid fuels

Road, rail or ship deliveries are used. Storage in silos, closed stockpiles, open stockpiles and in buildings are used depending on the type of fuel (e.g. coke, coal etc) and its' tendency to form dust.

Open stockpiles are not used frequently but those that exist are designed to give an even, sloping face to the wind and can have retaining walls to reduce the effect of wind and contain the material. Material can be reclaimed using underfed conveyor, grab crane or front-end loader.

Conveyor systems are designed to minimise the number of direction changes and the drop height at these changes to reduced spillage and dust formation. Closed, covered or open conveyors are used depending on the potential for dust formation; extraction and dust filtration is used if needed. In case of open conveyors dust can be produced if the belt is running too fast (i. e. more than 3.5 m/s). Belt scrapers are used to clean the return section of the belt to prevent spillage.

The moisture content of the fuel can be controlled to prevent the release of dust. Dust explosions are possible with dry and fine material.

Some open stockpiles are treated with water sprays or sealing agents (such as Poly Vinyl Acetate or molasses) to prevent dust formation in windy conditions, such as sealing agents can also prevent surface oxidation of the fuel. Solid matter can be washed into drainage systems and efficient settlement is often used to prevent emissions to water from open stockpiles.

Solid fuel can be distributed on site by truck, conveyor or by pneumatic “dense phase” system. Day storage or surge storage, usually in silos or hoppers, is used frequently. These systems usually incorporate dust extraction and filtration equipment.

2.4.1.4 Process chemicals and gases

Acids and alkalis and other chemical reagents are often used in the main process, in abatement equipment and may be produced during the process. They may be used to leach metals, precipitate compounds or can be used for off-gas or effluent treatment processes. Chemical compounds may be produced as part of the main process.

The supplier generally specifies the appropriate storage of these materials. Many of these reagents can react together and the storage and handling methods usually takes this into account by segregating reactive materials. Liquids are usually stored in drums or tanks in open or enclosed bunded areas, acid or chemical resistant coatings are used. Solids are generally stored in drums or bags (big bags) internally with isolated drainage systems, silos are used for some materials such as lime. Pneumatic transport systems are used.

Gases are used for a variety of purposes in the production of non-ferrous metals. The industry can use large quantities of process gases and the consumption of particular gases influences the method used for transport and distribution.

Oxygen is used to improve combustion, provide oxidation and improve conversion processes and natural gas or propane are used to reduce metal oxides. Carbon dioxide, nitrogen and argon are used to provide inert atmospheres and to degas molten metal. Chlorine is used in the chlorination step of the electrolytic magnesium production, to degas molten metal and to remove unwanted metallic components (e.g. magnesium). Carbon monoxide and hydrogen are used in the main processes. Hydrogen and sulphur dioxide are used to reduce oxides and salts. Chlorine and oxygen are used in leaching processes. Specific applications are discussed under individual metal production processes.

The operator can produce gases on site although contract gas production is encountered and these installations also supply other sites. Several sites use oxygen to improve combustion and nitrogen for spark suppression of pyrophoric materials. The same cryogenic or pressure swing process produces both gases and the low-grade nitrogen produced can be suitable for some inerting operations. In a similar way, combustion gases which have low oxygen content, are used to prevent auto ignition.

Gases can be transported by tanker and pipeline. Chlorine is usually stored as a liquid in drums or tanks and is distributed by evaporation and suction line, gas leakage is therefore prevented. Inventory and pressure control and monitoring can provide leakage detection for all gases.

Flow balancing and pressure decanting are used for the mixing of gases (e.g. argon/chlorine mixtures). For small volumes, pre-mixed gases can be supplied.

Distribution of gases within the site is normally achieved by pipelines, which are carried overhead using good damage protection systems. Health and Safety regulations govern the use and distribution of chlorine.

2.4.1.5 Residues

A variety of residues are produced by the processes in this sector. Many form the basis of raw materials for other parts of the industry. The section above describing secondary raw materials covers most of the techniques that are used. Later chapters describe in more detail the specific residues from the processes and the techniques for handling and storage.

2.4.2 Present emissions and consumption levels

Consumption of raw materials is dependent on the metal being produced and this data is included in chapters 3 to 12.

There are potential emissions of VOCs to air and of oils to water or land during loading, storage, unloading and transfer of liquids and gases. There are potential emissions of VOCs to air from tank breathing and pipeline leaks.

There are potential emissions of dust and metals to air and land from the loading and unloading operations, the transfer and storage of solid material and the re-suspension of dust from the storage areas and conveyors. Suspended solids, metals, oil and various anions such as sulphate (depending on the ore and its treatment) can be emitted to water.

Emissions from these sources are usually fugitive and are hard to quantify. Some estimates may be made from environmental sampling such as deposit gauges for dust or surface water samples. This chapter therefore concentrates on the techniques used that prevent emissions from raw material handling.

2.4.3 Techniques to consider in the determination of BAT

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau.

The applied techniques discussed above are all capable of preventing releases to all environmental media to a certain extent. The techniques that are used depend to a large extent on the type of material that is being used. For example large, heavy items are treated by a completely different range of techniques to fine, dusty material. These issues are specific to individual sites and materials. There are however, several techniques that are considered more effective in preventing releases from raw material handling. These techniques are:

- The use of liquid storage systems that are contained in impervious bunds that have a capacity capable of containing at least the volume of the largest storage tank within the bund. Various guidelines exist within each Member State and they should be followed as appropriate. Storage areas should be designed so that leaks from the upper portions of tanks and from delivery systems are collected and contained in the bund. Tank contents should be displayed and associated alarms used. The use of planned deliveries and automatic control systems to prevent over filling of storage tanks.

- Sulphuric acid and other reactive materials should also be stored in double walled tanks or tanks placed in chemically resistant bunds of the same capacity. The use of leak detection systems and alarms is sensible. If there is a risk of ground water contamination the storage area should be impermeable and resistant to the material stored.

- Delivery points should be contained within the bund to collect spilled of material. Back venting of displaced gases to the delivery vehicle should be practised to reduce emissions of VOCs. Use of automatic resealing of delivery connections to prevent spillage should be considered.

- Incompatible materials (e.g. oxidising and organic materials) should be segregated and inert gases used for storage tanks or areas if needed.

- The use of oil and solid interceptors if necessary for the drainage from open storage areas. The storage of material that can release oil on concreted areas that have curbs or other containment devices. The use of effluent treatment methods for chemical species that are stored.

- Transfer conveyors and pipelines placed in safe, open areas above ground so that leaks can be detected quickly and damage from vehicles and other equipment can be prevented. If buried pipelines are used their course can be documented and marked and safe excavation systems adopted.

- The use of well designed, robust pressure vessels for gases (including LPG’s) with pressure monitoring of the tanks and delivery pipe-work to prevent rupture and leakage. Gas monitors should be used in confined areas and close to storage tanks.

- Where required, sealed delivery, storage and reclamation systems can be used for dusty materials and silos can be used for day storage. Completely closed buildings can be used for the storage of dusty materials and may not require special filter devices.

- Sealing agents (such as molasses and PVA) can be used where appropriate and compatible to reduce the tendency for material to form dust.

- Where required enclosed conveyors with well designed, robust extraction and filtration equipment can be used on delivery points, silos, pneumatic transfer systems and conveyor transfer points to prevent the emission of dust.

- Non-dusty, non-soluble material can be stored on sealed surfaces with drainage and drain collection.

- Swarf, turnings and other oily material should be stored under cover to prevent washing away by rain water.

- Rationalised transport systems can be used to minimise the generation and transport of dust within a site. Rainwater that washes dust away should be collected and treated before discharge.

- The use of wheel and body washes or other cleaning systems to clean vehicles used to deliver or handle dusty material. Local conditions will influence the method e.g. ice formation. Planned campaigns for road sweeping can be used.

- Inventory control and inspection systems can be adopted to prevent spillages and identify leaks.

- Material sampling and assay systems can be incorporated into the materials handling and storage system to identify raw material quality and plan the processing method. These systems should be designed and operated to same high standards as the handling and storage systems.

- Storage areas for reductants such as coal, coke or woodchips need to be surveyed to detect fires, caused by self-ignition.

- The use of good design and construction practices and adequate maintenance.

2.5 Pre-processing and transfer of Raw Materials

2.5.1 Applied processes and techniques

Ores, concentrates and secondary raw materials are sometimes in a form that cannot be used directly in the main process. Drying/thawing may be needed for control or safety reasons. The material size may need to be increased or decreased to promote reactions or reduce oxidation. Reducing agents such as coal or coke and fluxes or other slag forming materials may need to be added to control the metallurgical process. Coatings may need to be removed to avoid process abatement problems and improve melting rates. All of these techniques are used to produce a more controllable and reliable feed for the main process and are also used in precious metal recovery to assay the raw material so that toll recovery charges can be calculated.

2.5.1.1 Thawing

Thawing is performed to allow frozen material to be handled. This occurs for instance when ores or concentrates or fossil solid fuels such as coal are discharged from a train or ship in the wintertime. Thawing can be achieved by using steam jets in order to just melt the ice and to be able to unload the raw material.

2.5.1.2 Drying

Drying processes are used to produce a raw material that is suitable for the main production process. The presence of water is often avoided for several reasons.

- It is dangerous when large volumes of steam are produced rapidly in a very hot furnace.
- Water can produce variable heat demand in a concentrate burner, which upsets the process control and can inhibit auto-thermal operation.
- Separate drying at low temperatures reduces the energy requirements. This is due to the energy required to super heat the steam within a smelter and the significant increase in the overall gas volume, which increases the fan duty.
- Corrosion effects.
- Water vapour may react with carbon to form H_2 and CO.

Drying is usually achieved by the application of direct heat from a burner or by steam jets, or indirectly using steam or hot air in heat exchanger coils. The heat generated from pyrometallurgical processes is also often used for this purpose as well as the CO rich off-gas that can be burned to dry the raw material. Rotary kilns and fluidised bed dryers are used. The dried material is usually very dusty and extraction and abatement systems are used to collect dusty gases. Collected dusts are returned to the process. Dried ores and concentrates can also be pyrophoric and the design of the abatement system usually takes this into account, nitrogen blanketing or the low residual oxygen in combustion gases can be used to suppress ignition. Dryer off-gases may contain SO_2 and treatment of the gases may be considered.

2.5.1.3 Crushing and size reduction

Crushing and size reduction is practised to reduce the size of products, residues or raw material so that is suitable for sale or further processing. Many types of crusher are used including cone crushers and ball crushers. Wet or dry materials are crushed and a blending stage can be included. The specific equipment used will depend on the raw materials to be treated. Dry crushing is potentially a major source of dust emission and extraction and abatement systems are used, collected dusts are returned to the process. Damp materials can be crushed where dust formation can cause problems and where wet pelletising stages follow.

Granulation is used to produce small particles of slag, which are suitable as shot blasting material, road fill or a material that can be reprocessed to recover the metal content. Molten slag is cast into a water bath or poured through a stream of water. Granulation is also used to produce metal shot. Granulation processes have the potential to form fine dust and aerosols, which have to be controlled.

Electronic components are a source of several non-ferrous metals and these may be ground in shredders or mills to liberate the circuit boards and other material from the metallic components so that separation can take place.

2.5.1.4 Battery breaking

Battery breaking is used to recover lead, nickel, cadmium and other materials from batteries. For lead-acid batteries, hammer mills are used to break the battery cases to liberate lead (as grids) and lead compounds (as paste) and allow the recovery of the plastic case material (mainly poly-propylene), the electrolyte is also removed and treated or used. Two-stage crushing can be used to control the particle size and prevent the lead oxide from being impacted into the plastic during a single stage mill. Plastic material is separated and washed to improve the quality and produce plastic that is suitable for recycling. The acid content of the batteries can contaminate land and water if it is not collected and handled properly, sealed acid resistant drainage systems can be used with dedicated collection and storage tanks. The milling stages can produce an acid mist, this can be collected in wet scrubbers or mist filters.

Ni/Cd batteries are pyrolised to remove any plastic coating and to open the batteries. Pyrolysis is carried out at low temperatures and the gases are treated in an afterburner and then a bag filter. Cadmium and nickel are recovered from the electrodes and steel from the casing material.

2.5.1.5 Blending

Blending is performed to mix ores or concentrates of varying quality and to combine fluxes or reductants, if necessary, with the ore to produce a stable feed to the main process. Blending can be achieved in proprietary blending equipment, in the grinding stage or during conveying, drying and storage stages. Accurate blends are produced using loss in weight storage systems, belt weighers or by volume from the loading equipment. Blending can be a very dusty operation and high levels of containment and extraction are used. Collected dusts are returned to the process. Wet mixing is also used to avoid the production of dusts; slurry is produced that is then de-watered and used in a pelletising process. Coating and binding agents may also be used for this purpose. Depending on the process the blended material may be needed to be pelletised before further processing such as sintering.

2.5.1.6 Briquetting, pelletising and other agglomeration methods

Many techniques are used to treat concentrates, flue dusts and other secondary material and they include the baling of wire or small scrap, compressing briquettes of material as mentioned before and extruding or rolling pastes to produce even sized balls of material. Coating and binding agents are used for this purpose to reduce dust development in subsequent process steps.

Briquettes and pellets containing a mixture of fine ore or concentrate, recycled dust and additional material such a reducing agents are often produced to ensure efficient smelting conditions. After adding binders or water the mixture is fed into a press, which often produces pillow shaped briquettes or pelletised in a rotary pelletising drum or a pelletising disc. The binding material must be of such properties that the briquettes have sufficient green strength to enable them to be handled easily and to remain unbroken when they are charged to the furnace.

Various types of binders can be used, such as molasses and lime, sodium silicate, steel slag or cement and they also reduce dust formation. Pitch can be added to improve the green strength. Coarse fractions of filter dust from the furnace bag house filter and filter dust from crushing and screening operations can be mixed with the other materials to be briquetted.

2.5.1.7 Sintering and calcination

These processes are used to increase the size of the raw material or the chemical composition so that it is suitable for further processing. Agglomeration and sintering allow a more even gas flow through a furnace bed and reduce dust formation, gas volume and fugitive emissions [tm 109, UNEP 1993].

Sintering and calcining are also used for this purpose and additionally it is used to adjust the chemical form of the mix or to convert any sulphur present e.g. calcination of dolomite into dolime in the production of magnesium. The main binding mechanism in ore sintering is archived by bringing the ore up to a temperature where the gangue minerals start to melt, whereby individual particles are fused together in a matrix of molten slag. In some case re-crystallisation, e.g. formation of new crystals across former grain boundaries will play some role in the sintering process. The sinter is usually crushed and classified and the fine materials are returned to the sintering process, sometimes the returned material is 2 - 4 times greater than the sinter produced. The feed particles are then sent to the smelter.

The sintering and roasting of sulphide ores are often carried out together at high temperatures and in this case the gases produced are high in sulphur dioxide. The oxidation of sulphur provides the heat necessary for the process. Generally the ore is blended with return sinter and fluxing agents and may be pelletised before sintering. In the case of oxides, coke is also added.

Sinter plants use a moving grate, continuous grate or a steel belt to carry the material through heating and cooling zones, some plants use steel pallets to contain the feed. The gases are drawn upwards or downwards through the bed (up-draught or down-draught sintering). A sintering machine that uses a combination of up-draught and down-draught stages is also used and is capable of minimising gas volumes and fugitive emissions and recovers heat efficiently. Sometimes a layer of sintered material is used between the grate and the blend is used to protect the steel grate.

The sintering of sulphide ores is exo-thermic, other materials use natural gas as a fuel. The hot gases are usually recycled to preheat the bed or the combustion air. The sinter is cooled by air draught on the bed or in a water quench. The sinter is then sieved and sometimes crushed to produce a final feed material of constant size. The fine materials are returned to the sintering process.

Calcining is performed in rotary, fluidised bed or multiple hearth furnaces, there are normally no addition of carbon during the process. Calcination of sulphide concentrates performs the roasting stage and is discussed in the chapters for metal production.

2.5.1.8 Fuming processes

These processes are used to fume volatile metals such as lead or zinc, from a substrate. The process uses high temperatures and a source of carbon to produce an inert slag by fuming or volatilising metals from the material. This allows the metals to be recovered usually as an oxide for further processing. Waelz kilns and slag fuming furnaces are used. Fuming is also achieved during batch converting processes when volatile metals are removed during the process.

2.5.1.9 De-coating and de-oiling

These operations are usually performed on secondary raw materials to reduce the organic content of the feed to some main processes. Washing and pyrolysis processes are used. Centrifuging can recover oil and reduce the load on the thermal system. Major variations in organic content can cause inefficient combustion in some furnaces and produce high volumes of combustion gases that contain residual organic compounds. The presence of coatings can also reduce the melting rate significantly [tm 121, Hoogovens 1998, tm 125, ETSU 1994]. These events can cause significant emissions of smoke, dioxins and metal dusts to air unless the gas collection and combustion systems are sufficiently robust. Sparks or burning particles can be produced that can cause significant damage to abatement equipment. In-furnace de-coating of contaminated scrap is also less efficient in most cases than de-coating shredded material in a separate kiln due the production of more dross [tm 125, ETSU 1994] but some furnaces are specially designed to receive organic contaminants.

The removal of oil and some coatings is achieved in a specially designed furnace such as a swarf dryer. In most cases a rotary furnace is used at low temperature to volatilise oil and water. Direct and indirect heating of the material is used. An afterburner operated at high temperature (more than 850 °C) is used to destroy the organic products produced in the furnace, and the gases are usually filtered in a fabric filter.

Mechanical stripping is also used frequently to remove insulation from cables and coatings from other materials. Some process use cryogenic techniques to make the coating brittle and therefore easier to remove. Washing with solvents (sometimes chlorinated) or with detergents can also be used. Solvent vapour systems with integral condensers are the most common. These processes are also used to de-grease production items. Treatment systems to prevent water contamination are used in these cases.

2.5.1.10 Incineration and pyrolysis

This is normally used to treat photographic film, sweepings, catalysts and other materials to concentrate the precious metals content or to recover nickel. It is also used to pre-treat catalysts to remove the organic content before further treatment. These processes are usually carried out at low temperature to prevent carry over of the metals. The gases produced from the incinerator are then treated in an afterburner and bag filter. The potential formation of dioxins needs to be considered for these processes.

Simple box kilns and rotary furnaces are used for the incineration or pyrolysis stage. Raw materials are fed into the box kilns in trays. The metal-rich ashes are collected or quenched before they are processed further.

2.5.1.11 Leaching procedures

Leaching or pre-leaching is used to remove impurities such as alkali and alkaline earths, magnesium, sulphate or chloride from some concentrates and secondary raw materials before further processing. Leaching is also used to reduce the content of cadmium, chloride and sulphate etc in residues or to recover them as by-products. Examples are - Waelz oxide can be washed to produce material that is suitable for use in a primary process; - Cadmium in filter dust can be removed before the dust is recycled to a smelter. Pre-leaching is also used to remove metals from complex matrices or to concentrate the precious metals that are used to coat catalysts. Ores such as quartz are washed and screened before use. Open or closed circuit washing processes are used, a bleed of liquor is used in a closed circuit system. Wastewater is treated before discharge.

2.5.1.12 Separation techniques

These processes are used to remove impurities from raw materials prior to their use. The separation techniques for ores and concentrates (such as flotation) are generally used at the mine when the material is concentrated or “beneficiated”, but these techniques are also used at several production sites to treat slag to remove metal rich fractions. Magnetic separation is used to remove items of iron.

Separation techniques are more frequently used for secondary raw materials and the most common is magnetic separation. Heavy media and density separation (swim/sink) is used by the scrap processing industry but may be encountered in the non-ferrous metals industry for example in the processing of battery scrap to remove plastic material. In this case the density and size difference of the various fractions is used to separate metal, metal oxides and plastic components using a water carrier. Air classification is also used to separate metals from less dense materials such as the plastic and fibres from electronic scrap. Flotation is also used to enrich leach residues.

Magnetic separation is used to remove pieces of iron to reduce contamination of alloys. Generally, over-band magnets are used above conveyors. Sloping hearths in a reverberatory furnace are used to melt zinc, lead and aluminium to leave large, higher melting point impurities (e.g. iron) on the hearth for further processing.

Moving electromagnetic fields (eddy current separation) are used to separate aluminium from other material. A variation on this technique uses this moving electromagnetic field to pump molten aluminium or other metals without direct contact between the metal and mechanical components.

Other separation techniques involve the use of colour, UV, IR, X-ray, laser and other detection systems in combination with mechanical or pneumatic sorters. These are used for example to separate Ni/Cd batteries from other battery types and the techniques are being developed for other applications.

2.5.1.13 Transfer and charging systems

These systems are used to convey the raw materials between pre-treatment stages and then into the main process. Techniques, similar to those used for raw materials are used and similar problems of dust production, containment and extraction exists. Collected material is reused.

Pre-treated materials may be drier than raw materials and more stringent methods are used to prevent dust emissions, water spray systems are generally not used but high standards of housekeeping are needed. Conveyors for the transport of dust forming materials are generally enclosed and in these cases efficient extraction and abatement systems are employed at exposed, sensitive areas such as conveyor change points. An alternative is the use of fine water sprays or mists. Bottom scrapers are used on conveyors to prevent carry over of material on the return section of the belt. Dense phase, pneumatic conveying systems are also used frequently.

2.5.2 Present emission and consumption levels

The potential emissions to all environmental media are similar to those from raw materials handling. In addition, there are releases to air of smoke, acid gases, fume and dust from thermal processes and dust from mechanical processes and releases of metals to water from granulating and filtering systems. The emissions from these processes are usually collected.

2.5.3 Techniques to consider in the determination of BAT

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau.

The techniques that are used depend to a large extent on the type of material that is being used for example large, heavy items are treated by a completely different range of techniques to fine, dusty material. These issues are specific to individual sites and materials. The pre-processing and transfer operations however often deal with materials that are dry or are likely to produce process emissions to any of the environmental media. More detailed design of the process equipment used at this stage is therefore needed and the processes need to be monitored and controlled effectively. The nature of the material (e.g. dust forming, pyrophoric) needs to be taken into account and the potential emissions of VOCs and dioxins in thermal processes needs to be assessed. Extraction and abatement systems in particular need to be carefully designed, constructed and maintained. The review of applied techniques in this section includes the issues that will be encountered in the various process options. The techniques listed for raw materials handling should also be referred to. The following items however are considered to be the most important.

- Use of pre-treatment and transfer processes with well designed robust extraction and abatement equipment to prevent the emission of dust and other material. The design of this equipment should take account of the nature of the emissions, the maximum rate of emissions and all of the potential sources.
- Use of enclosed conveying systems for dusty materials. These systems should be provided with extraction and abatement equipment where dust emissions are possible.
- Processes that “flow” directly into the following process if possible to minimise handling and conserve heat energy.
- Use of wet grinding, blending and pelletising systems if other techniques for the control of dust are not possible or appropriate.
- Thermal cleaning and pyrolysis systems (e.g. swarf drying and de-coating) that use robust after-burning equipment to destroy combustion products e.g. VOCs and dioxins. The gases should be held at a temperature greater than 850 °C (1100 °C if there is more than 1% halogenated organic material), in the presence of at least 6% oxygen for a minimum of 2 seconds. Lower residence times may as well result in the complete destroying of VOCs and dioxins but this should be demonstrated on a local level. Gases should be cooled rapidly through the temperature window of dioxin reformation.
- To reduce the impact of VOC’s, washing processes to remove oil or other contaminants should use benign solvents. Efficient solvent and vapour recovery systems should be used.
- Steel belt, up-draught or fully enclosed down-draft sintering processes are techniques to be considered. Steel belt sintering has several advantages for certain metal groups and can minimise gas volumes, reduce fugitive emissions and recover heat. These are discussed later. Off gas extraction systems should prevent fugitive emissions.
- The use of rotary kilns with wet ash quenching for the processes involving the volume reduction of material such as photographic film. Smaller installations may use a moving grate furnace. In both cases the combustion gases should be cleaned to remove dust and acid gases if they are present.
- If required to minimise the generation of smoke and fumes and to improve the melting rates, separation processes should be designed to produce clean materials that are suitable for recovery processes.
- Collection and treatment of liquid effluents before discharge from the process to remove non-ferrous metals and other components.
- The use of good design and construction practices and adequate maintenance.

Pre-treatment method	Materials	Metal group	Comment
Drying	Concentrates & fluxes	All	Dry feed to a smelter
Crushing	Slag	All	Mechanical or water based
	Batteries		Mechanical 1 or 2 stages. Potential acid emissions to all media.
Blending	Concentrates & fluxes	All	Use of conveying and blending stages
Agglomeration	Concentrates & fluxes Residues	All (Rarely Cu & Ni)	Coating and pelletising
Sintering	Concentrates & fluxes	Pb, Zn, Ferro-alloys	SO_2 and dust emissions
Fuming	Filter dusts, slags	Pb, Zn	Filter dusts from a variety of processes contain Pb and Zn
De-coating, de-oiling	Cable Swarf Centrifuging can recover oil and reduce the load on the thermal system.	Cu, Al, Ti etc.	VOC and dioxin emissions from thermal systems. Mechanical and cryogenic systems are available.
Incineration	Film, catalysts.	Precious metals.	VOC and dioxin emissions
Leaching	Raw materials Residues	Pb, Zn, PMs	
Separation	Plastic material Metals	Pb, Cd, PMs, Al	Air or liquid based systems
De-greasing	Products – using solvent or aqueous based systems.	Cu etc	Potential for chlorinated hydrocarbons

Table 2.3: Summary of pre-treatment methods

2.6 Metal Production and Process Control Techniques

Metal	Type furnace likely to be encountered	Comment
Copper	Flash Smelting Furnaces. Bath Smelting Furnaces. Electric Furnaces. Rotary Furnaces or converters. Blast furnaces. Shaft Furnaces. Induction Furnaces. Reverberatory Furnaces.	• A variety of applications depending on the raw material and process stage.
Aluminium	Molten Electrolyte Cells. Reverberatory Furnaces. Rotary and Shaft Furnaces. Induction Furnaces.	• Molten electrolyte cells only for primary.
Lead	Imperial Smelting Furnace (ISF). Flash Furnace (Kivcet). Bath Furnace (QSL, ISA Smelt/Ausmelt). Short rotary Furnace. Heated Kettle. Sinter machine.	
Zinc	ISF and New Jersey Distillation Fluidised bed roaster, sinter machine. Induction and crucible furnace. Slag fuming furnaces.	• Temperature control of melting is vital.
Precious Metals	Electric Furnace. Blast Furnace. Crucible Furnace, Rotary and Static Incinerator. Cupel and BBOC. Vacuum distillation	• A variety of applications depending on the raw material and process stage.
Mercury	Rotary Kiln. Tube furnace. Herreshoff furnace.	
Refractory Metals	Pusher Furnace. Band Furnace Batch Furnace Rotary Furnace Electron Beam Furnace. Vacuum Induction Furnace.	• Pusher, band, batch and rotary furnaces are used for powder production. • Electron beam furnace is used for ingot smelting
Ferro Alloys	Blast Furnace. Electric Arc Furnace, Electric Furnace. Reaction Crucibles, Herreschoff Furnace Metallo-thermic reactors	• The electric arc furnace is used as an open, semi-closed and closed furnace. • Herreshoff furnace is only used for Mo-roasting.
Alkali Metals	Molten Electrolyte Cells. Electric Furnaces, Induction Furnaces.	• Induction furnaces are mostly used for re-melting.
Nickel and Cobalt	Flash Smelting Furnaces. Bath Smelting Furnaces. Electric Furnaces, Reverberatory Furnaces. Converters. Rotary Kilns & Furnaces. Induction Furnaces.	• A variety of applications depending on the raw material and process stage.
Carbon and graphite	Pit Furnaces, Vacuum Furnaces. Electric Furnaces.	

Table 2.4: Typical furnace applications

There are several processes or combinations of processes used to produce and melt metals. Pyrometallurgical and hydrometallurgical processes are shown below. The order in which they appear is not significant and does not signify a ranking. The techniques described in the metal specific chapters give more details of the pyrometallurgical or hydrometallurgical process, the metals that they are used for and the specific advantages and disadvantages in those applications.

Furnaces are used for a variety of purposes in this industry such as roasting or calcining raw materials, melting and refining metals and for smelting ores and concentrates.

The same "type" of furnace or process may be used for a variety of purposes and this review is therefore intended to give an overview of the various applications [tm 22, EC 1991; tm 26, PARCOM 1996; tm 35, LRTAP 1995].

An important aspect of the choice of process is the relationship with the collection of fume and gases; sealed, semi-closed and open processes are encountered. The design of the fume collection system is strongly influenced by geometry, which in some instances can make fume collection difficult. The use of transfer systems that require collection hoods to be moved from a furnace is an illustration of this factor. The other important factor in the applicability of a particular process type is the type and variability of the raw material used, some process allow a range of materials to be used but others need a defined type of material. These issues are considered further in the individual metal production chapters under techniques to consider in the determination of Best Available Techniques. In a similar manner the operation and maintenance of these systems is also critical.

2.6.1 Furnaces for roasting, calcining etc

2.6.1.1 Rotary kilns

Rotary kilns use the same arrangement as a rotary furnace but operate without melting the charge.

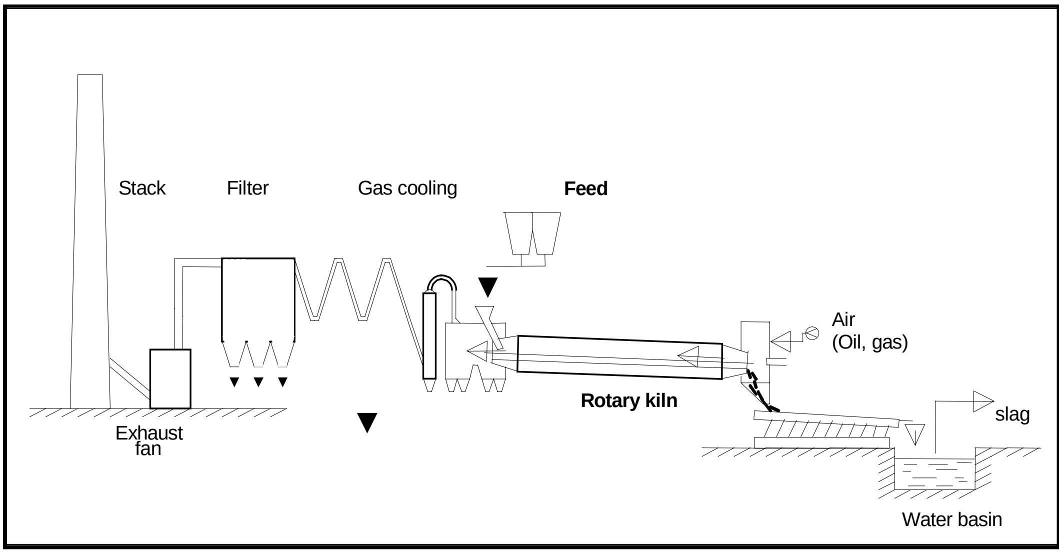


Figure 2.1: Rotary kiln
[tm 124, DFIU Cu 1999]

These kilns are used for a variety of fuming and calcining processes. Principal examples are the production of zinc oxide by fuming in a Waelz kiln; the production of calcine for the ferro nickel process; the calcination of aluminium hydroxide and the calcination of magnesium hydroxide to a light burnt magnesium oxide for electrolytic magnesium production. Other applications are the pre-treatment of a variety of raw materials at high temperatures, the incineration of photographic film and paper and the drying of concentrates and blends of material at lower temperatures.

2.6.1.2 Fluidised bed roaster

These furnaces are especially suitable when good temperature control is required for example for sulphating roasting and dead roasting of zinc concentrates as well as for Al_2O_3 calcining.

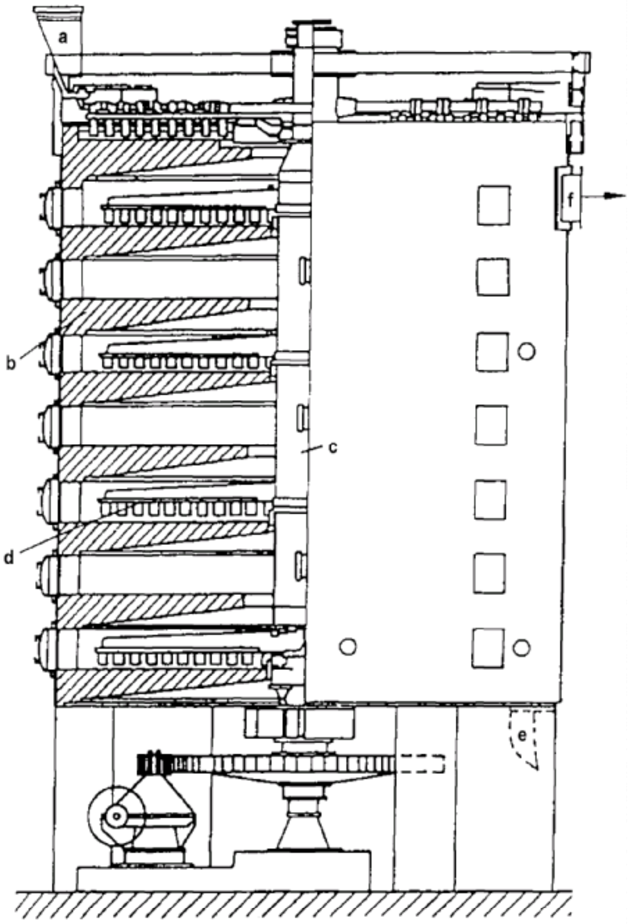
Combustion air is blown through tuyeres in a grid at the bottom of the furnace and through the fluid bed of material being roasted on the grid. The concentrate is fed on to the top of the bed. The oxygen reacts with the sulphides in the bed to produce oxides, the calcine. SO_2 gas is formed at about 900 to 1000 °C by the oxidation of sulphide to form oxide. At this temperature practically all of the iron is combined with heavy metal oxides to give ferrite in the presence of excess oxygen.

Part of the calcine is removed mechanically from the furnace but some is carried over in the gas stream and is removed in a waste heat boiler and EP system. The roasting removes some minor impurities like Cl, F, Se and Hg into the gas phase.

The heat evolved in the roasting is recovered as steam by cooling coils in the bed and in the waste heat boiler. Utilisation of the steam may vary somewhat dependent on the need at the plant site, but part of it is always used for heating in the process.

2.6.1.3 Herreshoff furnace

The furnace consists of a tower that contains a number of 8 to 12 annular shaped refractory brick hearths arranged vertically and enclosed in a cylindrical refractory lined steel shell. The feed to the furnace is usually of the outside of top hearth and material is moved to the centre of this hearth by rabble arms where it falls to the centre of the second hearth. The material flow on the second hearth is from the centre out where it falls to the outside of the third hearth. This zigzag flow is repeated until the roasted material is discharged. The rabble arms are attached to a central, vertical rotating, tube which is air cooled. Gas or oil burners are provided at various points in the furnace depending on the combustion characteristics of the material. The cooling air that is used to cool the central tube normally is used as pre-heated combustion air for the furnace.



a) Hopper; b) Circular hearth; c) Hollow shaft; d) Rabble arm with teeth; e) Discharge outlet; f) Gas outlet

Figure 2.2: The Herreshoff Furnace

This furnace is used to roast sulphide ores, to produce metal directly in the case of mercury or an oxide such as molybdenum oxide. Vaporised rhenium that is liberated in the roasting process of molybdenite can be recovered from the roaster off-gas by using a wet scrubbing system together with a subsequent rhenium recovery plant. The Herreshoff furnace is also used to re-generate activated carbon.

2.6.1.4 Sintering furnaces

The raw materials for the sintering plant are concentrates, ore fines, flue dusts and other secondary material. In the sintering plant the material is first agglomerated to the required extent and may be pelletised. The agglomerated material is fed to the sintering furnace in a layer or in carriers, heated gases are passed up (up-draft) or down (down-draft) through the bed.

In the Steel Belt Sintering machine a multi-compartment oven is used through which the green agglomerate is carried on a perforated steel conveyor belt. The agglomerate is dried in the drying compartment by circulating gas from the last cooling compartment. In the preheating compartment the temperature of the agglomerate is increasing so that the material is calcined and the carbon in the bed is ignited. Heating gas is taken from the second cooling compartment. In the sintering compartment the sintering temperature is achieved. Heating gas, in addition to the energy from burning of carbon and oxidation of iron, is taken from the first cooling compartment.

The front-end compartments are down draft, cooling air to the three cooling compartments is blown through the bed. In case additional energy is required to control the temperature profile in the compartments, CO-gas from the smelting process or natural gas is burned in the preheating and sintering compartments. Part of the product sinter or pellets is used as bottom layer on the steel belt to protect it from too high temperatures. The exhaust gases are cleaned in cascade scrubbers and/or bag filters. Dusts are recycled back to the agglomeration.

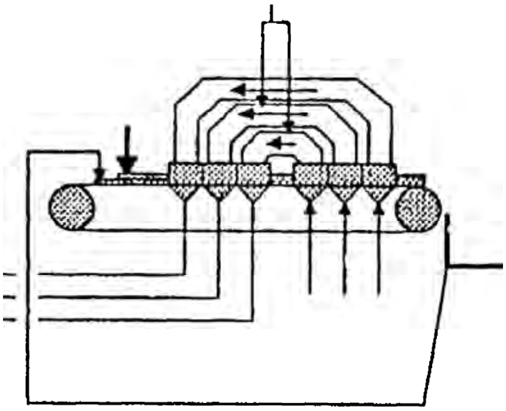


Figure 2.3: Steel belt sintering furnace

Sintering furnaces are applied to sintering of a variety of ores, dusts and sludges. The steel belt sintering furnace is used for chromite pellets, manganese ore and niobium concentrate but may have other applications.

2.6.2 Smelting furnaces

2.6.2.1 Reverberatory furnace

The reverberatory furnace is used for smelting concentrates and secondary material. Two general types exist, a simple bath furnace for smelting of calcine or concentrates and a reverberatory hearth furnace for melting or refining. Furnaces can sometimes be tilted to pour or blow metal. Tuyeres can be used for the injection of treatment gases or for the addition of fine material.

The furnace is constructed in a number of configurations depending on the particular metal and application, variations include the provision of sloping hearths and side wells for specific melting purposes, tuyeres and lances for the addition of gases.

Slag is usually removed by tapping.

When sulphide ores are smelted in a reverberatory furnace the sulphur dioxide concentrations are normally low due to the high volume of combustion gases and the low rate of sulphur elimination in the furnace.

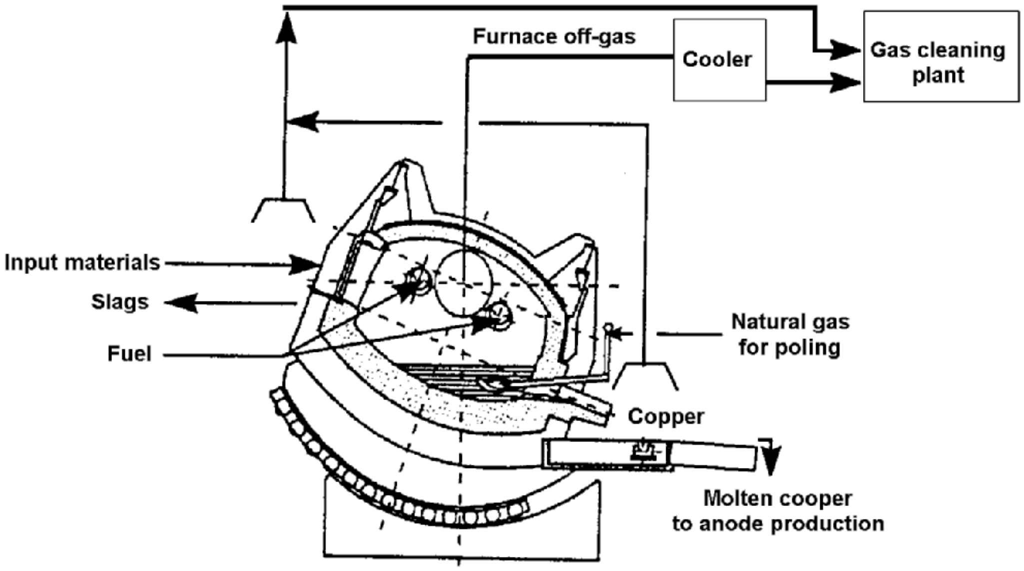


Figure 2.4: An example of a tilting reverberatory hearth furnace used for secondary materials [tm 124, DFIU Cu 1999; tm 226, VDI 2102 1999]

These furnaces are used for smelting a variety of primary and secondary raw materials and for fire refining.

2.6.2.2 The blast furnace (and Imperial Smelting Furnace)

This is a type of shaft furnace. It uses a heated air blast from tuyeres in the lower part of the furnace to burn coke that is mixed with the furnace charge of metal oxide or secondary material and fluxing agents, materials are often briquetted before charging. The combustion of a portion of the coke raises the furnace temperature and the remainder produces CO, which along with hydrogen produced by the water gas reaction reduces the metal oxides to metal. The reaction produces a gas that is rich in carbon monoxide. This can be collected and cleaned and burnt to pre-heat the blast-air or may be burnt off in a separate afterburner or in an oxygen rich part of the furnace. In some instances, raw materials such as zinc oxide dusts are fed via the tuyeres.

The metal collects on a hearth or crucible at the bottom of the furnace and may be tapped continuously or on a batch basis. When tapped batch-wise, the slag floats on top of the metal and the metal is tapped from a separate tap hole. Fume extraction and abatement is used during the tapping process.

The furnace shell is normally water cooled either over its entire height or in the lower part, the blast furnace can also be called a water jacket furnace. There are two variations of the blast furnace depending on the feeding method and the operating temperature used to melt the metal. Furnaces can be: - a) “hot top” where the charge material is fed via a “bell” or a conveyor via a transfer lock or b) “cold top” where the furnace is charged from a hopper and the feedstock provides the top seal itself.

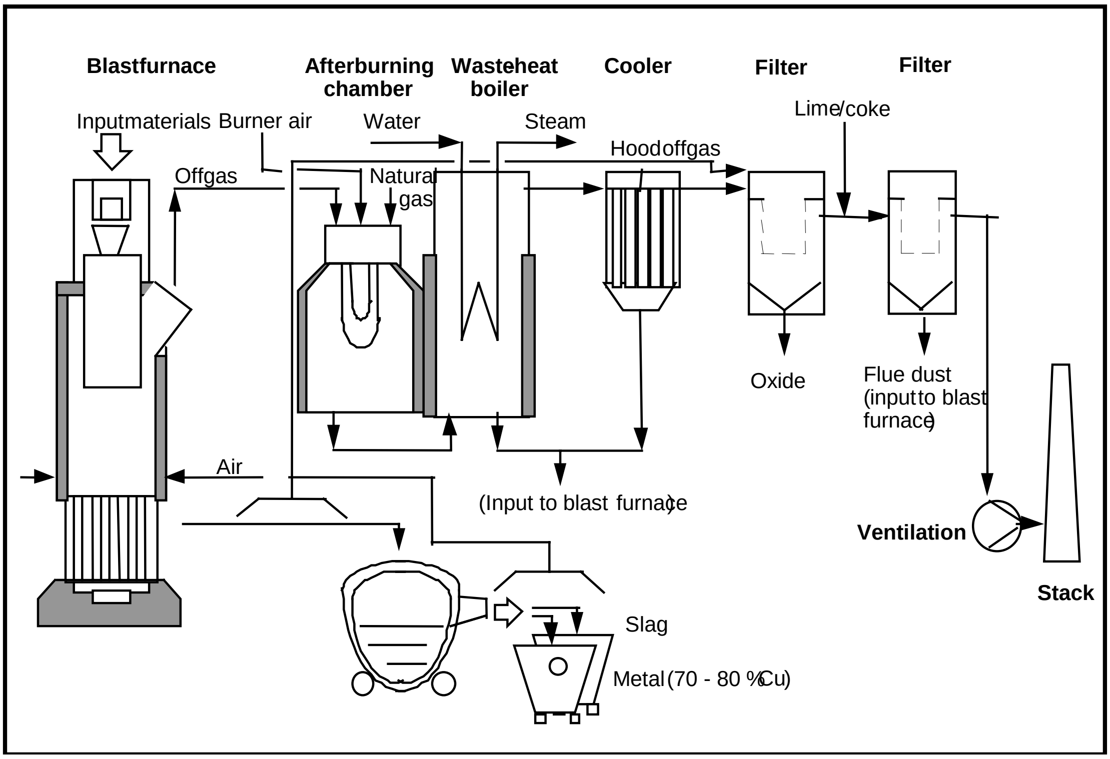


Figure 2.5: Blast furnace for secondary copper production
[tm 124, DFIU Cu 1999; tm 226, VDI 2102 1999]

Blast furnaces are used to smelt and recover a variety of metals including precious metals, copper and lead from primary and secondary raw materials as well as high carbon ferro-manganese. Recent developments allow the charging of fine materials into the furnace via the tuyeres and this can avoid briquetting and reduce the handling of dusty material.

One specific application of the blast furnace is the Imperial Smelting Furnace that is used for mixed lead/zinc concentrates. This furnace uses a molten lead splash condenser after the blast furnace section to collect zinc vapour released in the gases while lead collects on the hearth. The zinc and cadmium collected in the condenser is purified in a fractional distillation system (New Jersey Distillation Column).

2.6.2.3 Electric arc furnaces

Electric arc furnaces operate on the principle of passing a large alternating electrical current between a series of usually three carbon electrodes (for a three phase electrical supply) to produce electrical arcs. A DC (Direct Current) electrical supply can also be used and in this case the arc strikes between a number of electrodes and a carbon furnace lining.

The electric arc furnace can be divided in the following main components:
- Equipment for adding ores and concentrates or a mix of raw material to the furnace.
- Equipment to supply electrical energy to the furnace consisting of electrical grid, transformers, bus bar and the electrodes.
- The furnace body or shaft consisting of a shell, the lining and the furnace hood that protects the equipment from the heat and the chemical load.
- Equipment for tapping the metal and slag from the furnace.

The raw material may be charged to the furnace in different ways. For smaller furnaces the raw material can be charged manually by using a charging car. The charging car may sometimes also be used for the necessary stoking work to break down crust formation in the upper part of the furnace charge. Large electric arc furnaces are normally charged by charging tubes where the charge flows from the tubes to the hearth so that the material in the tubes form in case of a closed furnace a gas tight seal.

The electrical supply system will transform the electrical energy that normally is at high voltage down to low voltage–high current that is required for the process. Three furnace transformers are situated around the furnace in order to obtain electrical symmetry. The operation of separate transformers has some advantages on the furnace control. The electrodes are connected to the electrical supply system through the bus bar. The electrodes can be pre-baked or of the Søderberg type. They are made from graphite or carbon material and are consumed in the process, so that they have to be replaced continuously.

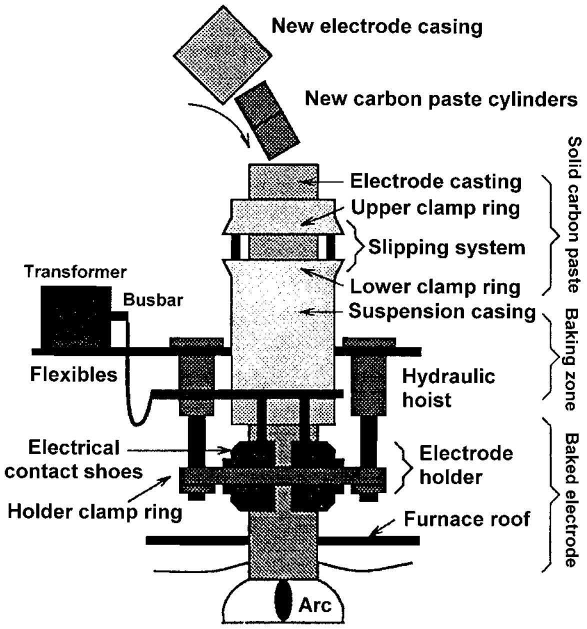


Figure 2.6: Søderberg electrode system in an electric arc furnace

The Søderberg system that is shown in figure 2.6 is based on an outer steel electrode casing which acts as a former for the carbon paste. The carbon paste is baked to a fixed electrode inside the steel casing when the electrode is heated as it approaches the warmer part of the furnace. Some of the heating is due to the electrical current in the electrode. Carbon from the electrodes can be consumed to reduce oxides to a metal or can be worn away by the action of the arc. Significant concentrations of carbon monoxide can be produced. Some installations use hollow electrodes which allows material to fed into the furnace through the electrode.

The raw material provides part of the resistance in the electrical circuit and promotes the formation of the electric arc, which produces the high temperatures. The depth of insertion of the electrodes regulates the resistance. Direct current arc furnaces exist and use anode pins or conducting hearths. The electric arc furnaces can be operated batch-wise or continuously.

The furnaces can be open, semi-sealed (with extraction commonly from a fourth hole in the hood) or totally sealed using feed chutes and sealing valves for charging. In the latter case all of the furnace gases are extracted efficiently and are cleaned and can be used to pre-heat feed materials or used as a source of fuel. The hoods and occasionally the furnace body can be water-cooled to control the process and prevent damage.

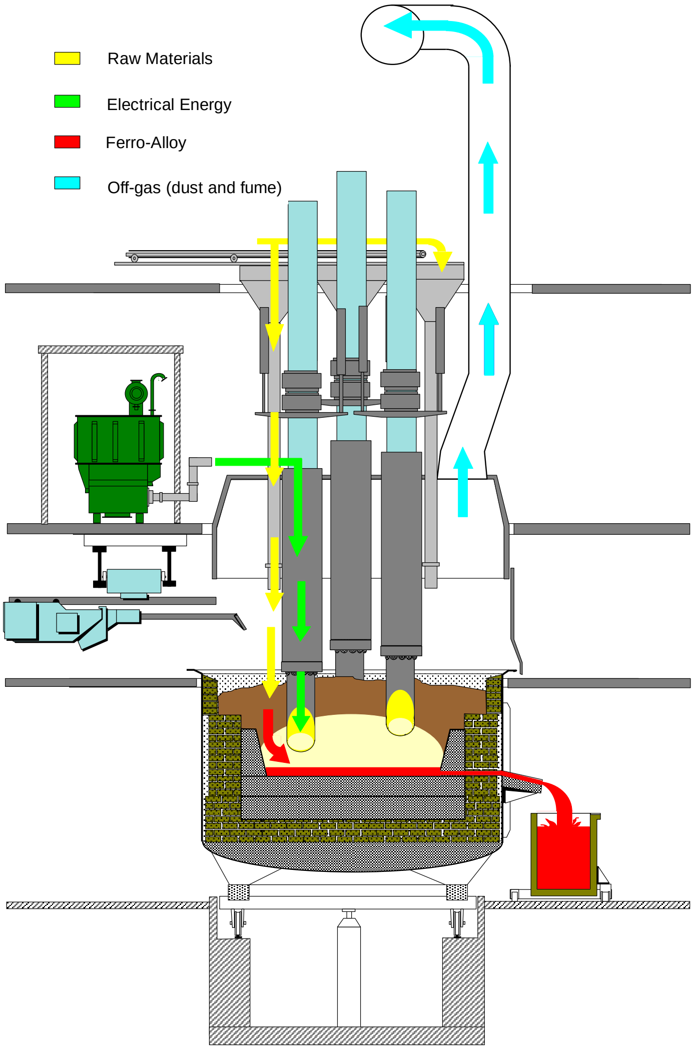


Figure 2.7: Rotary Electric Arc Furnace

These furnaces are used for smelting a range of ferro-alloys. They are also used for melting and refining refractory metals and high temperature alloys and in these cases they are operated under vacuum.

The furnace can be operated on a batch basis or continuously with a molten charge. In the latter case the electrodes are "submerged" in the slag and do not strike an arc (except during start up) but operate as an electric resistance furnace or Electric Submerged Arc Furnaces.

2.6.2.4 Electric (resistance) furnace

This type of furnace uses a similar arrangement to the electric arc furnace. Depending on the size of the furnace 3 to 6 Søderberg or pre-baked electrodes are immersed in the liquid layer. The melting temperature is maintained by means of electric resistance heating. The furnace is usually operated continuously.

Molten or solid raw materials are fed in a number of ways using launders, feed pipes or through a hollow electrode. Sealed or semi-sealed conditions are easy to maintain. In smelting processes the roasted ore concentrates are transferred on to the liquid melt either through the top of the furnace or sideways by individual chargers and the electrodes are immersed in the molten slag layer.

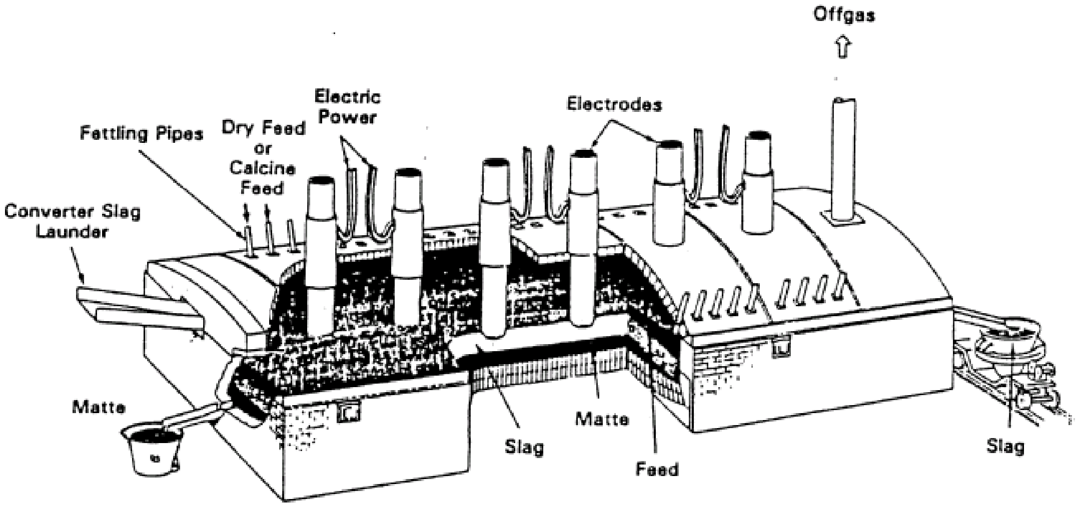


Figure 2.8: Electric Furnace for concentrate or calcine smelting

They can be operated in a number of ways using coke and slagging agents depending on the application. The carbon electrodes are consumed as oxides are reduced but the gas volumes produced during operation are kept to a minimum as there are no gases produced by the combustion of a fuel. These furnaces are usually sealed and the gases are easily collected and treated to remove and if possible re-use dust, CO and sulphur dioxide.

These furnaces are used in the production of a number of metals from primary and secondary raw materials including precious metals, lead and copper and for slag cleaning [tm 124, DFIU Cu 1999]. Some slags from primary smelting e.g. Cu, are usually cleaned in circular furnaces. They are also used for the recovery of precious metals in particular silver.

2.6.2.5 Refractory lined pits and crucibles

These are simple pits formed in Al_2O_3 or other refractory material and refractory lined steel cylinders that are placed to from crucibles, which contains the process. They are commonly used for metallo-thermic reactions. Refractory lined pits and crucibles are often used in the production of special ferro-alloys such as ferro-vanadium and ferro-molybdenum as well as for refractory metals.

2.6.2.6 The ISA Smelt/Ausmelt furnace

This furnace uses a steel lance for the injection of fuel gas, oil or coal and oxygen or air into a cylindrical bath furnace. The lance is submerged in the molten bath and relies on the formation of a coating of slag to prevent rapid deterioration.

Other raw materials are fed into the furnace by sealed conveyor where they react at a high rate and are melted. The submerged combustion lance stirs the bath and produces a slag along with the desired metal or matte. The separation of the molten phases requires a separate settling furnace from where the phases are tapped separately. The furnace can be used on a batch basis when conditions in the furnace, such as the gas blown through the lance are changed at the end of a batch. Examples of a batch operation are a) the smelting of copper/lead secondary material to a copper lead matte in a first stage followed by conversion of the matte to blister copper by blowing with oxygen; b) the treatment of zinc leach residues. Continuous operation is possible using two furnaces in series e.g. as suggested for the ISA lead production process.

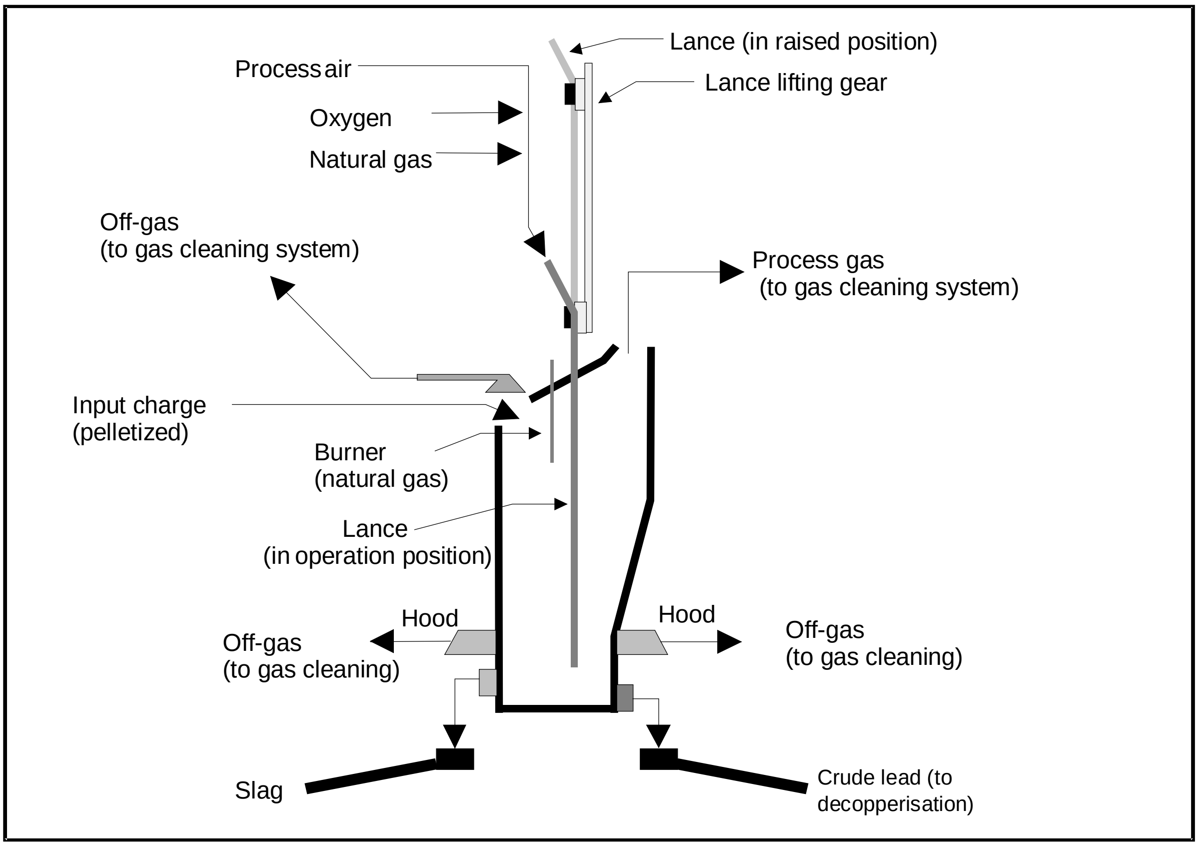


Figure 2.9: The Ausmelt/ISA Smelt process
[tm 124, DFIU Cu 1999]

The furnace uses a robust hood and extraction system to collect and treat fume from the furnace system and tapping operations. When sulphide concentrates are smelted the gases are passed to a sulphur removal system.

There are a number of applications for this type of furnace including the production of copper matte from concentrates (ISA Smelt) and converting, production of lead from primary and secondary materials (ISA Smelt), treatment of spent pot lining and fuming of zinc (Ausmelt) [tm 38 - 45, Ausmelt 1997]. The ISA Smelt furnace is also used for the production of copper and lead from mixed feed. This furnace is used for continuous direct smelting furnace as well as for batch and stepwise operations. When smelting copper concentrate to matte the process uses moist feed that is fed continuously with fluxes into the furnace.

2.6.2.7 The Top Blown Rotary furnace

This is a rotating and tilting furnace that uses lances for heating and blowing purposes. The furnace is small and is usually housed in an enclosure to contain secondary emissions, which are treated. Rotation of the furnace promotes good mixing of the charge and complete reaction of the components but can lead to abrasion of the refractory lining.

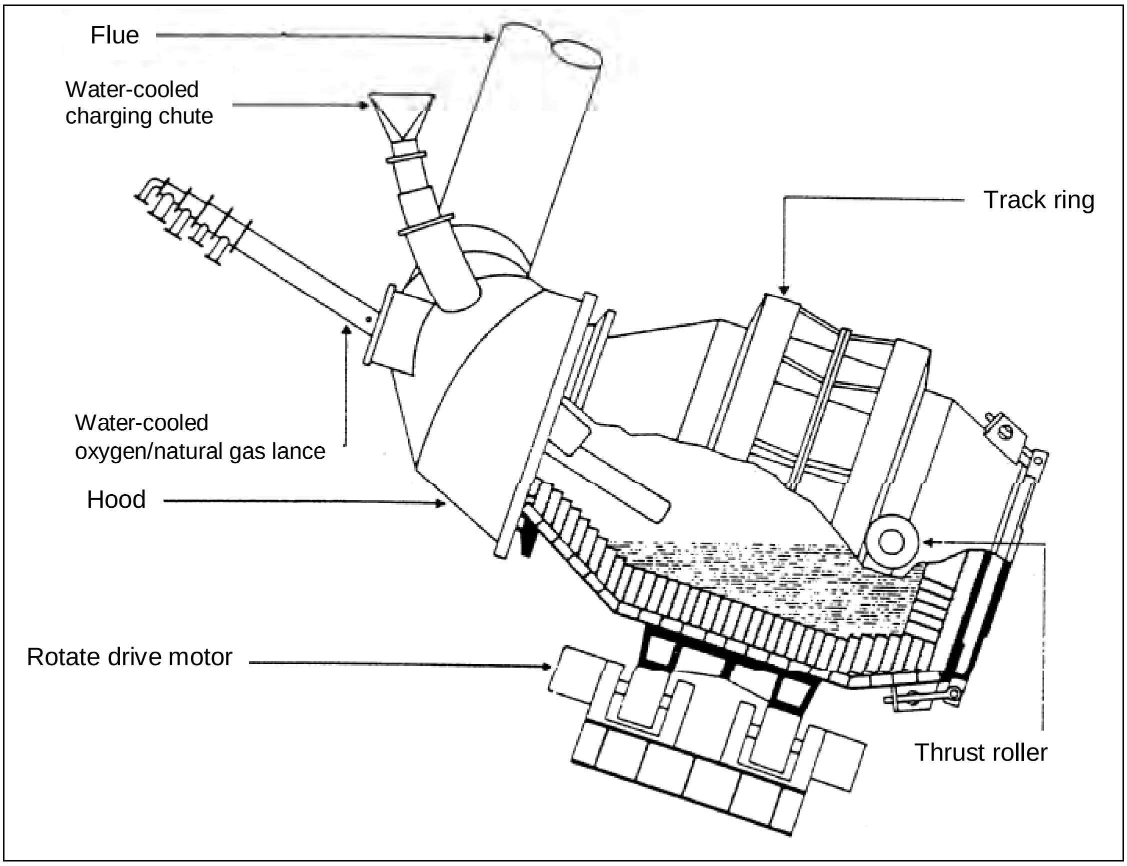


Figure 2.10: Top Blown Rotary Furnace

Oxygen and fuel are added via the lances, which blow on to the surface of the melt. The use of oxygen results in the production of low off-gas volumes and high sulphur dioxide when sulphides are smelted. The process is normally carried on a batch basis and it is common to use a number of these furnaces for smelting, converting and slag cleaning.

The furnace is used for smelting, converting and slag treatment. It is used to produce primary and secondary copper and lead, ferro-nickel and for the recovery of precious metals.

Other commercial designs of tilting rotary furnaces are also used for smelting and examples are the mini-smelter and the tilting, rotating oxy-fuel furnace (TROF).

2.6.2.8 The Noranda, El Teniente, Baiyin and Vanyucov processes

The Noranda Reactor uses a cylindrical refractory lined furnace for smelting. Pelletised concentrate and additives are charged on to the bath of molten slag at the top end of the furnace. Burners fired by natural gas or oil situated at both ends produce the heat necessary for processing. Oxygen-enriched air is blown into the molten bath through tuyeres, causing sulphur and iron to oxidise.

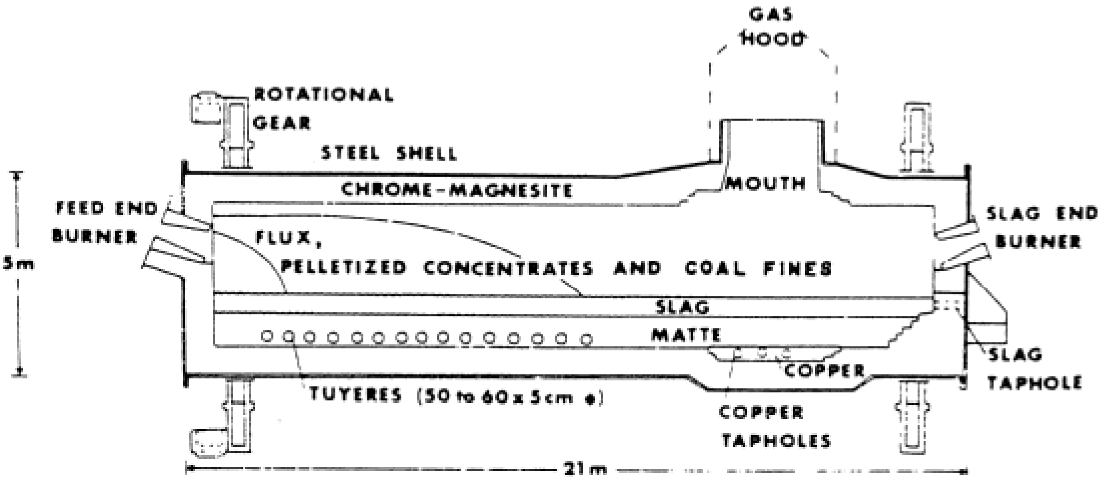


Figure 2.11: The Noranda Reactor

During continuous smelting in the furnace the melt segregates into two liquid phases: slag and matte. Due to their various densities they settle to form two layers. Matte is tapped periodically from the bottom of the furnace and the slag flows out continuously opposite the charging end. The furnace is sealed and extracted and the launders are provided with extraction.

This process is used to smelt copper concentrates and can produce blister copper when using concentrates with low impurity levels or high-grade matte. The normal operating practice is to produce a copper-rich matte to undergo further conversion.

The El Teniente, Baiyin and Vanyucov processes are similar to the Noranda process. In the El Teniente process wet concentrates are added to the furnace using a Gar gun and dry concentrates are added via the tuyeres. Initially a matte was seeded into the furnace to help the process and produce white metal. The Baiyin process uses a rectangular furnace that is divided into smelting and settling zones. In the Vanyucov process the oxygen enriched air is blown into the slag layer rather than the matte layer.

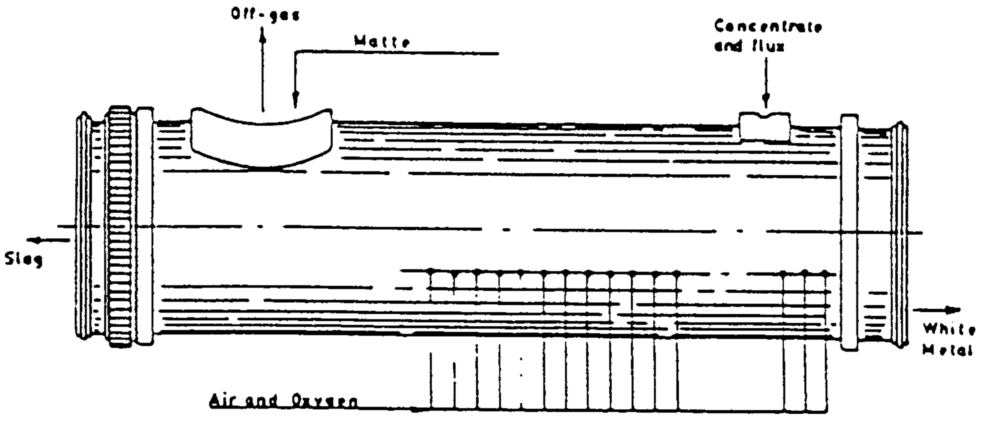


Figure 2.12: El Teniente Reactor

2.6.2.9 The Mitsubishi process

This process employs three interconnected furnaces, a bath smelting furnace, an electric slag cleaning furnace and a converting furnace. Gravity flow is used between the furnaces and avoids the transfer by ladle. All of the furnaces are sealed and extracted, heat from the process gases is recovered and treated to remove dust and sulphur dioxide.

The dried concentrates, air, oxygen and additives are charged into the bath furnace by means of lances and subsequently melted to form matte (60 - 65% copper content) and slag. This mixture flows continuously through a channel into the electric hearth furnace that serves as a settling furnace to separate the slag. Matte is continuously discharged from the settling furnace through a siphon into the converting furnace.

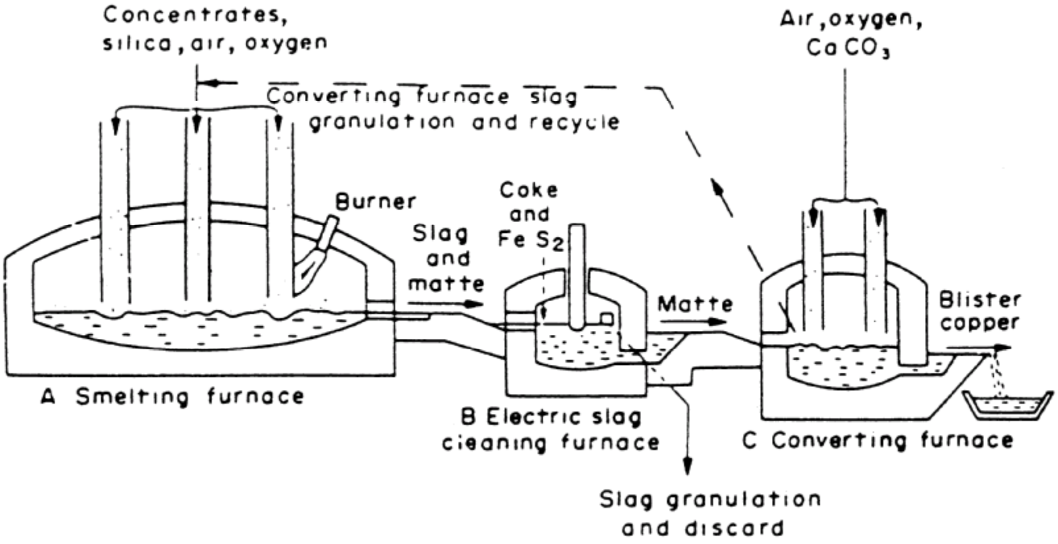


Figure 2.13: The Mitsubishi Process

In the converter air, oxygen and additives are blown on to the liquid bath via water-cooled lances to produce blister copper. The converter slags are recycled to the smelting furnace, which can also be fed with anode scrap. It is possible that the converter stage could be used with other smelting furnaces.

This process produces blister copper continuously.

2.6.2.10 QSL furnace

The furnace is a horizontal cylinder divided into an oxidation zone and reduction zone. The furnace is lined with chrome-magnesite bricks to cope with a temperature of 1250 °C. Tuyeres at the furnace bottom supply oxygen to the oxidation zone and a mixture of air and coal dust to the slag reduction zone. Raw material can be moist and sized from large lumps to fine material. They are fed into the top of the furnace mixed with coal and fluxes.

The oxidation zone produces lead bullion, sulphur dioxide and a lead rich slag. This flows into the reduction zone so that a further quantity of lead bullion is produced, this flows in the reverse direction to the lead tap hole. Slag is tapped from the reduction end and then granulated. Lead bullion is tapped from the oxidation end and then refined. Hoods and complete enclosures exhaust the outlets and launders. The exhaust gases are used from heat recovery and then de-dusted before passing to a sulphuric acid plant. Other process gases are cleaned in bag filters.

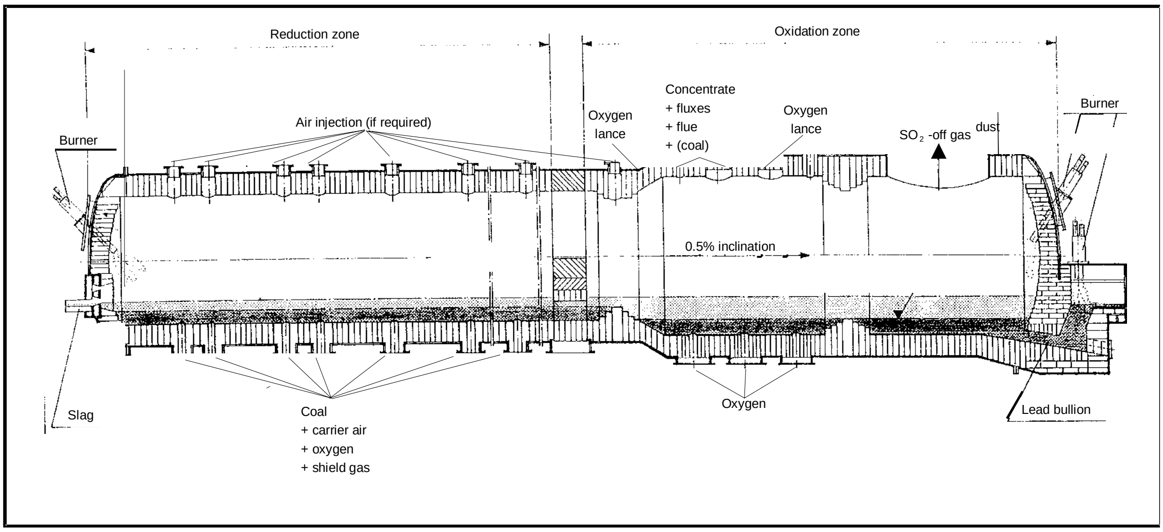


Figure 2.14: QSL Process
[tm 102, DFIU Zn 1999]

The QSL process was designed to produce lead from concentrates and some secondary materials in a single bath furnace and to maximise energy recovery.

2.6.2.11 Cyclone smelting furnaces

These include the Flame Cyclone Reactor (FCR) and the Contop reactor. With these high-intensity flash-smelting processes the copper concentrates and flux are smelted with oxygen in cyclone-type combustion chambers. In the Contop process, the cyclone is disposed vertically and the reacted mixture falls into a settling chamber below the cyclone. In the FCR process, the combustion takes place in a vertical reaction shaft and the separation of the matte and slag occurs in a further horizontal reactor. Slag and white metal or copper rich matte are separated in the fore-hearth and tapped off. The white metal or matte is processed in a standard converter.

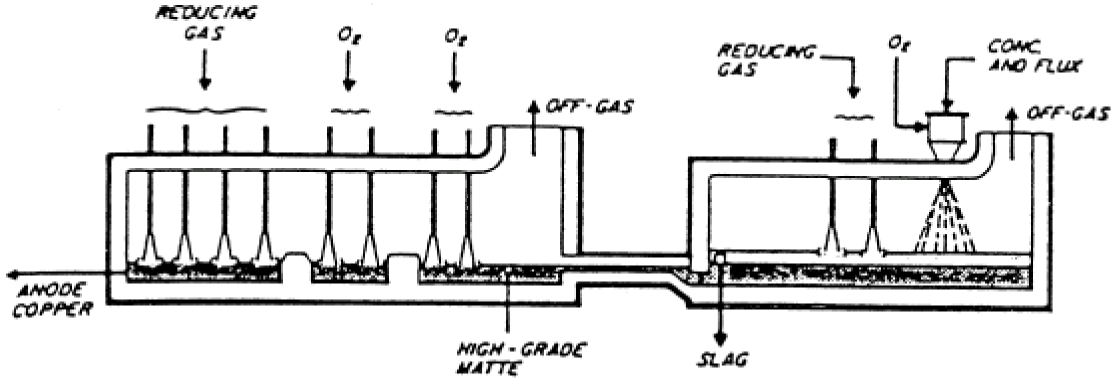


Figure 2.15: Contop Process

These processes are mainly used to smelt copper concentrates.

2.6.2.12 The Outokumpu Flash Furnace

This is a flash smelting process. The dried concentrates are smelted by utilising the energy content of the concentrates for the production of the heat needed for the smelting of concentrate and flux. The concentrate feed mixture is fed continuously with oxygen enriched air through a concentrate burner into the vertical reaction shaft of a sealed furnace where the reactions between oxygen and concentrate takes place rapidly in suspension. The heat of reaction melts the particles. The fused particles produce matte and slag. Sulphur dioxide is formed at the same time. In older installations process air preheating to about 200- 800 ℃ was used to achieve autogeneous operation, but at the time of writing the majority of installations achieve autogeneous operation by using oxygen enrichment to about 30 – 90% oxygen in process air. The degree of oxygen enrichment is determined by the concentrate quality and the heat balance requirements. The continuous off gas flow leaves the furnace through the uptake shaft for heat recovery and particulate removal. It has a high, constant sulphur dioxide concentration and sulphur is recovered from the gas mainly by conversion to sulphuric acid after particulates are removed.

The molten slag and matte particles are settled out of the gas in a horizontal settler part of the furnace forming a molten bath where the phases separate without an external settler. The matte is tapped out of the furnace to ladles or led via launder to granulation depending on the method of conversion used. The slag is tapped continuously or semi-continuously out of the furnace and can be further processed in a slag furnace or in a slag flotation circuit for copper recovery. In some installations the low copper content in slag allows the slag produced in the primary smelter to be discarded or used directly.

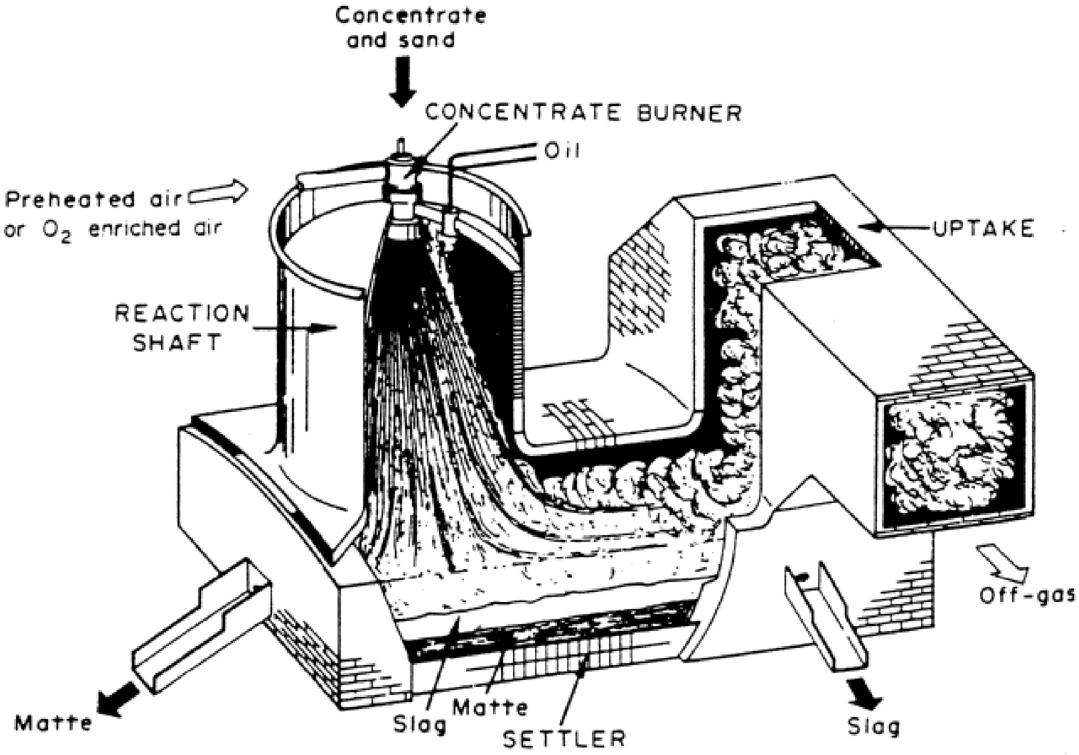


Figure 2.16: The Outokumpu Furnace

The flash furnace is established for the production of copper and nickel matte and blister copper directly from concentrates. The furnace produces a high-grade matte and so the main part of the sulphur in the concentrate is released in the smelter gases and enables the conversion process (e.g. the discontinuous Peirce-Smith converter) to eliminate the remaining sulphur more easily.

The furnace has been used on a demonstration scale for the production of lead bullion and for fuming of Jarosite waste.

The same type of furnace is also used in the Flash Converting process for the conversion of ground, granulated matte into blister copper. The process has similar features to the flash smelting process i.e. autogeneous operation with oxygen enriched air and a continuous flow of off gas with a high sulphur dioxide content.

2.6.2.13 The INCO furnace

This is a flash furnace similar to the Outokumpu Flash Furnace but uses pure oxygen to operate autogeneously. Copper ore concentrate blended with slagging agents are blown horizontally into the furnace from both ends and the off gases are collected at the centre of the furnace.

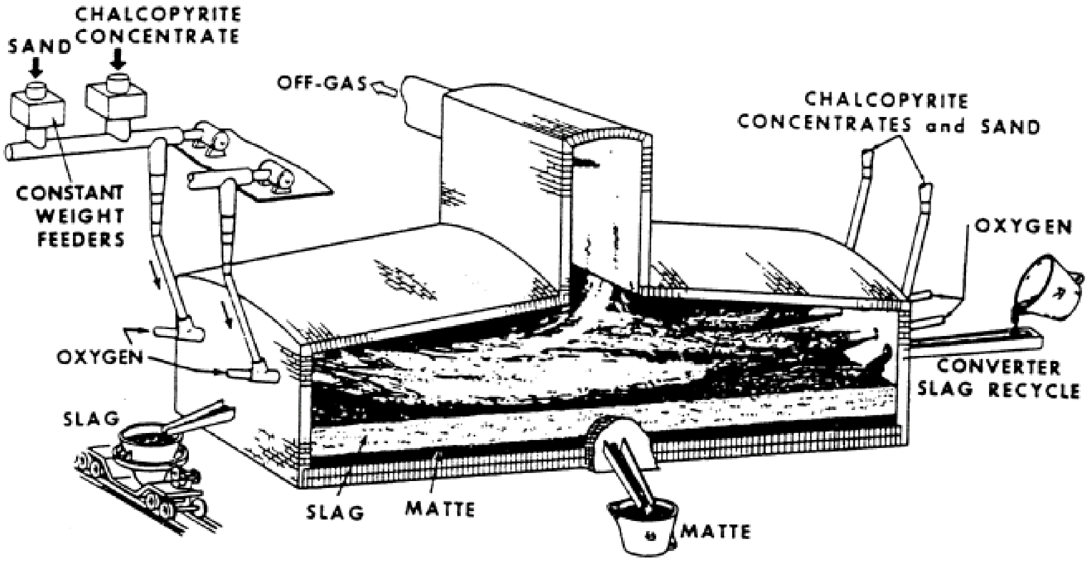


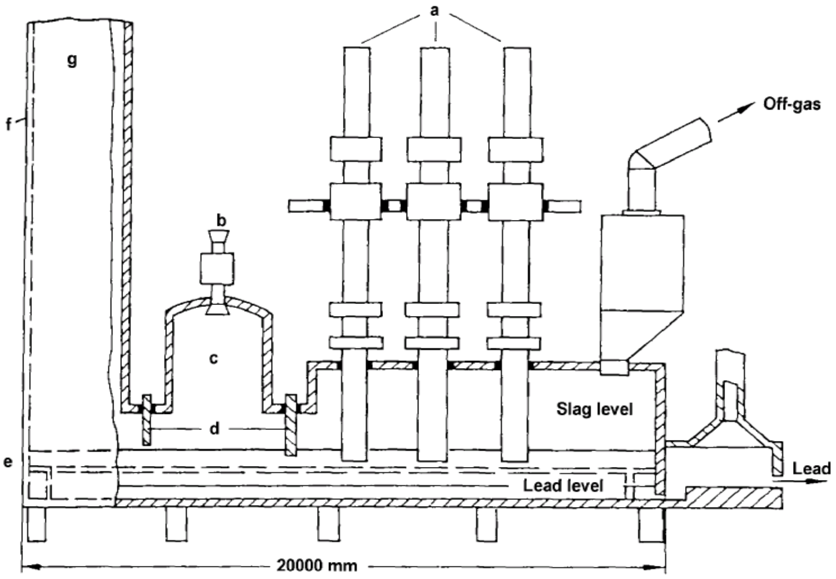
Figure 2.17: The INCO Furnace

The concentrates are roasted and melted in suspension in the furnace and fall into the settler in the same manner as the Outokumpu Flash Furnace. The heat produced by roasting is sufficient for an auto-thermal smelting process. The slag, which has a medium copper content, flows out continuously at one end of the furnace and the matte is tapped periodically at the centre of one sidewall. The waste gas contains up to 75% SO_2.

2.6.2.14 The Kivcet (KSS) furnace

This is a flash furnace similar to the Outokumpu Flash Furnace. Dry and blended charge components and oxygen are fed continuously through burners at the top into an oxidation shaft. At the same time coke breeze is added.

The charge is ignited as it enters the reaction shaft, temperatures up to 1400 °C are reached and complete de-sulphurisation takes place immediately. The coke breeze is only heated as it falls down the shaft. The coke floats on the slag bath and reduces PbO. Partly reduced slag and bullion flow under a submerged partition wall into the reduction section of the furnace, which is electrically heated and where additional coke or coal is added for final reduction.



a) Electrodes; b) Concentrate burner; c) Smelting shaft; d) Partition walls;
e) Belt of water-cooled elements; f) Water-cooled refractory lining;
g) Gas removal shaft

Figure 2.18: The Kivcet Furnace

Lead bullion is sent for refining, the slag may be sent to a Waelz kiln. the flue dust from the oxidation is directly sent back to the furnace. The flue dust from the reduction stage is treated in an ISF. The process is also used for copper production.

2.6.3 Converters

2.6.3.1 The Peirce-Smith Converter

These converters are run batch-wise and use tuyeres to blow air or oxygen into the matte to react the matte in two stages to produce blister copper or high-grade nickel matte and slag. They are also used for the production of ferro-nickel and some metal oxides.

Large volumes of hot gases are produced during the blowing periods and are collected by means of hoods over the converter opening. The space between the converter housing and the hood allows the access of bypass air, which causes dilution of the SO_2-rich effluent gases. The SO_2 concentration varies depending on the process cycle. During initial blowing SO_2 concentrations can be considerably higher than 10%, during the subsequent blowing period, and when the converter is turned away from the hood, SO_2 concentrations are much lower and often nil. The varying SO_2 concentration does not provide a satisfactory feed to the acid plant, which requires a relatively steady flow. This is overcome in multi-converter plants by converter scheduling to attain a relatively steady flow. The gases can also be mixed with the much stronger smelter gases. The use of oxygen for enriching the blast air will also increase the SO_2 content however the enrichment is limited due to the rapid increasing refractory wear. Water-cooled hoods are now being used in some plants.

The converter is charged via ladles with liquid matte and the slags produced during the conversion of the matte and the blister copper produced are subsequently poured into ladles from the converter. During these tapping processes, fugitive emissions are released. The use of additional fume extraction facilities (e.g. secondary hoods and air curtains) and the control of converter positioning to prevent blowing during the converter roll out, can reduce these emissions. Through-hood and tuyere charging systems are also used so that it is not always necessary to tilt the converter away from the hood during the charging of metal scrap and fluxes.

The general drum furnace format adopted by this type of converter is also used **for Anode Furnaces** where the blister or black copper produced by the converter are refined. These furnaces use tuyeres for further air blowing followed by the addition of a reducing agent (usually natural gas or propane) to remove the final traces of sulphur and then convert copper oxide to copper.

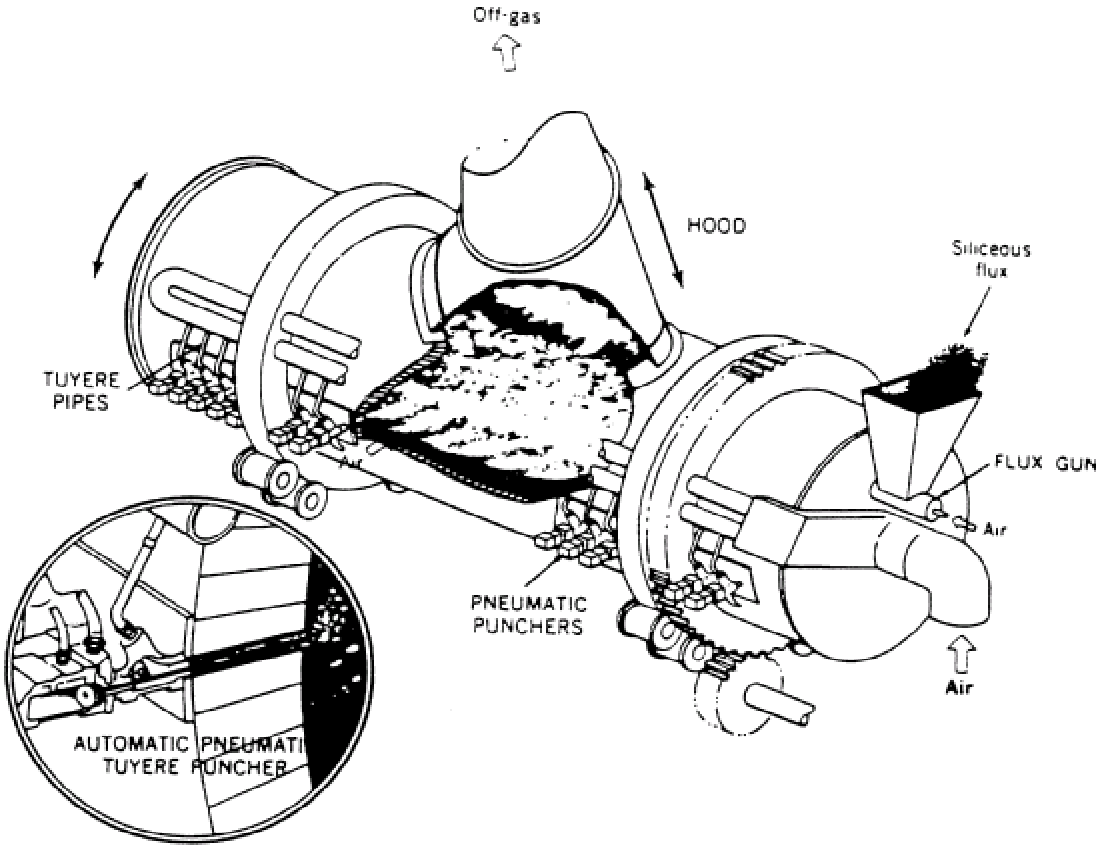


Figure 2.19: The Peirce-Smith Converter

This is by far the most common matte-converting vessel and is used to produce copper and high-grade nickel matte and for refining ferro-nickel.

2.6.3.2 The Hoboken Converter

This operates on the same blowing principle as the Peirce-Smith Converter but the large escape of gas that usually occurs when the converter is tilted for charging and tapping the slag and crude copper is avoided.

The effluent gas is sucked off through the flue at the end of the converter. The siphon minimises gas escape during all phases of operation. The converter is charged through a small opening at the top of the casing and charging is therefore possible during blowing without tilting the converter because of the shorter process duration. Dilution of the effluent gases due to infiltrated air is small, so that the steady average concentration of SO_2 is higher than for the Peirce-Smith converter. However, the SO_2 concentration will still vary throughout the cycle.

The end result is that there is a smaller loss of SO_2 from the converter. The smaller opening used for charging can create problems due to slag build-up.

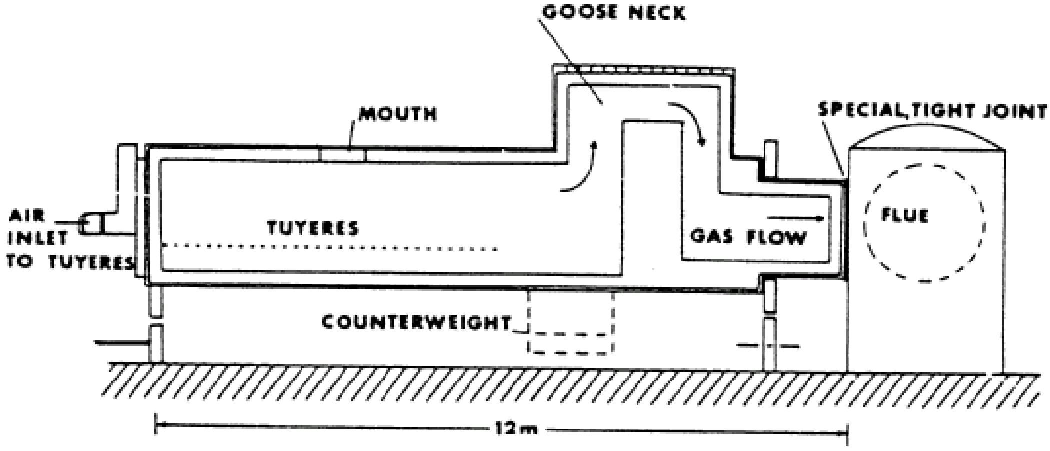


Figure 2.20: The Hoboken Converter

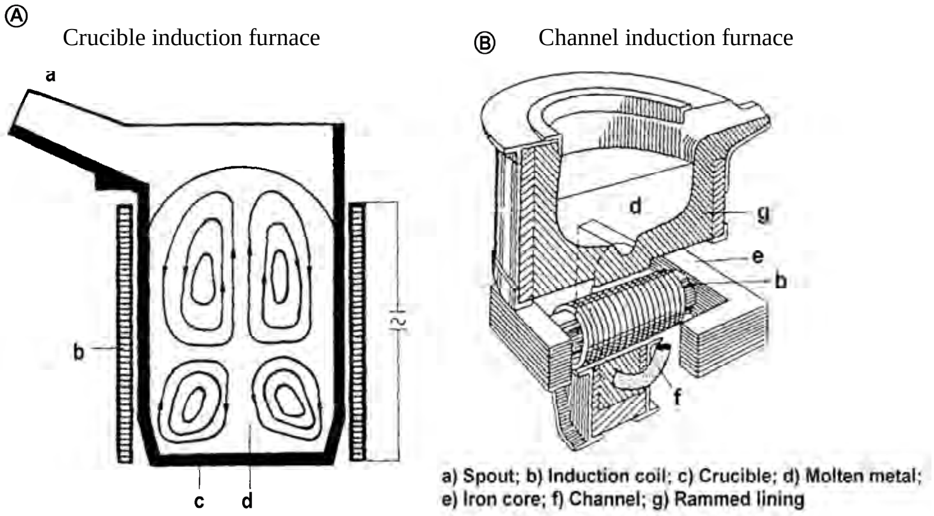
2.6.3.3 Other converters

The ISA Smelt/Ausmelt furnace, the TBRC, the converter stage of the Mitsubishi process and the Noranda converter are also used as converters. These furnaces use molten matte as the feed material. The OBM converter is used for ferro-nickel. The Flash converter (Kennecott/Outokumpu) is also used, in this case ground matte is used as the feed material. The Mitsubishi Converter and the Flash Converter are the only continuous Converters in metallurgy at the time of writing.

2.6.4 Melting and refining furnaces

2.6.4.1 Induction furnaces

They are simple crucibles or channels that are heated by an external electrical coil, channel induction furnaces are mainly used for melting items with large dimensions. In one case the channel furnace is used to melt aluminium cans.


Ⓐ Crucible induction furnace

Ⓑ Channel induction furnace

a) Spout; b) Induction coil; c) Crucible; d) Molten metal; e) Iron core; f) Channel; g) Rammed lining

Figure 2.21: Induction Furnaces

Current is induced in the metal that has been charged into the furnace and heat is generated. The furnaces are equipped with fume extraction hoods and dust abatement that can be used during drossing and pouring operations. Access to an induction furnace for charging and tapping means that a movable hooding system is often used. The hoods are robust so that they can withstand some mechanical impact. Alternatively, efficient fixed or lip extraction is used. The efficiency of this furnace can be low for some materials but can be increased particularly if the feed material is small. Large items can be cut to improve efficiency and also to allow the fume collection hoods to be deployed properly. Some continuous processes also retain a “heel” of molten metal in the bottom of the furnace between charges if the operation allows it.

These furnaces are used for small melting capacities up to 30 t commonly for copper, brass, zinc and aluminium. They may also be operated under vacuum, for example when melting super alloys, high alloyed steel, pure metals and in some cases for metal distillation. The temperature of the furnace can be automatically controlled to minimise the production of fume when melting volatile or oxidisable metals such as zinc or alloys containing zinc.

These furnaces are also used to “Hold” molten metal for alloying and casting. The current induced in these furnaces causes the metal to be stirred electro-magnetically, which promotes mixing of the charge and any alloying materials that are added.

2.6.4.2 Indirectly heated kettles

These are simple crucibles that are heated externally by the combustion gases from gas or oil combustion, electricity or for lower temperatures by thermal fluid. Contact with a direct flame is avoided to prevent local hot spots at the base of the crucible and good temperature control can be maintained in the melt so that oxidation and vaporisation of the metal is prevented.

These kettles are used mainly for melting clean lead and lead alloys and zinc and its alloys.

2.6.4.3 The shaft furnace for melting of metal

This is a simple vertical furnace with a collecting hearth (inside or outside the furnace) and burner system at the lower end and a material charging system at the top. The burners are usually gas fired and are designed to produce an oxidising or reducing atmosphere. This allows the metal to be melted with or without oxidation. Metal is fed into the top of the furnace and is melted as it passes down the shaft. Independent control of the fuel/air ratio is usually provided for each burner. Continuous CO or hydrogen monitoring is also provided for each row of burners and monitor the combustion gases from each burner in turn. Combustion gases are usually extracted and cleaned. An afterburner is used sometimes to decompose any carbon monoxide, oil, VOCs or dioxins that are released. The addition of oxygen above the melting zone has been used to provide after-burning in the upper levels of shaft or blast furnaces.

The furnace is used to melt pure metal but occasionally metal that is contaminated with organic material is used. If oily metal is fed into the furnace it passes through the temperature gradient that exists between the charging area and the burners. The low temperature can produce a mist of partially burnt organic material. The shaft furnace is also used to pre-heat the charge material before smelting.

2.6.4.4 The Contimelt process

The process comprises two interconnected furnaces, a hearth shaft furnace and a drum furnace. The first is a vertical rectangular furnace with a horizontal collecting chamber which is fed with blister or black copper and other raw materials. Oxy-gas burners supply heat and the feed is melted to produce a fire-refined copper and a small amount of slag that is separated.

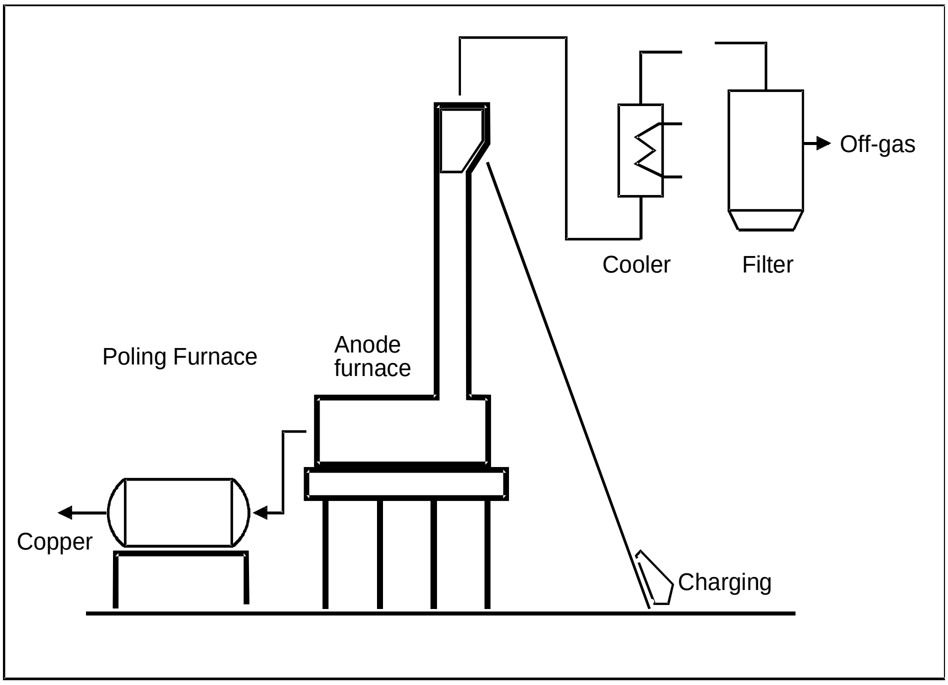


Figure 2.22: Contimelt Process
[tm 124, DFIU Cu 1999]

Molten copper flows via a siphon and launder to a horizontal cylindrical furnace where it is de-oxidised using natural gas. Refined copper is then cast as anodes. Gases from the second furnace are passed to an afterburner. They are then combined with gases extracted from the first furnace and pass to a waste heat boiler, burner air pre-heater, cooling stage and finally a bag filter.

The furnace operating conditions can be controlled to minimise oxidation of the metal. The arrangement allows heat recovery by steam generation or charge pre-heating.

This is a continuous 2-stage process to melt and treat black and blister copper, high grade copper scrap and anode scrap to produce copper anodes. A similar development in the aluminium industry is the Meltower process [tm 116, ALFED 1998]. This process uses a vertical melting tower and incorporates charge pre-heating using the hot exhaust gases.

2.6.4.5 Electron beam furnaces

The very high melting temperatures of refractory metals like tungsten, tantalum or niobium do not allow melting in a normal melting furnace. For high melting point metals the electron beam furnace has been developed, using accelerated electrons as an energy source to impart their energy into the furnace charge. The electron beam melting is used to produce high purity inclusion free metals. The ability to melt high purity metals is due to the perfectly clean high temperature heat source (electrons) and the water-cooled copper hearth. The melted metal freezes against the copper, so that the melt is only in contact of its own solid. Electron beam melting and refining is a well-established process for the production of ultra clean refractory metals such as vanadium, niobium, tantalum, molybdenum and tungsten.

2.6.4.6 The rotary furnace

This is a refractory lined rotating cylinder fitted with burner at one end. A charging door is provided at one end and the burner can sometimes be housed in this. Oxy-fuel firing can be used. The furnaces can be either “long” or “short” and several variants exist.

- Short rotary furnaces: Smelting of secondary lead, precious metals etc.
- Long rotary furnaces: Melting and recovery of aluminium scrap etc.
- Thomas furnace: Melting and refining copper scrap etc.
- Rotary furnace with submerged tuyeres: Refining of blister or black copper, slag cleaning etc.

Furnace rotation can be varied to give a complete reaction of the charged material and high efficiency. Raw materials are usually charged via an end door, this is usually enclosed and extracted to prevent fume emissions. The furnaces use oil or gas fuel and oxy-burners are commonly used, heat from the burner is transferred to the refractory wall and the charge is heated by the refractory during rotation.

Slags and metal produced during the process can be tapped from a tapping hole at the door end or at the mid-point of the furnace. The tapping hole is orientated by partial rotation of the furnace to maintain the separation of the metal and slag. Tapping from the door end allows fume to be collected from a single enclosure and extraction system. Tilting rotary furnaces are also used, they show improved recovery rates for some feed stocks and can have less reliance on fluxes.

A variety of metals can be smelted or melted in these furnaces.

2.6.4.7 The reverberatory furnace

This is a refractory lined, rectangular or circular bath furnace that is fired by wall or roof mounted burners. Varieties of fuels are used and oxy-fuel burners can be used to increase the melting rate. Extraction and treatment of the combustion gases is used and the furnaces are partially sealed. Hoods and covered launders provide extraction during tapping and charging.

Slag or dross can be removed by raking or by tapping.

Many designs have large access doors that allow large objects to be charged. This introduces the problem of sealing and extraction during charging. Water cooling of the doors can reduce this problem by reducing warping of doors. Sealed charging carriages are used and charging pipes can be used for concentrates. In a similar manner, door sealing can be affected by material being incorrectly charged to furnace. In some cases spilt metal or slag can solidify in the opening or in other cases wire or cable can prevent the doors from closing properly.

The melting efficiency of a reverberatory furnace usually is not great because of poor heat transfer from the burner. Efficiency has been improved in practice by the use of oxygen enrichment or by using combinations of gas and solid fuel to extend the flame length.

These furnaces are used for batch melting, refining and holding a variety of metals.

2.6.5 Summary of furnaces

Furnace	Metals Used	Material Used	Comment
Steam coil dryer Fluid bed dryer Flash dryer	Cu and some others	Concentrates	
Rotary Kiln	Most metals for drying. Fuming ZnO. Calcining alumina, Ni and ferro alloys. Burning film in precious metals. De oiling Cu and Al scrap	Ores, concentrates and various scrap and residues.	Drying, calcining and fuming applications. Use as an incinerator.
Fluidised bed.	Copper and zinc Al_2O_3	Concentrates. $Al(OH)_3$	Calcining and roasting.
Up Draught sintering machine.	Zinc and lead.	Concentrates and secondary.	Sintering.
Down Draft sintering machine	Zinc and lead.	Concentrates and secondary.	Sintering.
Steel Belt sintering machine	Ferro-alloys, Mn, Nb.	Ore.	Other applications possible
Herreshoff	Mercury and refractory metals Mo (rhenium recovery)	Ores and concentrates.	Roasting, calcining.

Table 2.5: Drying, roasting, sintering and calcining furnaces

Furnace	Metals Used	Material Used	Comment
Enclosed refractory lined crucibles	Refractory metals, special ferro-alloys	Metal oxides	
Open Pit	Refractory metals, special ferro-alloys.	Metal oxides	
Baiyin	Copper	Concentrates	
Electric Arc Furnace	Ferro Alloys	Concentrates, ore	
Contop/Cyclone	Copper	Concentrates	
Submerged Electric Arc Furnace	Precious metals, copper, ferro alloys.	Slag, secondary materials, concentrates.	For the production of ferro-alloys the open, semi closed and closed types are used.
Rotary	Aluminium, lead, precious metals	Scrap and other secondary	Oxidation and reaction with substrate.
Tilting Rotary Furnace	Aluminium	Scrap and other secondary	Minimises salt flux use.
Reverberatory	Aluminium, copper, others	Scrap and other secondary	Smelting of oxidic Cu material, refining.
Vanyucov	Copper	Concentrates	
ISA Smelt/Ausmelt	Copper, lead,	Intermediates, concentrates and secondary materials.	
QSL	Lead	Concentrates and secondary	
Kivcet	Lead Copper	Concentrates and secondary	
Noranda	Copper	Concentrates	
El Teniente	Copper	Concentrates	
TBRC TROF	Copper (TBRC), Precious metals	Most secondary inc. slimes	
Mini Smelter	Copper/lead/tin	Scrap	
Blast Furnace and ISF	Lead, lead/zinc, copper, precious metals, high carbon ferro-manganese.	Concentrates, most secondary	For ferro-manganese production it is only used together with energy recovery.
Inco Flash Furnace	Copper, nickel	Concentrates	
Outokumpu Flash Smelter	Copper, nickel	Concentrates	
Mitsubishi Process	Copper	Concentrates and anode scrap	
Peirce Smith	Copper (converter), Ferro-alloys, Metal Oxide Production	Matte and anode scrap	
Hoboken	Copper (converter)	Matte and anode scrap	
Outokumpu Flash Converter	Copper (converter)	Matte	
Noranda Converter	Copper (converter)	Matte	
Mitsubishi Converter	Copper (converter)	Matte	

Table 2.6: Smelting and converting furnaces

Furnace	Metals Used	Material Used	Comment
Induction	Most	Clean metal and scrap.	Induced stirring assists alloying. Vacuum can be applied for some metals
Electron Beam	Refractory metals	Clean metal and scrap.	
Rotary	Aluminium, lead	Various scrap grades.	Fluxes and salts used for complex matrices.
Reverberatory	Aluminium (primary and secondary)	Various scrap grades.	Bath or hearth configuration can vary. Melting or holding
Contimelt	Copper	Copper anode and clean scrap.	Integrated furnace system.
Shaft	Copper	Copper cathode and clean scrap.	Reducing conditions.
Drum (Thomas)	Copper	Clean copper scrap	Melting, fire refining
Heated Crucibles (indirect kettles)	Lead, zinc	Clean scrap.	Melting, refining, alloying.
Direct heated crucibles	Precious metals	Clean metal	Melting, alloying.

Table 2.7: Melting Furnaces

2.6.6 Electrochemical processes

2.6.6.1 Electro-winning

An electrolytic cell is used consisting of an inert anode of lead or titanium and a cathode, placed in an aqueous electrolyte containing the metal solution. The cathode is either a thin blank of pure metal (starter sheet) or a former sheet made from stainless steel or aluminium (permanent cathode plate). Metal ions pass from solution and are deposited onto the cathode, gases such as chlorine or oxygen are evolved at the anode. Chlorine is collected in a sealed anode compartment but oxygen is usually released and may entrain some of the electrolyte and produce an acid mist, which may need to be collected and returned to the process. Depleted electrolyte is normally returned to the process.

Copper, cobalt, nickel, tin, zinc and precious metals are produced in this manner. When using permanent cathode plates the pure metal deposits can be stripped or scraped off, melted and cast into the required shape.

2.6.6.2 Electro-refining

An electrolytic cell is used consisting of a cast anode of the metal to be refined and a cathode, placed in an electrolyte containing the metal solution. The cathode is either a thin blank of pure metal (starter sheet) or a former sheet made from stainless steel (permanent cathode plate). Metal ions are dissolved from the impure anode and pass into solution from where they are deposited onto the cathode.

Copper, precious metals lead and tin are refined in this manner. When using permanent cathode plates the pure metal deposits can be stripped or scraped off, melted and cast into the required shape.

During electro-refining other metals contained in the anodes are separated, soluble metals are dissolved in the electrolyte and insoluble metals like the precious metals, Se and Te form an anode slime that settles in the electrolytic cells. Anode slimes are periodically removed from the cells and the valuable metals recovered. In some cases anode bags are used to contain the slimes.

A portion of the electrolyte is bled from the system and other metals recovered from it.

2.6.6.3 Molten salt electrolysis

An electrolytic cell is constructed using inert cathodes and anodes (steel or carbon) so that the high electrolyte temperatures can be withstood. Molten metal is deposited at the cathode and is removed periodically by vacuum or displacement. Gases such as chlorine or oxygen are evolved at the anode; chlorine is collected and recycled or sold. For aluminium, oxygen reacts with the carbon anode, which is continuously consumed.

Molten salt electrolysis can be used to produce aluminium, lithium, sodium and magnesium.

2.6.7 Hydrometallurgical processes

Acids and NaOH, sometimes also Na_2CO_3 are used to dissolve the metal content of a variety of ores and concentrates before refining and electro-winning. The material to be leached is usually in the form of the oxide, either as an oxidic ore or an oxide produced by roasting [tm 137, Copper Expert Group 1998]. Direct leaching of zinc concentrate is also done at both elevated and atmospheric pressure. Some copper sulphide ores can be leached with sulphuric acid or other media sometimes using natural bacteria to promote oxidation and dissolution, but very long residence times are used. Air or oxygen or chlorine can be added to leaching systems to provide the appropriate conditions, and solutions containing ferric chloride are also used. The solutions that are produced are treated in a number of ways to refine and win the metals. Common practice is to return the depleted solutions to the leaching stage where appropriate to conserve acids and alkaline solutions.

2.6.7.1 Heap leaching

Open heap leaching is usually carried out at the mine. Material is crushed and ground to allow intimate particle/acid contact and then formed into natural heaps on an impervious liner. Acid is sprayed onto the heaps and percolates through the mass [tm 130, Chadwick 1994]. It is collected on the liner and is re-circulated to allow the metal content to build up. Leaching time of a single heap can vary from 100 days for copper oxide ore to 500 days for copper sulphide ore.

2.6.7.2 Atmospheric leaching (open tank)

Atmospheric leaching of oxides and concentrates is carried out in open or partially enclosed tanks by re-circulating the mixture to maintain temperature and acid concentration. The system is usually operated in a number of tanks in series. This is followed by sedimentation to separate the residue and purification and winning of the metal solution. Some leach residues can be leached further when the acid strength and temperature are increased. The use of a number of leaching stages can improve the leaching efficiency but can result in the dissolution of more impurities particularly iron, which subsequently has to be removed.

2.6.7.3 Pressure leaching (autoclave)

Pressure leaching or autoclaving can be carried out as a complete leaching process or as part of a series of leaching stages. Acid or alkaline resistant pressure vessels are used and liquor is re-circulated to allow the reactions to proceed. Oxygen, air or chlorine can be added to increase oxidation. Pressure reduction stages can result in the production of acid mists and they are designed to contain them.

2.6.7.4 Solvent extraction

Metals can be extracted from aqueous solutions with certain organic solvents that are insoluble in water. The aqueous and organic phases are dispersed in each other and by controlling the pH of the mix and the complexing agent used, the target metal is selectively extracted into the organic phase. After phase separation a pure metal solution is obtained by re-extracting the metal from the organic phase into a secondary aqueous phase (stripping), from which the metal can be won in different ways. The following figure shows the principle for such a process.

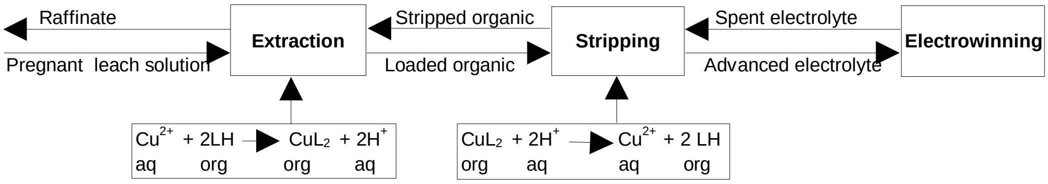


Figure 2.23: Solvent extraction (SX) processing stages

2.6.8 Process control techniques

The principles of Best Available Techniques include the concepts of how a process is designed, operated, controlled, manned and maintained. These factors allow good performance to be achieved in terms of emission prevention and minimisation, process efficiency and cost savings. Good process control is used to achieve these gains and also to maintain safe conditions.

Process operation and control has developed recently in this sector and is applied to a variety of processes. The following techniques are used: -

Sampling and analysis of raw materials is commonly used to control plant conditions. Good mixing of different feed materials should be achieved to get optimum conversion efficiency and reduce emissions and rejects.

Feed weighing and metering systems are used extensively. Loss in weight silos, belt weighers and scale weighers are use extensively for this purpose.

Microprocessors are used to control material feed-rate, critical process and combustion conditions and gas additions. Several parameters are measured to allow processes to be controlled, alarms are provided for critical parameters: -

- On-line monitoring of temperature, furnace pressure (or depression) and gas volume or flow is used.
- Gas components (O_2, SO_2, CO) are monitored.
- On-line monitoring of vibration is used to detect blockages and possible equipment failure.
- On-line monitoring of the current and voltage of electrolytic processes.
- On-line monitoring of emissions to control critical process parameters.

Monitoring and control of the temperature of melting furnaces to prevent the production of metal and metal oxide fume by overheating.

Process gases are collected using sealed or semi-sealed furnace systems. Interactive, variable speed fans are used to ensure that optimum gas collection rates are maintained and can minimise energy costs.

Solvent vapours are collected and recovered as far as possible. Further removal of solvent vapours is practised to prevent the emission of VOC and odours.

Operators, engineers and others should be continuously trained and assessed in the use of operating instructions, the use of the modern control techniques described and the significance of and the actions to be taken when alarms are given.

Levels of supervision are optimised to take advantage of the above and to maintain operator responsibility.

Environmental management and quality systems are used.

Hazard and operability studies are carried out at the design stages for all process changes.

Robust maintenance systems are used. There is growing use of dedicated maintenance staff forming part of the operator teams who supplement the dedicated maintenance teams.

General comments on some process design aspects are given in various sections of this document; these design aspects are used commonly in this sector. Full process design is approached with care using professional engineers who have experience and knowledge of the process and of the environmental impact and requirements.

Slag, metal and matte are analysed on the basis of samples taken at intervals. On-line analysis of these streams is an emerging technique.

For some processes special regulations such as the Seveso or Waste Incineration Directives may have to be taken into account.

2.7 Off Gas Collection Techniques

The process steps involved in the production of non-ferrous metals involve the potential production of dust, fume and other gases from material storage, handling and processing. The techniques for the prevention of fugitive emissions from the storage and handling stages are covered earlier in this chapter and this section deals with process gases. The techniques involved follow the hierarchy of prevention, minimisation and collection of fume.

Furnace sealing (or the use of sealed furnaces) combined with process control is the technique that should be applied to wherever possible to prevent or contain emissions from process plant. The section covering furnaces indicates where furnace sealing is possible and where other collection techniques may be used to provide integral gas collection.

Other techniques are available to collect the emissions that are not preventable or contained [tm 75, Theodore 1994; tm 76, Scapa 1998; tm 78, IEA 1997; tm 79, Soud 1995]. Gases and fume that escape from the processes are released into the working area and then escape into the surrounding environment. They therefore affect operator health and safety and contribute to the environmental impact of the process. Process gas collection techniques are used to prevent and minimise these fugitive emissions.

Fugitive emissions are very important but are hard to measure and quantify. Methods of estimating ventilation volumes or deposition rates can be used to estimate them. One reliable method has been used over a number of years at one site [tm 163, Steudtner 1998]. The method that is used to measure the volume and composition of fugitive dust emissions has proved to be reliable [tm 161, Petersen 1999] and the results of the monitoring exercise are reproduced below. The results show that the magnitude of fugitive emissions can be much more significant than collected and abated emissions. The lower the controlled emissions, the more significant the fugitive emissions. Fugitive emissions can be more than two to three times the quantity of controlled emissions.

	Dust emission kg/a	
	Before additional secondary gas collection (1992)	**After additional secondary gas collection (1996)***
Anode production t/a	220000	325000
Fugitive emissions: -		
Total Smelter	66490	32200
Smelter roofline	56160	17020
Controlled emissions (Primary smelter): -		
Smelter/acid plant	7990	7600
Secondary hoods stack	2547	2116
Note. * Emissions after an investment of 10 million Euros to give an improved fugitive gas capture and treatment system. Additional energy = 13.6 GWh/a		

Table 2.8: Comparison of abated and fugitive dust loads at a primary copper smelter [tm 161, Petersen 1999]

Light detection and ranging techniques (LIDAR) may also be used to measure some fugitive gaseous components such as SO_2 and VOCs.

2.7.1 Applied techniques

Dust, fume and gases are collected by using sealed furnace systems, by total or partial enclosure or by hooding [tm 75, Theodore 1994]. Sealed furnaces can be charged from sealed lance or burner systems, through hollow electrodes, through hoods or tuyeres or by docking systems that seal onto the furnace during charging. Hoods are designed to be as close as possible to the source emission while leaving room for process operations. Movable hoods are used in some applications and some processes use hoods to collect primary and secondary fume.

2.7.1.1 Use of energy

Gas collection requires the movement of significant volumes of air. This can consume vast amounts of electrical power and modern systems focus the design on capture systems to increase the rate of capture and minimise the volume of air that is moved [tm 124, DFIU Cu 1999]. The design of the collection or hood system is very important as this factor can maintain capture efficiency without excessive power consumption in the remainder of the system. Sealed systems such as sealed furnaces can allow a very high capture efficiency to be attained.

Ducts and fans are used to convey the collected gases to abatement or treatment processes. The effectiveness of collection depends on the efficiency of the hoods, the integrity of the ducts and on the use of a good pressure/flow control system. Variable speed fans are used to provide extraction rates that are suitable for changing conditions such as gas volume, with minimum energy consumption. The systems can also be designed to take account of the characteristics of the plant that it is associated with, e.g. the abatement plant or sulphuric acid plant. Good design and maintenance of the systems is practised.

2.7.1.2 Design criteria

Collector systems and extraction rates are designed on the basis of good information about the characteristics of the material to be collected (size, concentration etc), the shape of the dust cloud at the extremes of operation and the effects of volume, temperature and pressure changes on the system.

Correct measurement or estimation of the gas volume, temperature and pressure are made to ensure that sufficient rates of extraction are maintained during peak gas flows. Some of the characteristics of the gas and dust are also critical to good design to avoid problems of abrasion, deposition, corrosion or condensation and these are measured. Another significant factor is the provision of access to furnace filling or tapping areas while maintaining good rates of collection, operator experience is used at the design stage to provide this.

2.7.2 Techniques to consider in the determination of BAT

2.7.2.1 Some examples of the techniques to consider

The techniques to consider are based on the application of the principles of good practice recorded above. Good practice relies on the professional design and maintenance of the collection systems as well as on-line monitoring of emissions in the clean gas duct. The following examples are used to illustrate good practise, it is not an exhaustive list and other examples may also be applicable.

- The use of sealed furnaces can contain gases and prevent fugitive emissions. Examples are sealed smelting furnaces, sealed electric arc furnaces and the sealed point feeder cell for primary aluminium production. Furnace sealing still relies on sufficient gas extraction rates to prevent pressurisation of the furnace. The point feeder cell illustrated is usually connected to a well-sized extraction system that provides a sufficient rate of extraction to prevent the escape of gases during the opening of cell covers for short periods e.g. anode changes.

This technique is applicable to new or extensively modified processes only.

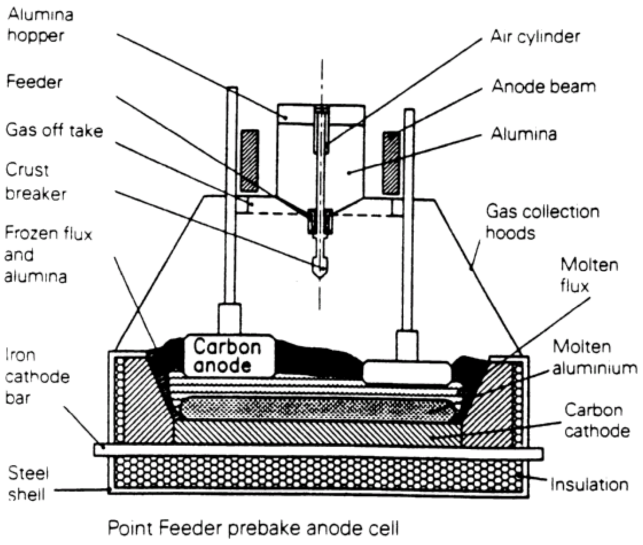


Figure 2.24: Point feeder prebake anode cell

- The use of sealed charging systems for the furnaces to prevent fugitive emissions during furnace opening. Examples are the use of charging skips that seal against a furnace feed door and the use of through-hood charging systems. These techniques may be applicable to some new and existing processes particularly for non-continuous processes.

- An important established practise to achieve good extraction is the use of automatic controls for dampers so that it is possible to target the extraction effort to the source of fume without using too much energy. The controls enable the extraction point to be changed automatically during different stages of the process. For example, charging and tapping of furnaces do not usually occur at the same time and so the charging and tapping points can be designed to be close together so that only one extraction point is needed. The extraction point is also designed to allow good access to the furnace and give a good rate of extraction. The hooding is constructed robustly and is maintained adequately**.**

  An example of this is an adaptation of a short rotary furnace. The feed door and tapping holes are at the same end of the furnace and the fume collection hood allows full access for a slag ladle and feed conveyor, it is also robust enough to withstand minor impacts during use.

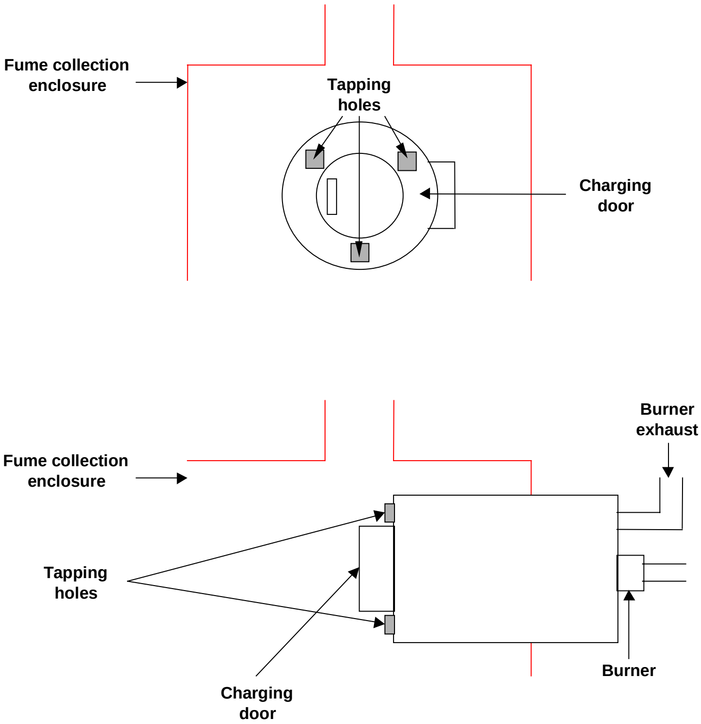


Figure 2.25: Coincident charging and tapping system

This principle is easily applied to a short rotary furnace but the principle of targeting the extraction effort to a changing source of fume is also be achieved by automatically controlling dampers to extract the main source of fume during the operating cycle e.g. charging, tapping etc.

The short rotary furnace and the TBRC may also be totally enclosed.

These techniques may be applicable to all new and existing processes particularly for non-continuous processes.

- If sealed furnaces are not available for example when retrofitting an existing open furnace, maximum sealing to contain furnace gases can be used.

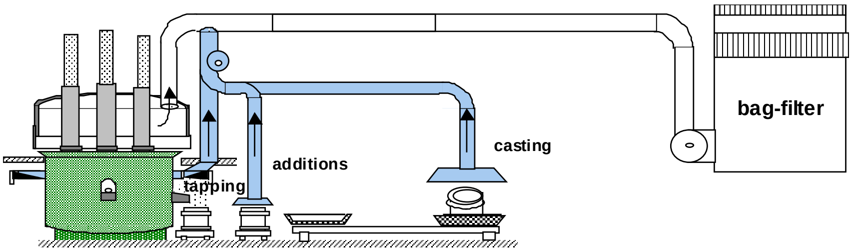


Figure 2.26: Fourth hole fume collection

An example of this is the use of a “fourth hole” in the roof of an electric arc furnace to extract the process gases as efficiently as possible and is shown in the above figure.

- Maintenance of the collector hood, the ducts, the filter system and the fan is vital to ensure that collection or extraction rates remain at the designed level. Physical damage from collision or abrasion, deposition in ductwork and deposition on fan blades are some of the problems that can be encountered. Regular inspection and preventative maintenance is used to ensure this. This technique is applicable to all new and existing processes.

- The collection of gases from a batch converter can be difficult as ladle transfers interfere with the collection hoods. Some installations collect all of the fume from the roof-line at the expense of a high energy cost. Another installation uses a system of up to 3 hoods in addition to the main hood. These hoods can be connected either to the sulphuric acid plant (hood 1) or to the secondary cleaning system (hoods 2 & 3). During filling and pouring operations the individual hoods are motor driven to the positions that ensure optimal collection efficiency. The gas treatment system is shown later in figure 2.28.

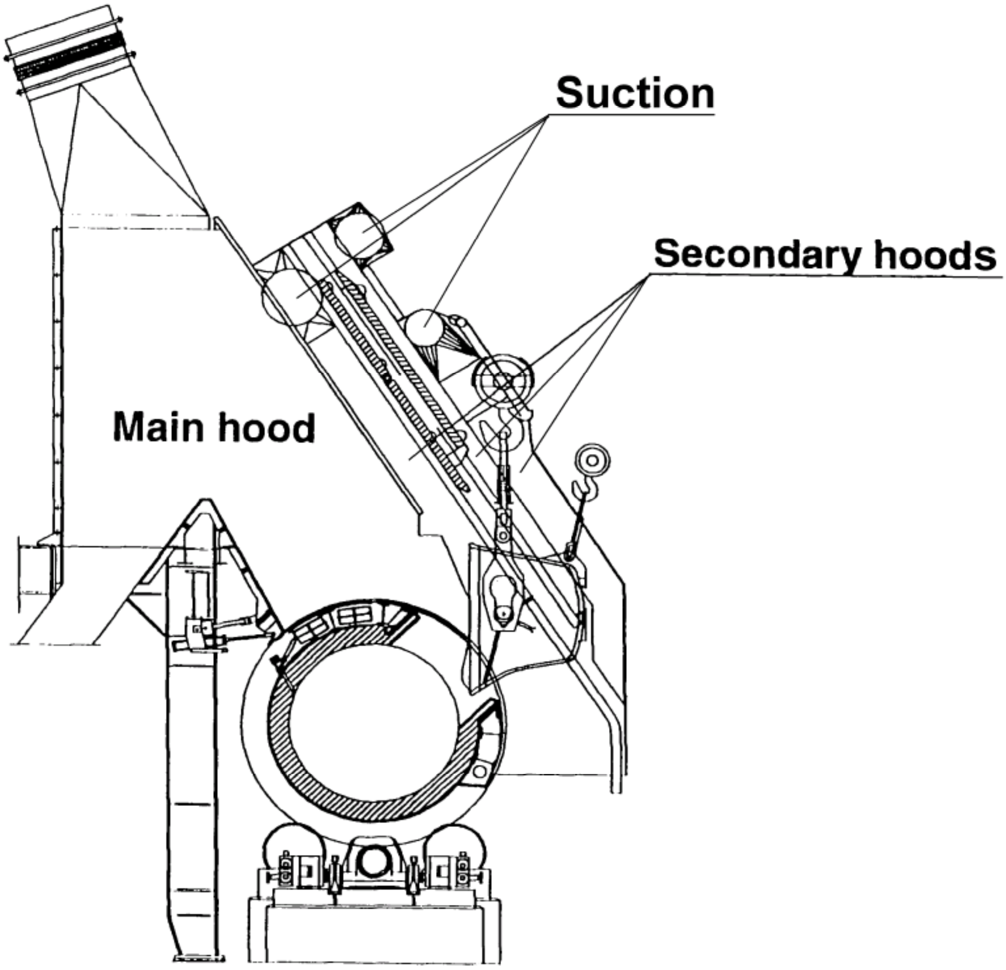


Figure 2.27: Secondary hooding system for a converter
[tm 201, Velten 1999]

2.7.2.2 Fugitive emissions

Good extraction is used to prevent fugitive emissions as illustrated above but some systems cannot collect all of the process gases and they are emitted into the workspace and are then exhausted from roof vents. These emissions are notoriously difficult to measure but there are techniques that can be used effectively.

- Environmental samples can be taken to measure the impact of fugitive emissions. In this case samples of air or dust are collected at a series of points determined by an atmospheric modelling exercise. Correlation with atmospheric conditions is needed to estimate releases.

- Fugitive releases from a building such as a furnace room can be measured by taking samples from the building ventilators. The flow of gases from the ventilators can be estimated by measuring the temperature difference between the flow from the ventilators and the ambient air [tm 163, Steudtner 1998].

As reported above, fugitive emissions can be highly significant, therefore if fugitive emissions cannot be prevented or minimised to an acceptable level, secondary fume collection systems can be used as illustrated by the examples below.

a) Some furnaces can be equipped with secondary hoods in order to prevent fugitive emissions during charging or tapping as described above. The fan suction is provided directly at the source of fume to optimise the reduction of fugitive emissions.

Alternatively, the air could be extracted at the roof ventilator, but a large volume of air would have to be handled which might not be cleaned effectively in a fabric filter. Other disadvantages are high energy consumption, high investment, more waste (used filter media). Secondary fume collection systems are designed for specific cases. Energy use can be minimised by automatically controlling the point of extraction using dampers and fan controls so that the systems are deployed when and where they are needed, for example during charging or during “roll out” of a converter.

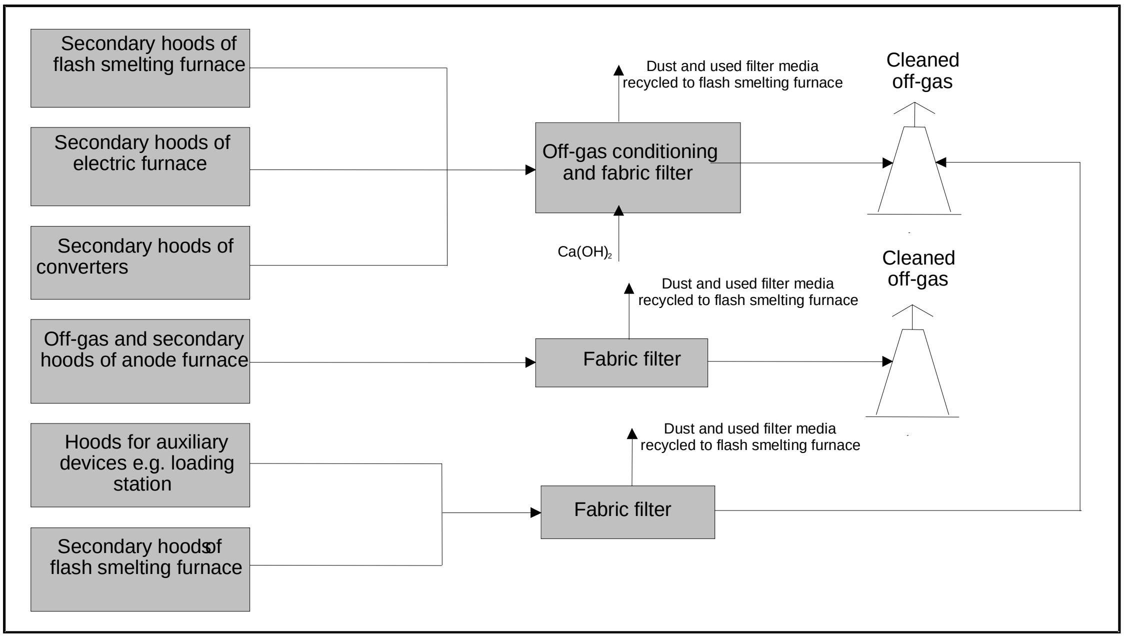


Figure 2.28: Outline secondary fume collection system for a primary copper process [tm 124, DFIU Cu 1999]

In the above process the air flow rate is controlled via a closed-cycle control system by reducing dampers. Ventilator fans with speed control are used in order to minimise the energy consumption. 580000 Nm^3/h of secondary gases are captured and cleaned in fabric filters. 13.6 GWh/a of electrical energy are consumed and 700 kg of dust is collected per hour [tm 124, DFIU Cu 1999].

b) The following example shows how tapping fume from a blast furnace can be collected by a secondary fume collection system.

The de-dusting equipment is composed of various hoods located above the tap hole of a blast furnace, the main metal runner and the device where the liquid metal is poured into the torpedo ladle. The collected fume is cleaned in a separate bag filter. The hooding system (viewed from the top of the blast furnace) is shown in the following figure.

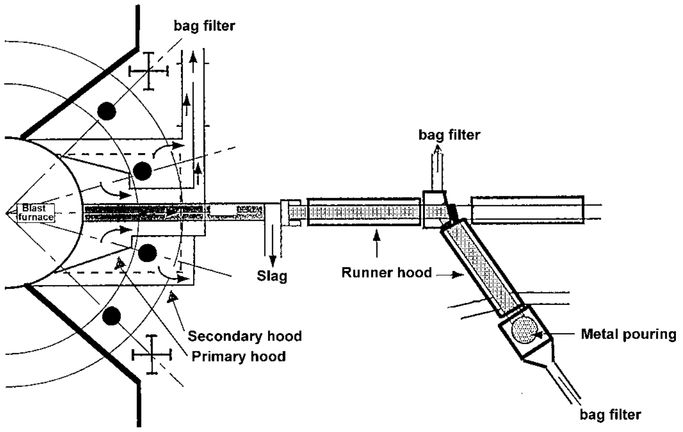


Figure 2.29: Tap-hole fume collection
[tm 195, SFPO 1999]

2.8 Air Abatement and Recovery Techniques

Collected gases are transferred to abatement plant where contaminants are removed and some components recovered. Dust and acid gases are commonly removed and valuable or toxic metal components are recovered for use in other processes. The design of the abatement process is critical, factors such as efficiency, suitability of the method and the input and output loading of the material to be collected are used.

2.8.1 Applied processes and techniques

The following abatement techniques are used in the non-ferrous metal industry, their operating principles are given.

2.8.1.1 Dust and particle removal

The following techniques are used for the removal of particles such as dust and fume from the various processes used by the Industry.

2.8.1.1.1 Electrostatic precipitators

The electrostatic precipitator (EP) is used extensively in the industry and is capable of operating over a wide range of conditions of temperature, pressure and dust burden. It is not particularly sensitive to particle size, and collects dust in both wet and dry conditions. Corrosion and abrasion resistance is built into the design [tm 75, Theodore 1994; tm 78, IEA 1997; tm 79, Soud 1995: tm 222, VDI 3678 1998].

The EP consists of a series of high voltage discharge electrodes and corresponding collector electrodes. Particles are charged and subsequently separated from the gas stream under the influence of the electric field generated between the electrodes. The electrical field is applied across the electrodes by a small direct current at a high voltage (100kV). In practice an EP is divided into a number of discrete zones (up to 5 zones are commonly used).

Particles are removed from the gas stream in four stages.

- application of an electrical charge to the dust
- placement of the charged dust in an electrical field
- capture of the dust onto the collecting electrode
- removal of the dust from the surface of the electrode

The discharge electrodes must be rapped or vibrated to prevent dust build-up and their mechanical strength must be compatible with transmission of the rapping blow or vibration. The mechanical reliability of the discharge electrodes and their supporting frame is important as a single broken wire can short out an entire electrical field of the precipitator.

The performance of an EP follows the Deutsch Formula, which relates efficiency to the total surface area of collector electrodes, the volumetric flow rate of the gases and the migration velocity of the particles. Therefore, for a given dust, maximising the surface area of the collector electrodes is very important and current practice is to use wide electrode spacing. This practice relies in turn on good rectifier design and control.

The industry uses good rectifier design, which includes the use of separate rectifier sections for each zone or portion of a zone of the EP. This allows the applied voltage to be varied in the inlet and outlet zones to take account of the reduced dust load towards the outlet and gives the ability to operate the zones at progressively higher voltages without sparking. Good design is also practised by the use of automatic control systems. They maintain the optimum high tension (HT) voltage applied to the electrodes in a particular zone without sparking. An automatic monitor is used to apply the maximum voltage without sparking and constantly varies the HT. Fixed HT power supplies are unlikely to provide optimal collection efficiencies.

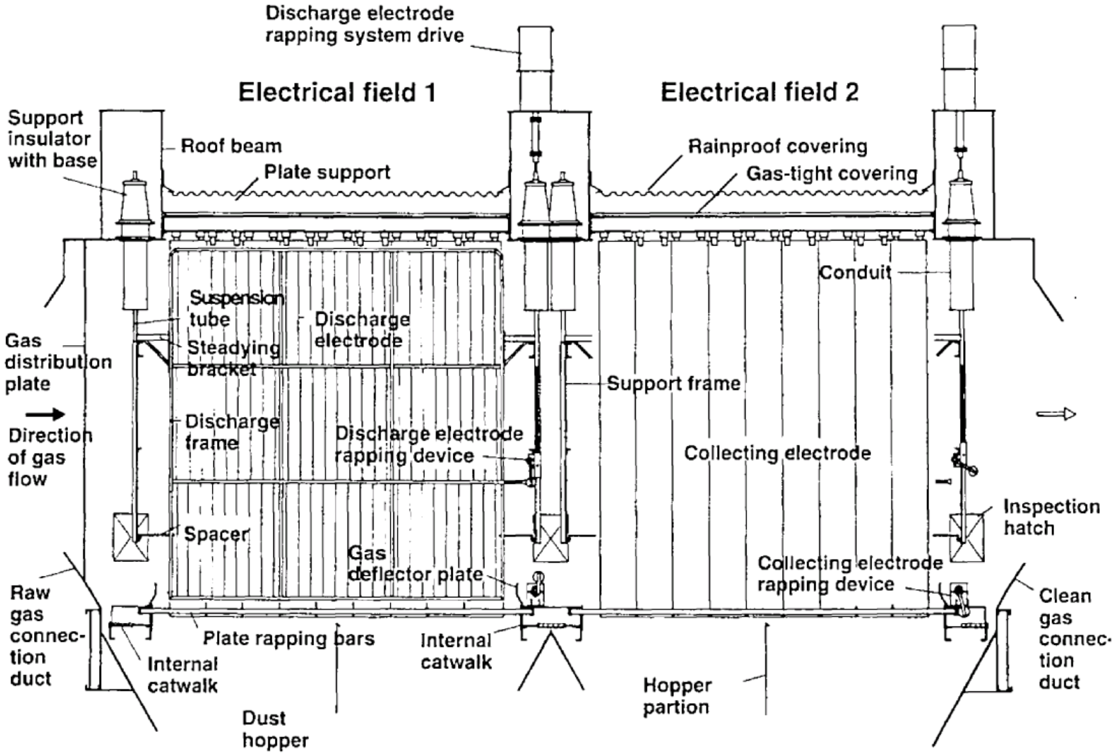


Figure 2.30: Typical arrangement of an electrostatic precipitator (only two zones shown) [tm 198, Lurgi 1999]

The resistivity (the inverse of the conductivity) of the dust is particularly important. If it is too low the particles reaching the collector electrode lose their charge easily and dust re-entrainment can occur. When the dust has too high a resistivity an insulating layer is formed on the electrode, which hinders normal corona discharge and leads to a reduction of the collection efficiency. Most dusts have a resistivity within the correct range and collection can be improved by conditioning the dust. Ammonia and sulphur trioxide are commonly used. The resistivity can also be reduced by reducing the gas temperature or by adding moisture to the gas.

The EP usually does not achieve final dust concentrations as low as those achieved by a fabric filter. To achieve the best performance from a precipitator the gas flow through units are optimised to give a uniform flow to prevent gas bypassing the electrical field. Correct design of inlet ducting and the use of flow distribution devices within the inlet mouthpiece are used to achieve uniform flow at the inlet to the precipitator. Under these circumstances dust emissions in the range 5 - 15 mg/Nm^3 can be achieved.

2.8.1.1.2 Wet electrostatic precipitator

Wet electrostatic precipitators operate on the same principles. In this case the collected dust is removed from the collector plates by flushing with a suitable liquid, usually water, either intermittently or by continuous spray irrigation. They offer advantages with certain dusts that adhere to conventional plates or when other components in the gas stream interfere with the operation for example in the case of a cool, damp gas. A liquid effluent is produced that requires further treatment.

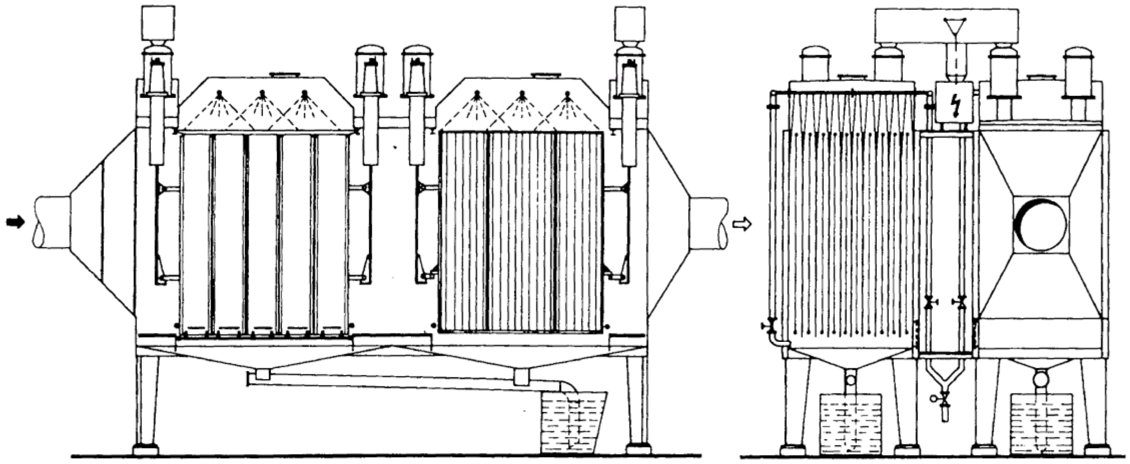


Figure 2.31: Wet electrostatic precipitator
[tm 198, Lurgi 1999]

2.8.1.1.3 Cyclones

Cyclones were installed in many of the processes in the 1980s and are still in widespread use. The cyclone is an inertial gas-cleaning device. Dust becomes separated from the gas stream when the direction of gas flow is changed and the dust continues in the original direction by virtue of its inertia and is deposited on a collection surface.

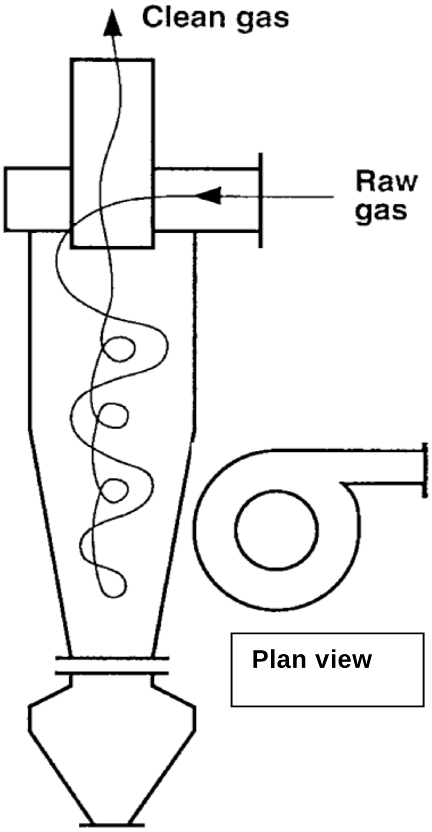


Figure 2.32: Arrangement of a cyclone
[tm 198, Lurgi 1999]

The inlet gas is channelled into a spiral flow. Centripetal forces operating within the spiral provide the change of direction, and the particles above a critical mass will be deposited on the cyclone walls.

Cyclones are not generally suitable for controlling emissions directly from the processes in this industry sector. The efficiency in collecting fine dust is too low to deal effectively with furnace releases. Operational experience has shown that they are not capable of meeting modern release standards. However, cyclones are used effectively as a primary collector in conjunction with another technique, particularly on larger processes where throughput can vary [tm 75, Theodore 1994; tm 220, VDI 3476 1990].

2.8.1.1.4 Fabric or bag filters

Fabric filter systems are used for many applications within this industry sector, due to their high efficiency in controlling the fine particulate matter encountered in melting operations [tm 75, Theodore 1994; tm 79, Soud 1995; tm221, VDI 3677 1997]. However, due to their tendency to blind in certain circumstances and their sensitivity to fire, they are not suitable for all applications. Settling and cooling chambers but also waste heat recovery boilers are used before bag-houses to reduce the likelihood of fires, to condition the particles and to recover the heat content of the off-gas before de-dusting.

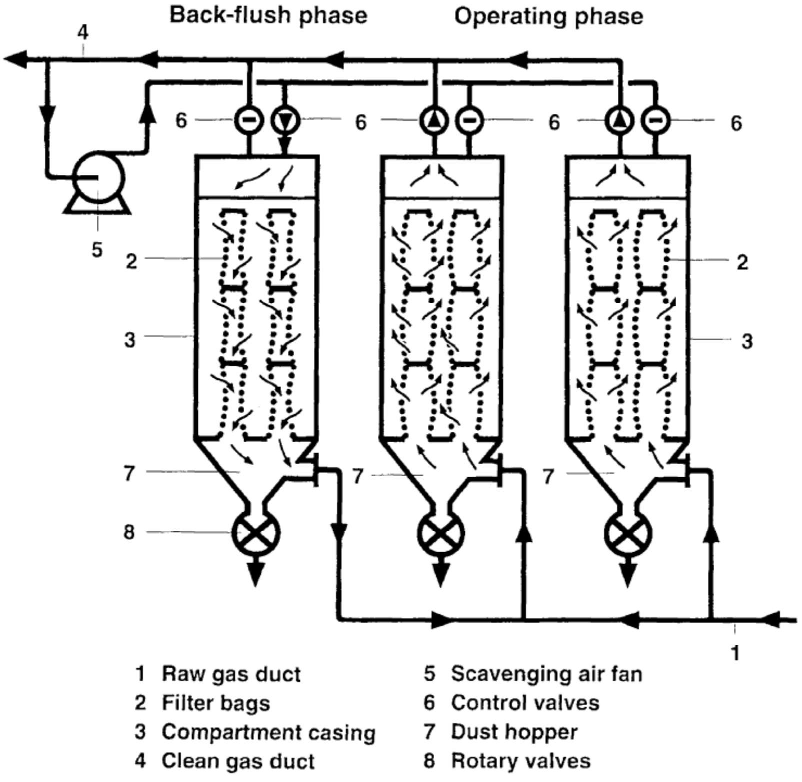


Figure 2.33: General arrangement of a fabric filter (with one compartment in the cleaning cycle) [tm 198, Lurgi 1999]

The basic principle of fabric filtration is to use a fabric membrane which is permeable to gas but which will retain the dust. The bags are usually supported on a metal frame and each bag will incorporate a method of sealing into the bag house structure. Initially, dust is deposited both on the surface fibres and within the depth of the fabric, but as the surface layer builds up it itself becomes the dominating filter medium. As the dust cake thickens, the resistance to gas flow is increased. Periodic cleaning of the filter media is therefore necessary to control the gas pressure drop across the filter. The direction of flow of the gas to be treated can be either from the inside of the bag to the outside or from the outside of the bag to the inside.

Fabric filters are normally classified according to the method by which the filter media are cleaned. Regular dust removal from the fabric is important in order to maintain effective extraction efficiency, but it also influences the operating life of the fabric.

The most common cleaning methods include reverse air flow, mechanical shaking, vibration and compressed air pulsing. Acoustic horns are also used for the cleaning of bags. The normal cleaning mechanisms do not result in the fabric returning to its pristine condition and the particles deposited within the depth of the cloth help to reduce the pore size between the fibres, thus enabling high efficiencies to be achieved on sub-micron fumes.

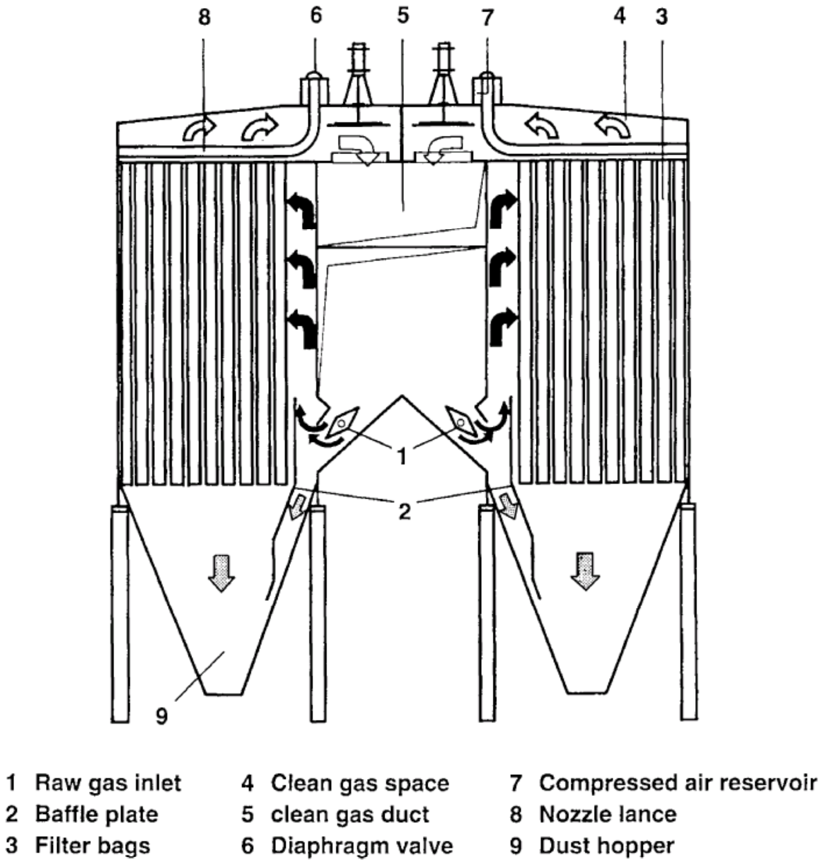


Figure 2.34: Reverse pulsed jet cleaning system
[tm 198, Lurgi 1999]

Fabric filters are designed on the basis of anticipated filtration velocity which is defined as the maximum acceptable gas velocity flowing through a unit area of fabric ($m^3/s \div m^2$ - expressed in m/s). Filtration velocities generally lie in the range 0.01 to 0.04 m/s according to the application, the filter type and the cloth.

Fabric selection takes into account the composition of the gases, the nature and particle size of the dust, the method of cleaning to be employed, the required efficiency and economics. The gas temperature is also considered, together with the method of gas cooling, if any, and the resultant water vapour and acid dew point.

Characteristics of the fabric considered include chemical resistance, fibre form and type of yarn, fabric weave, fabric finish, abrasion and flex resistance, strength, collecting efficiency, cloth finishes and cloth permeability.

A comparison of the most commonly used parameters of different filter systems is shown in the following table [tm 144, Elkem 1998].

Parameter	Pulse Jet Filter	Membrane Fibre-Glass Filter	Fibre Glass Filter
Air to cloth ratio	80 –90 m/h	70 – 90 m/h	30 – 35 m/h
Temperature limits	200 ºC	280 ºC	280 ºC
Bag type	Polyester/Nomex®	Gore-Tex® membrane/fibre glass	Fibre glass
Bag size	0.126 x 6.0 m.	0.292 x 10 m	0.292 x 10 m
Cloth area per bag	2.0 m^2	9.0 m^2	9.0 m^2
Cage	Yes	No	No
Pressure drop	2.0 kPa	2.0 kPa	2.5 kPa
Bag life	Up to 30 months	6 –10 years	6 – 10 years

Table 2.9: Comparison between different bag filter systems
[tm 144, Elkem 1998]

Wear of the filter bags results in a gradual reduction in performance, which can be measured. Damage or catastrophic failure of several bags is a danger when corrosion occurs, abrasive material is filtered or when there is the danger of fire. Simple on-line monitoring systems such as pressure drop indicators or dust telltale devices give only a rough indication of performance.

Triboelectric or optical devices are used to measure the trend in the dust emitted from the bag-house to identify possible failure and they can be used to detect dust peaks during a cleaning cycle. When these measurements are integrated with a zoned cleaning system the zone that contains damaged bags can be identified and local repairs made [tm 126, Robson 1998]. Temperature measurement and alarms are also used.

There exist a number of different bag filter designs using different kinds of filter materials, which in principle all achieve low emission values that means dust emissions below 5 mg/Nm^3. The use of the membrane filtration techniques (surface filtration) results additionally in an increasing bag life, high temperature limit (up to 260 ºC) and relatively low maintenance costs. The membrane filter bags consist of an ultra-fine expanded PTFE membrane laminated to a backing material. The particles in the off-gas stream are captured on the bag surface. Rather than forming a cake on the inside or penetrating into the bag fabric, particles are repelled from the membrane thus forming a smaller cake. This technique is applicable for all new and existing plants and may also be used for rehabilitation of existing fabric filters[tm 144, Elkem, 1998].

These synthetic filter cloths such as Gore-Tex® and Tefaire® (Teflon/Fibreglass) have enabled fabric filters to be used in a wide range of applications and to have an extended life. The performance of modern filter materials under high temperature or abrasive conditions has improved recently and cloth manufacturers can help to specify the material for specific applications. With the correct design and suitable dust, very low dust emissions (< 1 mg/Nm^3) are achieved and greater life and reliability repay the expense of modern fabrics.

Bag house filters in some ferro alloy processes use pressure filters with fans on the dirty fume/gas side. Recent developments have led to a closed suction filter with fans on the clean-gas side. This technique is used in most of the other metal sectors and combines the advantages of gentle bag cleaning that means longer bag life, low operating and maintenance costs and due to the closed filter a defined gas volume[tm 144, Elkem, 1998].

2.8.1.1.5 Ceramic and metal mesh filters

There are several examples where these filters are used in the correct application in this industry [tm 76, Scapa 1998] and very high dust removal efficiencies are achieved. Fine particles including PM_{10} are removed.

Low-density ceramic filters operate in a similar manner to bag filters as far as operating principles, general arrangement and cleaning operations are concerned. Instead of cloth bags and their metal supports, rigid elements that resemble candle filters are used. They have a high degree of thermal resistance and it is often the limitations of the housing that determines the upper operating temperature. Expansion of the support system as temperature rises is also a major factor as the sealing of the filter elements in the housing can be affected, resulting in leaks from the “dirty” gas stream into the clean gas stream. On-line failure detection systems are used in the same way as bag filters.

Ceramic filters are made from alumino silicates and can be pre-coated with a variety of materials to improve chemical or acid resistance. The filter elements are relatively easy to handle when new but become brittle after exposure to heat and can therefore be broken during maintenance or by violent attempts to clean them.

The presence of “sticky” dusts is also a potential problem as they may not be cleaned from the element during the normal cleaning cycle and would cause a significant increase in pressure drop. The effect of temperature on the material to be collected is therefore an important factor in the design of a plant. With the correct design and suitable dust, very low dust emissions down to 0.1 mg/Nm^3 are achieved.

Similar performance at high temperatures has also been reported using a re-designed metal mesh filter. The development allows the rapid establishment of a dust cake layer after cleaning while the zone is "off-line".

2.8.1.1.6 Wet scrubbers

Particle collection by liquid scrubbing occurs by three main mechanisms: inertial impacting, interception and diffusion. The particle size to be collected is an important factor [tm 75, Theodore 1994; tm 223, VDI 3679 1998] and the wet-ability of the material to be collected can also be significant.

Experience shows that the efficiency of wet scrubbers is strongly dependent upon their total energy usage, particularly upon the pressure drop across the collection zone. Moreover, provided the liquid is evenly dispersed within the scrubber, similar pressure drops will often give similar efficiencies on the same dust for quite different scrubber designs. Thus, it is not possible to design a wet scrubber that has high efficiencies without a high-energy consumption unless the dust concerned is particularly easy to wet. A variety of designs for high-energy scrubbers exist based on radial flow, jet, venturi and cascade principles and scrubbers have an application with dusts that are difficult to remove with other techniques. In general the gases are then used in another process (e.g. as a fuel gas) and are not emitted. They are also used in conjunction with wet EPs to cool and clean gases before contact sulphuric acid plants and to absorb acid gases. This is reported later in 2.8.1.2.

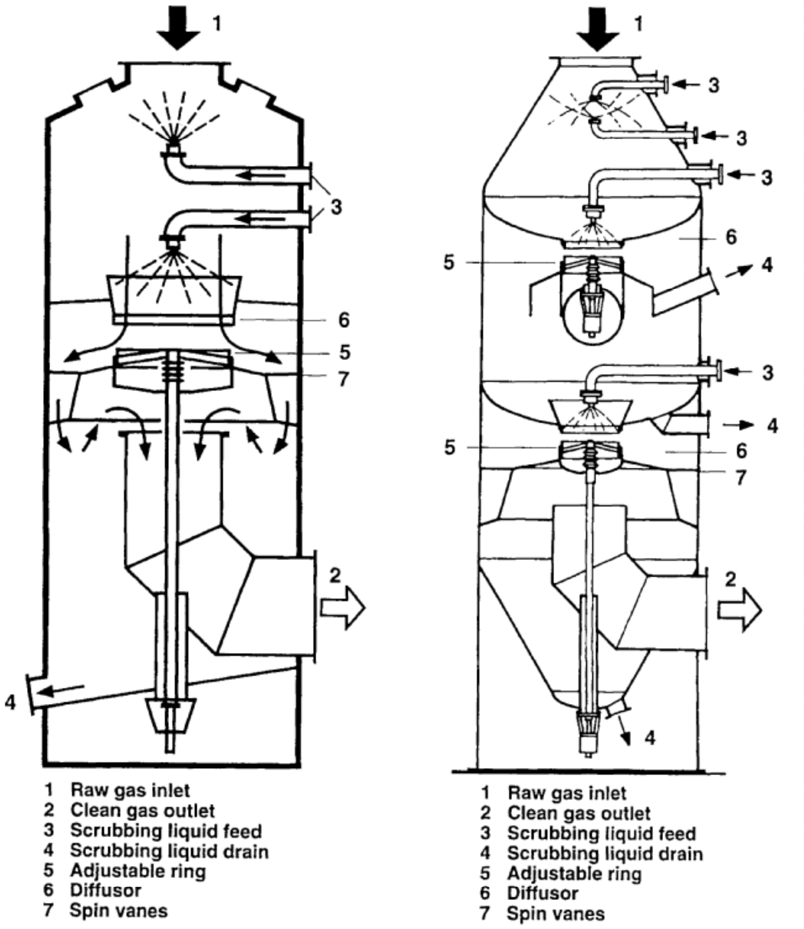


Figure 2.35: Radial flow scrubber
[tm 198, Lurgi 1999]

Cascade wet scrubbers are often used for the de-dusting of CO rich off-gases from sealed electric arc furnaces, the gas is used as high CV gas. It is also used to treat gases from a steel belt sintering machine, the dust is very abrasive but easily wetted and < 4 mg/Nm^3 has been achieved, the use of scrubber allows gas cooling to be achieved at the same time as dust removal. Bag filter life would be severely restricted and rapid fabric wear would result in poor performance.

2.8.1.1.7 Afterburners and flares

Combustion systems are used in the industry to oxidise CO, particulate or gaseous carbonaceous material in a gas stream [tm 217, VDI 2442 1987; tm 218, VDI 2443 1995; tm 220, VDI 3476 1990]. Three types are used:

- High temperature afterburners, where the gases are typically heated to between 850°C to 1000°C and held for a minimum of 0.5 seconds (provided there are no chlorinated components) and the results can confirm destruction of VOC present. Afterburners employ a burner system (not necessarily used continuously) and can employ a regenerative system to utilise the thermal energy in the gas and carbon compounds by using refractory support beds. A manifold system is needed to change the direction of the gas flow to clean the bed.

- Catalytic incinerators, where the decomposition is carried out on a metal catalyst surface at lower temperatures, typically 350°C to 400°C.

- Flares designed to burn waste gases e.g. excess CO.

Afterburners destroy organic compounds including dioxins by thermal oxidation and produce dust, carbon dioxide, water, oxides of sulphur and nitrogen, and other combustion products. Further abatement is necessary to remove these products.

Afterburners are particularly useful in de-oiling and de-coating operations, which can produce a high concentration of organic components. The presence of these components in a furnace produces a high volume of combustion products and would result in a very short residence time in a furnace and the emission of partially combusted gases.

2.8.1.2 Gas scrubbing systems

Gases such as NH_3, SO_2, HF, HCl and NO_x are produced in several processes, for example sulphur dioxide is produced during smelting and hydrogen fluoride is produced during electrolysis. Prevention and reduction techniques are available for these gases [tm 224, VDI 3927 1998]. Reduction of these gases is often possible by process control or fixing the material in a slag or matte. The use of low NO_x burners and staged combustion air for furnaces and other combustion plant can prevent the formation of these gases.

Organic components and dioxins and some metallic components can also be emitted from some processes and can be adsorbed using similar techniques.

The following techniques are used to remove gaseous components. More information is given in the metal specific chapters.

2.8.1.2.1 Wet scrubbing

Wet scrubbing systems are used in the industry to remove gaseous components at low concentrations, to remove particles and also to control temperature (by adiabatic cooling). Whilst the basic technology for these applications is similar, the design criteria for particulate and gaseous component removal are very different. Wet scrubbing systems are often used for all three processes simultaneously and so the design is inevitably a compromise and significant cross media effects such as the production of additional wastewater may result depending on the application. Some processes used elsewhere in the world for SO_2 removal have a dual alkaline medium and use lime as the second medium to regenerate the alkali and remove sulphate as gypsum, which is sold.

Various scrubbing media are used ranging from seawater to alkali solutions. The application for which a scrubber is used determines the factors that should be measured to monitor performance. The parameters that are used include; pressure drop and liquor flow, temperature, turbidity, conductivity and pH [tm 12, HMIP Zn 1993; tm 14 HMIP Pb 1993]. Potentially significant cross media effects exist and need to be taken into account locally.

2.8.1.2.2 Dry and semi-dry scrubbers

Adsorption techniques such as dry scrubbing are used to absorb acid gases and adsorb metallic or organic components. Lime, magnesium hydroxide, limestone, zinc oxide and alumina are frequently used for both applications and dual alkaline scrubbers are used elsewhere in the world. Activated carbon (or coke) is used to remove metal (mercury) and organic substances, for which it is usually more effective.

Adsorption is achieved using packed towers or by injecting the reagent into the gas stream and using a reactor tower. Bag filters are most frequently used down stream to collect the partially reacted scrubbing medium and provide a further surface area for further absorption to take place. The scrubbing medium can be recycled several times within the scrubbing network to allow full use of the absorptive and adsorptive capacity. In the case of alumina and zinc oxide, they are subsequently used in the main process. Fluorides absorbed by alumina are recovered by the electrolysis process.

A variant on dry scrubbing is semi-dry scrubbing. In this case a slurry of the reactant (usually lime) is injected into a reactor with the gas stream. The water is evaporated, provided the gas temperature is high enough and the gaseous components react with the particles. The particles of the reacted reagent are then removed from the gas stream. Dry scrubbing is often less effective than wet or semi-dry scrubbing, particularly with less reactive gases such as SO_2. The effectiveness of the reactant is often related to the "reactivity" of the reagent and suppliers of lime can often produce material at a reactivity that is suitable for certain applications.

When these processes are used to remove SO_2 they are known as flue gas de-sulphurisation (FGD). They are used to reduce the SO_2 content of gases from anode furnaces and other low strength sources and for tail gas scrubbing of the gases from a sulphuric acid plant. Gypsum is produced and can be sold in some circumstances.

2.8.1.3 Gas recovery systems

In addition to the use of wet, dry and semi-dry scrubbing systems to remove gaseous components reported above, this industry makes extensive use of recovery systems to recover gases from process gas streams. HCl can be absorbed in water and NO_x can be absorbed in water or hydrogen peroxide.

The following examples are used in the industry to close the material cycles: -

a) The hydrochloric acid loop: - For processes involving dissolution, hydrochloric acid, HCl, is used in combination with excess chlorine. By using evaporation and collection in water, an azeotropic acid (in concentrations about 20% w/w) is obtained. This is re-used in different parts of the process.

b) The nitric acid loop: - Silver and palladium are often dissolved in nitric acid, HNO_3. A significant quantity of nitrogen oxide off-gases (NO and NO_2) can be captured with oxygen or hydrogen peroxide in special cascade scrubbers. Problems are encountered by the long time needed to oxidise small quantities of NO and the reduction of gas absorption by exothermic reactions. Therefore cooling and several combined scrubbers are necessary to reach the limit values avoiding brown fumes from the stack. The resulting nitric acid from the first scrubber usually has concentrations about 45% by weight and can be reused in several processes.

c) The chlorine loop: - Chlorine is used in wet processes to dissolve metals and in dry chlorination steps at elevated temperatures to refine them. In both cases closed systems are used, e.g. using U-tubes with water and sealed electrolytic cells. Chlorine gas can be recovered or hypochlorite solutions produced. Hypochlorite is also used as an oxidising agent in scrubber solutions for various refining processes.

d) The ammonium chloride loop: - The relatively small solubility of ammonium chloride, NH_4Cl, in evaporated solutions at room temperature makes it possible to reuse crystalline precipitates of this salt.

2.8.1.4 Sulphur capture

Sulphur that is present in raw materials can be incorporated into slags or mattes using appropriate reagents, mattes can be used in the processes. Sulphur that is not captured in the matte or slag from a smelting process is usually present as SO_2 and can be recovered as elemental sulphur, liquid SO_2, gypsum or sulphuric acid. The presence of markets for these products influences the choice of end product but the most environmentally safe option is to produce gypsum or elemental sulphur in the absence of reliable outlets for the other products. Sulphur dioxide is produced from roasting and smelting of sulphide concentrates and the associated conversion processes. These processes are operated so that the maximum concentration of sulphur dioxide is produced to improve the efficiency of sulphur recovery. The recovery of sulphur eliminates cross media issues.

The following techniques are available for sulphur recovery [tm 24, DFIU Sulphur 1996]: -

a) Gases with up to 1% sulphur dioxide.

The Wellman-Lord re-generable process involves the reaction of weak gases with sodium sulphite and water to produce sodium bisulphite. Concentrated sulphur dioxide can be stripped from this solution and liquid sulphur dioxide produced or other products made such as sulphur.

2,3-dimethylaniline (DMA) (Asarco process) scrubbing can absorb sulphur dioxide, which is then removed by reaction with water to produce sulphuric acid or liquid sulphur dioxide.

Peracidox process, oxidation with hydrogen peroxide to produce sulphuric acid.

Sulphacid process, oxidation with an active carbon catalyst to produce sulphuric acid.

Flue gas de-sulphurisation (FGD) in a dry or semi-dry scrubber using lime to produce gypsum. This system is used extensively in power plants.

Double alkaline scrubbing with caustic soda absorption and gypsum precipitation.

Alumina absorption and gypsum precipitation (Dowa process).

Magnesium sulphate precipitation.

b) Gases with higher concentrations of sulphur dioxide.

i) Absorption of sulphur dioxide in cold water (e.g. cold seawater) followed by vacuum stripping and recovery as liquid sulphur dioxide. These processes are used in conjunction with a sulphuric acid plant to recover sulphur dioxide that is not dissolved. The potential for the production of liquid sulphur dioxide depends on the existence of a local market.

ii) Production of sulphuric acid. The production of sulphuric acid by burning sulphur to produce sulphur dioxide is a well-established chemical process. These installations benefit from a constant, high concentration of the gas and therefore have fewer process limitations. Gases from a roaster or smelter do not have these characteristics and are more difficult to operate and may not achieve the same level of conversion.

The smelter gases from the furnace are cleaned and cooled and may be dried. The sulphur dioxide in the gas is then converted to sulphur trioxide in a “contact process” when the gases are passed through a vanadium pentoxide catalyst bed. Sometimes the catalyst is doped with caesium oxide, which may improve performance particularly when the SO_2 concentration is low and variable or when the temperature is low. Improved catalysts are used to increase the conversion efficiency in single and double contact plants.

In a **single contact plant** the gases pass through a series of four or more catalyst beds to obtain high conversion efficiency. The production of sulphur trioxide is exothermic and if the sulphur dioxide content is high enough to generate sufficient heat, the gases are cooled between each pass. With gases that have a low sulphur dioxide content, heat may have to be added before the passes. The sulphur trioxide formed is then absorbed in 98% sulphuric acid, which is then diluted to give sulphuric acid. The WSA process is a development of the single contact plant.

The presence of sulphur trioxide inhibits the conversion of sulphur dioxide and a **double contact process** is therefore most commonly used to achieve more efficient sulphur dioxide conversion when the sulphur dioxide content of the gas is sufficiently high. In this case sulphur trioxide is absorbed after the second or third pass, allowing conversion of more sulphur dioxide in the subsequent passes. This is followed by a further sulphur trioxide absorption stage. The use of a double contact plant increases the removal efficiency of sulphur dioxide from < 98% to > 99.5%. It has also been reported that the use of a caesium doped catalyst can improve this to 99.9% but this data refers to a process that has a high, even concentration of sulphur dioxide feed gas [tm 140, Finland Cu 1999].

Dust removal before the contact process is essential to protect the catalyst and to produce a pure acid. This reduces the concentration of most metals, for example zinc, to acceptable levels in the acid that is produced and prevents the poisoning of the catalyst. The pre-treatment of the gas stream usually involves several stages depending on the contaminants present in the gas stream. The stages can include cooling with heat recovery, hot electrostatic precipitator, scrubbing to remove mercury etc. and a wet electrostatic precipitator.

The weak acid generated in the gas cleaning section contains typically 1 - 50% H_2SO_4. Halides will be presents as HCl (10 - 1000ppm) and HF (10 - 1000 ppm including H_2SiF_6). The acid may also contain metals such as copper, zinc and iron (individually up to 2500 ppm), mercury (up to 1900 ppm) and lead (up to 50 ppm). Arsenic may be present up to levels of 10000 ppm. Other elements, such as aluminium, nickel, chromium, cadmium, bismuth, antimony, etc. may also be present depending on the contaminants present in the smelter feed. The weak acid will also be saturated with SO_2 (typically between 2000 and 5000 ppm depending on the SO_2 strength). This acid can be decomposed and the gases passed to the acid plant, be treated and disposed or used e.g. if there is a leaching process nearby.

Any NO_x that is present in the gases treated in the sulphuric acid plant is absorbed in the acid that is produced. If the concentrations are high then a brown acid is produced and this may not be acceptable to potential customers. The problem is therefore one of potential sales.

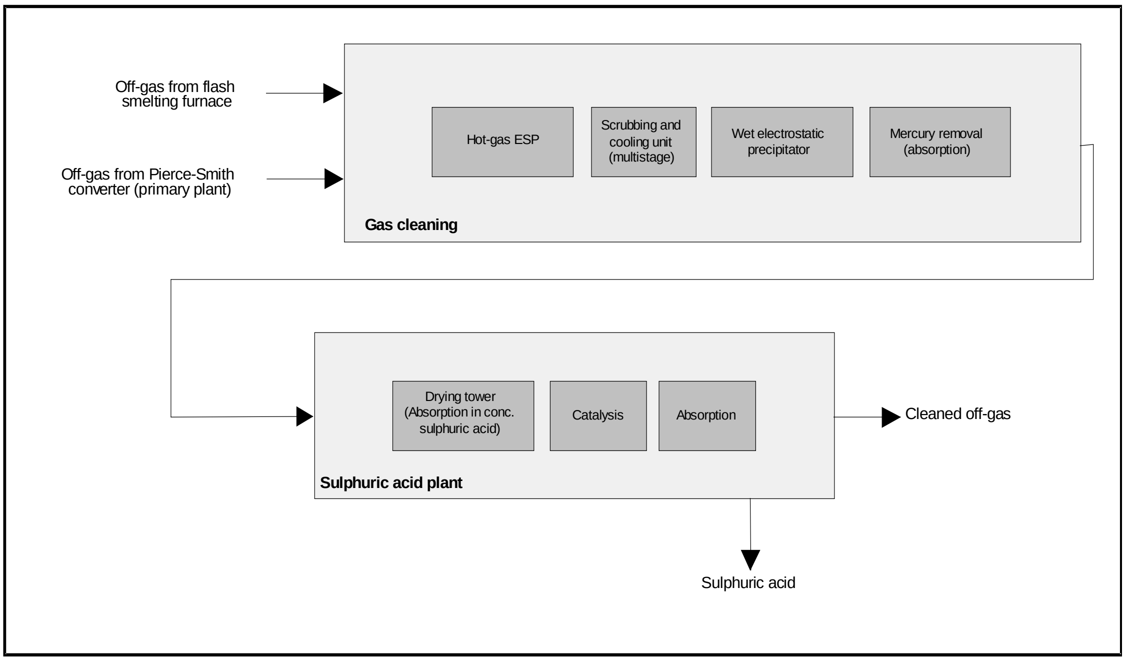


Figure 2.36: Typical gas cleaning train for a sulphuric acid plant

The sulphuric acid production process removes any residual dust and metals and they are transferred to the acid that is produced. The removal of dust and metals before the contact process means that these are not significant components in the gases emitted to air. Acid mists can be emitted from the stack and candle filters are used where they are needed to eliminate these mists. It is reported that high fluoride levels in the gas increases the likelihood of producing acid mists [tm 106, Farrell 1998]

Sulphuric acid plants are used to remove sulphur dioxide produced during the sintering, roasting and smelting of a wide range of sulphidic ores and concentrates. The metals produced are copper, nickel, lead, zinc and several mixed metal streams.

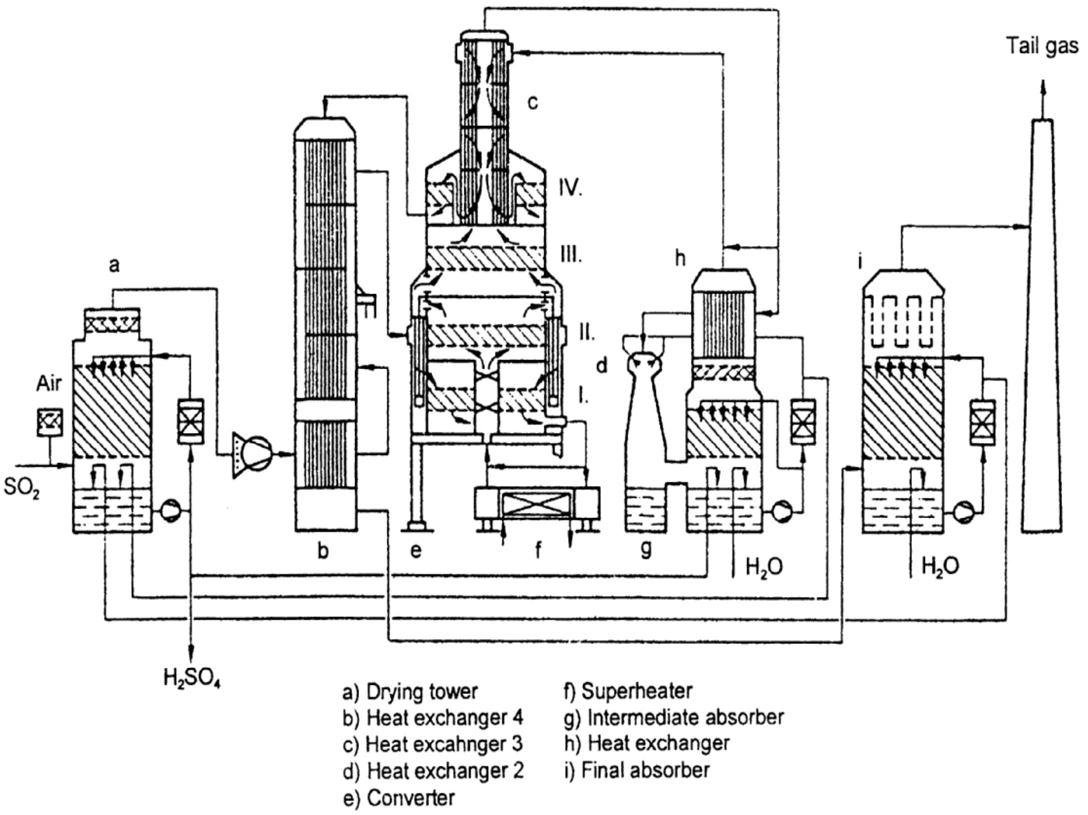


Figure 2.37: A Typical Double Absorption Sulphuric Acid Plant

2.8.1.5 Total carbon and VOCs

Total carbon and VOCs are produced by poor combustion and during various operations such as degreasing of components, solvent extraction processes and from the “breathing” of tanks used to store solvents and fuel. Solvents may be aromatic, aliphatic, chlorinated organic or water based, the eco-toxicity varies between solvents and this is taken into account to use the most benign solvent and to determine the abatement system that is used on a site by site basis. Containment is practised to prevent solvent emissions and mixer/settlers can be used that minimise contact with air. Solvent or fuel vapours need to be extracted and removed from the exhaust gases.

The techniques used to remove or destroy VOCs are afterburners and scrubbers detailed above and concentrations $< 10 mg/Nm^3$ can be achieved. Bio-filters and reactors are also used [tm 159, VDI 1996]. Activated carbon traps and chiller / condenser systems are used and allow the material to be recovered for re-use. In one solvent extraction process, ventilation air is cooled and removes solvent down to a level of 0.2 kg per tonne of cobalt produced. VOCs can also be emitted during delivery of solvents etc. Back venting of displaced gases is used to minimise the emission of VOCs.

2.8.1.6 Dioxins

Dioxins are relevant to the production of metals [tm 225, VDI 3460 1997] particularly the production from secondary raw materials or in processes that need chlorination such as the electrolytic production of magnesium from seawater and dolomite. Dioxins or their precursors may be present in some raw materials and there is a possibility of de-novo synthesis in furnaces or abatement systems. Dioxins are easily adsorbed onto solid matter and may be collected by all environmental media as dust, scrubber solids and filter dust.

This industry relies on sources of secondary raw materials from the scrap industry. Although there are agreed scrap grades, the impurities present may lead to the formation of dioxins during incomplete combustion or by de-novo synthesis. The presence of dioxins in EAF dust and the presence of poly chlorinated biphenyls on transformer scrap are potential direct sources of dioxins.

The presence of oils and other organic materials on scrap or other sources of carbon (partially burnt fuels and reductants, such as coke), can produce fine carbon particles which react with inorganic chlorides or organically bound chlorine in the temperature range of 250 to 500 °C to produce dioxins. This process is known as de-novo synthesis and is catalysed by the presence of metals such as copper or iron. Pre-selection or treatment of the feed material to minimise the amount of precursors or organic matter is therefore a very important measure to prevent the formation of dioxins.

Although dioxins are destroyed at high temperature (above 850 °C) in the presence of oxygen, the process of de-novo synthesis is still possible as the gases are cooled through the "reformation window". This window can be present in abatement systems and in cooler parts of the furnace e.g. the feed area. Care taken in the design of cooling systems to minimise the residence time in the window is practised to prevent de-novo synthesis. Sufficient oxygen needs to be present in the hot gases and oxygen injection can be used to ensure complete combustion.

Activated carbon can be injected into the gas stream where dioxins are absorbed on to the surface. High efficiency dust filtration is then used to remove the dust and dioxins. Dioxins may be also absorbed onto other particulate matter and can be removed using high efficiency dust filtration. The collected dusts may have high dioxin concentrations and may need to be disposed or treated carefully. Catalytic oxidation systems are also available for the destruction of dioxins and it has been reported that fabric filters that incorporate a catalytic layer are used.

These are all considered to be techniques to consider depending on the application, they can all be incorporated into existing processes. The most effective and economically viable technique will depend on the specific site, safety aspects and operational stability as well as economic factors are taken into account. Emission levels of better than 0.5 ng per cubic metre TEQ can be achieved using one or more of these techniques to the clean gas side of the system. Lower values better than 0.1 ng per cubic metre TEQ can be achieved by one or a combination of these techniques.

2.8.1.7 Removal of other impurities

In addition to their interference with the recovery of sulphuric acid and sulphur dioxide, other non-ferrous metals that are present in the ores and concentrates have an adverse environmental impact. They need to be removed if they have not already been removed. They also have a value and so they are recovered separately from the metal of prime interest. Additional purification stages are therefore used to remove and recover them and these are reported in the metal specific chapters.

2.8.1.7.1 Non-ferrous metals

Pyrometallurgical processes are used to remove impurities from the desired metal by volatilising and/or slagging other metals. For example Zn, Bi, Pb, Sn, Cd, As and Ga may be volatilised under the operating conditions in the furnace and are fumed from the melt. The choice of operating temperature influences this stage of the process and these metal oxides can be collected using an appropriate dust removal technique. The metals are then recovered from the collected flue dusts in a number of ways. Slag cleaning furnaces and slag fuming processes are also operated to remove volatile metals that are collected as flue dusts. These flue dusts and other residues therefore form the raw materials for a variety of metals.

Volatile metals and their oxides are also found in dusts and residues from other processes for example dust from steel making. These residues provide the raw material for other processes to recover zinc and other volatile metals. In these processes a rotary kiln (Waelz Kiln) or an ISA Smelt furnace is used to fume the metal and enrich zinc and lead in a mixed oxide which can then be recovered in other pyrometallurgical processes.

Tanks and other equipment used in hydro-metallurgical plants are mostly ventilated to atmosphere to ensure a safe work place. This ventilation air may contain an acidic mist that contains metal compounds from the solution. Removal techniques comprise wet scrubbers or de-misters. The de-mister elements are placed in the gas stream in the vent stack or on top of the cooling towers and the separated solution flows back to the main reservoir.

2.8.1.7.2 Mercury

Mercury is volatile at the temperatures encountered in most abatement processes and other techniques may be needed to remove it [tm 26, PARCOM 1996; tm 139, Finland Zn 1999; tm 225, VDI 3460 1997]. In the case of mercury removal before a sulphuric acid plant, any residual mercury will be present in the acid that is produced, the product specification is normally < 0.1 ppm and is equivalent to ~ 0.02 mg/Nm^3 in the cleaned gas and all processes are reported to achieve this.

- Boliden/Norzink process. This based on a wet scrubber using the reaction between mercuric chloride and mercury to form mercurous chloride (calomel), which precipitates from the liquor. The process is placed after the washing and cooling step in the acid plant, so the gas is dust and SO_3 free and the temperature is about 30 °C. The gas is scrubbed in a packed bed tower with a solution containing $HgCl_2$. This reacts with the metallic mercury in the gas and precipitates it as calomel, Hg_2Cl_2. The calomel is removed from the circulating scrubbing solution and partly regenerated by chlorine gas to $HgCl_2$, which is then recycled to the washing stage. The mercury product bleed is either used for mercury production or stored. Mercuric chloride is a very toxic compound of mercury and great care is taken when operating this process.

- Bolchem process. This process step is located in the acid plant like in the Boliden-Norzink process, but the removal is effected by 99% sulphuric acid. This acid comes from the absorption part of the acid plant and it oxidises the mercury at ambient temperature. The resulting mercury containing acid is diluted to 80% and the mercury is precipitated as sulphide with thiosulphate. After filtering off the mercury sulphide the acid is returned to the absorption. No acid is therefore consumed in the process.

- Outokumpu process. In this process the mercury is removed before the washing step in the acid plant. The gas at, about 350 °C, is led through a packed bed tower where it is washed counter currently with an about 90% sulphuric acid at about 190 °C. The acid is formed in situ from the SO_3 in the gas. The mercury is precipitated as a selenium-chloride compound. The mercury sludge is removed from the cooled acid, filtered and washed and sent to the production of metallic mercury. Part of the acid is then recycled to the scrubbing step.

- Sodium thiocyanate process. This process is used at a zinc roaster. The SO_2 gas is washed with a solution of sodium thiocyanate and the Hg is removed as sulphide. Sodium thiocyanate is regenerated.

$$3Hg + 8SCN^- + 4 H^+ + SO_2 \Rightarrow 2[Hg(SCN)_4]^{2-} + HgS + 2H_2O$$

- Activated Carbon Filter. An adsorption filter using activated carbon is used to remove mercury vapour from the gas stream.

Two processes are available to reduce the mercury content in sulphuric acid produced during the production of non-ferrous metals.

- Superlig Ion Exchange process. This process uses ion exchange to remove mercury from the product acid and achieves a concentration of mercury < 0.5 ppm.

- Potassium iodide is added to the acid, which has to be at least 93% strength, at temperature of about 0 °C. Mercury iodide, HgI_2, is then precipitated.

The Norzink and Outokumpu processes are most commonly used but other processes have been reported elsewhere [tm 26, PARCOM 1996]: -

- Selenium Scrubber. This is also based on a wet scrubber and uses the reaction between amorphous selenium in sulphuric acid and mercury to remove high concentrations of mercury vapour: -

- Selenium Filter. A dry scrubbing process which uses amorphous selenium to react with mercury vapour to form mercury selenide: -

- Lead Sulphide process. A dry scrubbing process using lead sulphide nodules as the media removes mercury from the gas stream.

2.8.1.8 Use of oxygen enrichment in combustion systems

The combustion/oxidation systems used in the production of non-ferrous metals often feature the use of tonnage oxygen directly or oxygen enrichment of air or in the furnace body. This enrichment is used to allow auto-thermal oxidation of sulphide based ores, to increase the capacity or melting rate of particular furnaces and to provide discrete oxygen rich areas in a furnace to allow complete combustion separately from a reducing zone.

Oxygen can achieve the following improvements [tm 125, ETSU 1994]: -

- The increase in the heat released in the furnace body allowing an increase in the capacity or melting rate. The ability to operate some processes auto-thermally and vary the extent of oxygen enrichment “on-line” to control the metallurgical process and prevent emissions.

- A significant reduction in the volume of process gases produced as the nitrogen content is reduced. This allows a significant reduction in the size of downstream ducts and abatement systems and prevents the loss of energy involved in heating the nitrogen.

- An increase in the concentration of sulphur dioxide (or other products) in the process gases allowing conversion and recovery processes to be more efficient without using special catalysts.

- The use of pure oxygen in a burner leads to a reduction of nitrogen partial pressure in the flame and therefore thermal NO_x formation may be reduced. This may not be the case with oxygen enrichment in or near the burner as the higher gas temperature may promote thermal NO_x formation. In the latter case oxygen can be added downstream from the burner to reduce this effect and maintain the improvement in melting rate.

- The production of tonnage oxygen on site is associated with the production of nitrogen gas separated from the air [tm 127, ETSU 1994]. This is used occasionally for inert gas requirements on site. Inert gases are used for abatement systems when pyrophoric materials are present (e.g. dry Cu concentrates), for de-gassing molten metal, for slag and dross cooling areas and fume control of tapping and pouring operations.

- Injection of oxygen at discrete points in a furnace downstream of the main burner allows temperature and oxidising conditions to be controlled in isolation from the main furnace operations. This allows the melting rate to be increased without an unacceptable increase in temperature. An example is the provision of an integral after-burning zone in a blast furnace.

2.8.1.9 Process control techniques for collection and abatement equipment

Process operation and control is used extensively in this sector. The following techniques are used:

- Reagent metering systems are used extensively.

- Microprocessor control of reagent feed and plant performance is used. On-line monitoring of temperature, pressure drop, particulates or other pollutants emitted, EP current and voltage and scrubber liquor flow and pH is used. Alarms are provided to indicate operational problems.

- Operators are trained and assessed in the use of operating instructions and the use of the modern control techniques described.

- Levels of supervision are optimised to take advantage of the above and to maintain operator responsibility.

- Environmental management and quality systems are used.

- Robust maintenance systems are used. There is growing use of dedicated maintenance staff forming part of the operator teams and they supplement the dedicated maintenance teams.

2.8.2 Current emission and consumption levels

The main emission and consumption data for HF, HCl, VOCs, dioxins NO_x and CO are found in the metal specific chapters but achieved emissions are given in the table below for a number of abatement and treatment examples.

Technique.	Particle Size um.	% Collection Efficiency at 1µm.	Maximum Operating Temperature °C.	Range of Achievable Emissions mg/Nm^3.	Comments
Hot EP	< 0.1	> 99 Depending on design.	450	< 5 - 15 (Pre abatement > 50)	4 or 5 zones. Usual application is pre-abatement
Wet EP	0.01	< 99	80	< 1 - 5 Optically clear	EP with 2 zones in series. Mainly mist precipitation.
Cyclone.	10	40	1100	100 - 300	Coarse particles. Used to assist other methods.
Fabric Filter.	0.01	> 99.5	220	< 1 - 5	Good performance with suitable dust type.
Ceramic Filter.	0.001	99.5	900	0.1 - 1	Very good performance with suitable dust type.
Wet Scrubber.	1 - 3	> 80 - 99	Inlet 1000 Outlet 80	< 4 - 50	Good performance with suitable dusts. Acid gas reduction.

Table 2.10: Example of current emissions from some dust abatement applications (dust mg/Nm^3)

Substance	Unit	Measured value
SO_x (as SO_2)	mg/Nm³	100 – 1100
SO_3	mg/Nm³	20 – 40
NO_x (as NO_2)	mg/Nm³	20 – 45
Cl^- (as HCl)	mg/Nm³	2 – 7
F^- (as HF)	mg/Nm³	1 – 4
Cd	mg/Nm³	0.001 - 0.02
Hg	mg/Nm³	0.001 - 0.07
Tl	mg/Nm³	0.001 - 0.02
As	mg/Nm³	< 0.01 - 0.02
Se	mg/Nm³	< 0.01 - 0.02
Sb	mg/Nm³	< 0.01 - 0.5
Pb	mg/Nm³	< 0.01 - 0.5
Cu	mg/Nm³	< 0.01 - 0.5
PCDD/PCDF	**ng TEQ/m³**	**0.001 - 0.01**
Gases from flash furnace and Pierce Smith Converter 290000Nm^3/h inlet SO_2 6 - 8.4% > 99.6 % conversion, producing 2000 t/d acid		

Table 2.11: An example of the concentrations of main constituents in the cleaned gas from a sulphuric acid plant
[tm 124, DFIU Cu 1999]

Method	SO_2 Input%	SO_2 Output mg/Nm^3	Notes
Double Contact – 4 Pass	> 5%	450	> 99.5% conversion
Single Contact – Cs_2O doping in final pass	< 3%	750	> 99% conversion Low/Variable SO_2 Input
Single Contact – Cs_2O doping + WSA condenser.	< 3%	850 (300 ppm)	> 99% Conversion
Double Contact – 5 Pass	15%	500 - 1000	99.8% conversion. Very high SO_2 input
Double Contact – 5 pass Cs_2O doping of catalyst, high O_2 content feed gas.	14%	< 285 (100 ppm)	99.9% conversion. Very high, constant SO_2 input

Table 2.12: Example of the performance of some existing sulphuric acid plants

2.8.3 Techniques to consider in the determination of BAT

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau.

2.8.3.1 General principles

The choice and design of a suitable abatement technique is particularly important. Several techniques exist and although some may seem to offer a very high performance, problems may be encountered unless the characteristics such as the loading and nature of the gases, dust and other components are fully considered. For example the fabric filter using modern materials is considered to offer better environmental performance than other techniques for dust removal however it cannot be considered to be universally applicable due to problems of stickiness and abrasion with some types of dust. These issues are specific to individual sites and materials and the operator should take these factors into account in a professional design brief.

The volume, pressure, temperature and moisture content of the gas are important parameters and have a major influence on the techniques or combination of techniques used. In particular the dew point will be affected by all of these parameters and their variations throughout a production cycle must be taken into account.

The characterisation of the nature of the dust or fume is very important to identify any unusual properties (hygroscopic, pyrophoric, sticky, abrasive etc). The particle size and shape, wet ability and density of the material are also factors to optimise the choice of technique. The dust concentration and its' variability should also be taken into account producing a reliable, robust design. These issues are discussed along with others in the sections on techniques to consider for the 10 groups of metals if the variation in dust characteristics is relevant.

Many operators have identified that performance may deteriorate with time as equipment wears and maintenance is needed. Modern systems should be used to continuously monitor performance by direct measurement of the gases emitted (for example dust, CO, SO_2). Alternatively critical control parameters can be monitored. Alarm systems should be incorporated in these systems.

2.8.3.2 Particle removal

2.8.3.2.1 Electrostatic precipitators

EPs that are correctly designed, constructed and sized for the application are techniques to consider [tm 75, Theodore 1994; tm 78, IEA 1997; tm 79, Soud 1995: tm 222, VDI 3678 1998]. Hot electrostatic precipitators will be used as the pre-cleaning stage before sulphur dioxide removal. Wet electrostatic precipitators are particularly applicable for wet gases such as those from granulation systems or as final abatement. Different performance is therefore required for these applications and affects the design parameters such as the size and number of fields and the cleaning method.

The following features are considered to be important: -

- Use of adequate number of fields, the number depends on the residual dust content, the dust resistivity and design criteria such as gas velocity and distribution and electrode design. Use of four or more fields is generally to be considered as a final abatement stage.

- The use of materials of construction that are appropriate for the material handled.

- Pre charging, pulse energisation and alternating polarity power supplies should be considered.

- Wet EP's or moving electrode EP's can be used for difficult dusts or moist gases.

These features above can be applied only to new EP.

- Conditioning of the gas, the use of good distribution of gas flow and dust, the use of power off rapping, the automatic (micro-processor) control of the power system for each field are also features that can be incorporated.

This feature can be applied to most existing installations.

2.8.3.2.2 Fabric or bag filters

Filters that are correctly designed, constructed and sized for the application are techniques to consider [tm 75, Theodore 1994; tm 79, Soud 1995; tm221, VDI 3677 1997]. They incorporate the following features: -

- Particular attention to the choice of filter material and the reliability of the mounting and sealing system. Good maintenance should be practised. Modern filter materials generally are more robust and have a longer life. The extra cost of modern materials is more than compensated by the extra life in most cases.

- Addition of lime or other reactants (e.g. activated carbon) in order to capture gaseous components such as SO_x or to remove dioxins.

- Operating temperature above the dew point of the gas. Temperature resistant bags and mountings are used at higher operating temperatures.

- Continuous dust monitoring using dust impingement, optical or triboelectric devices to detect filter bag failure. The device should interact if possible with the filter cleaning system so that individual sections, which contain worn or damaged bags, can be identified.

- The use of gas cooling and spark arrestment where necessary, cyclones are considered to be suitable methods of spark arrestment. Most modern filters are arranged in multiple compartments and damaged compartments can be isolated if required.

- Temperature and spark monitoring can be used to detect fires, inert gas systems can be provided or inert materials (e.g. lime) may be added to the off-gas where there is a danger of ignition.

- Pressure drop can be monitored to control the cleaning mechanism.

All of these techniques are suitable for new processes. They may also be applicable to existing fabric filters and can be retrofitted. In particular the bag sealing system can be improved during annual maintenance periods and filter bags can be changed for more modern fabrics during the normal replacement pattern and can also reduce future costs.

2.8.3.2.3 Ceramic filters

Filters that are correctly designed, constructed and sized for the application are techniques to consider [tm 79, Soud 1995]. They can incorporate the following features: -

- Particular attention paid to the choice and the reliability of the housing, mounting and sealing systems.

- The use of temperature resistant housing and mountings.

- Continuous dust monitoring using dust impingement, optical or triboelectric devices to detect filter failure. The device should interact with the filter cleaning system if possible so that individual sections, which contain worn or damaged elements, can be identified.

- Gas conditioning provided where necessary.

- The use of a pressure drop to monitor and control the cleaning mechanism.

All of these techniques are suitable for new processes. They may also be applicable to existing ceramic filters and can be retrofitted. In particular the sealing system can often be improved during normal maintenance periods.

2.8.3.2.4 Wet scrubbers

Scrubbers that are correctly designed, constructed and sized for the application are techniques to consider when the nature of the dust or the gas temperature precludes the use of other techniques [tm 79, Soud 1995] or when the dust is particularly suitable for removal in a scrubber. Their use can also be considered when gases need to be removed simultaneously with dust or when they form part of a chain of abatement techniques for example in de-dusting prior to a sulphuric acid plant. Sufficient energy should be applied to ensure the wetting and interception of the particles.

Wet Scrubbers should incorporate a monitoring system for pressure drop, liquor flow and (if acid gases are being abated) pH. The scrubbed gases should exit the scrubber to a mist eliminator.
These scrubber control features can also be applied to most existing installations.

2.8.3.2.5 Afterburners and flares

Installations that are correctly designed, constructed and sized for the application are techniques to consider to remove VOCs, dioxins, organic or carbon particles or combustible gases such as CO or H_2 . Heat recovery should be used where possible. The main requirements for effective combustion in an afterburner are: -

- Residence time in the combustion chamber or regenerative system must be sufficiently long in the presence of sufficient oxygen to ensure complete combustion. Destruction efficiency of 99% will usually require a residence time of 2 seconds at the relevant temperature depending on the presence of chlorinated compounds. Lower residence times and temperatures may as well result in the complete destroying of VOCs and dioxins but this should then be demonstrated on a local level under realistic operating conditions. Gases should be cooled rapidly through the temperature window of dioxin reformation. Turbulence is necessary to provide efficient heat and mass transfer in the combustion zone, and to prevent “cool spots”. This is usually achieved by using burners that generate a swirling combustion flame, and by incorporating baffles in the combustion chamber.

- An operating temperature 200 °C - 400 °C above the auto-ignition temperature of the most stable substance, minimum operating temperatures are above 850 °C. Where the gas stream contains chlorinated substances temperatures must be increased to 1100 °C – 1200 °C, and rapid flue gas cooling is required to prevent the re-formation of dioxins.

- Catalytic units operate at lower temperatures and flares require turbulence, air, and an ignition source. If necessary, supplementary fuel can be added.

- The burners should have microprocessor control of the air/fuel ratio to optimise combustion.

- The performance of the combination of equipment, operating temperature and residence time should be demonstrated to show effective destruction of the materials present in the feed gas.

These features can also be applied to most existing afterburner installations. Operating temperatures can be optimised and it is possible that the use of oxygen enrichment rather than air will increase the gas residence time (smaller gas volume) as well as increasing the operating temperature [tm 217, VDI 2442 1987; tm 218, VDI 2443 1995; tm 220, VDI 3476 1990].

Abatement Type	Potential Uses	Potential Problems	Associated emission mg/Nm^3	Reason for choice
Fabric Filters	Most with good sealing and modern fabrics.	Clogging, fires, sealing.	1 - 5	Performance for suitable dusts if well monitored. Potential to recycle dust to process.
Wet Electrostatic Precipitator	Improved performance for wet gases	Wire breakage & shorting.	< 5 Optically clear	Performance for suitable dusts, low pressure-drop but effluent produced.
Electrostatic Precipitator	Most with good control systems and gas distribution.	Variation in particles, wire breakage & shorting	5 - 10 (< 50 as pre-abatement)	Low pressure-drop, reliable, Low maintenance.
Wet Scrubbers	Only some dusts are suitable. Cleaning fuel gases or gases for acid plant.	Lower performance & blockages	< 20	Pre-cleaning of gases prior to other methods. Removal of acid gases and mists.
Ceramic Filters	Higher temperature operation.	Fragility, clogging & sealing.	< 1	Dust must be suitable. Housing material limits upper temperature
Cyclones	Pre-abatement	Poor performance. Limited efficiency for fine particles	< 50	Pre-cleaning of gases prior to other methods.
Emissions are given as daily averages based on continuous monitoring during the operating period.				

Table 2.13: Overview of dust abatement techniques

Abatement Type	Application	Measured dust emission mg/Nm^3	Comment
Fabric Filter (180000 – 250000 Nm^3/hr)	Secondary lead – batteries - PE removal.	0.7 to 3.4 (monthly average).	short rotary furnace, France
Fabric Filter (26000 Nm^3/hr)	Cadmium – battery recycling.	< 1 (monthly average).	
Cascade Scrubber	Ferro-chrome sinter plant.	< 4	Very abrasive dust – past fabric filter failures.
Fabric Filter	New Jersey zinc distillation	3 – 10	
Cyclone + E P + Wet EP	Lead Batteries in Ausmelt Plant	1 – 2	
Fabric Filter	Ferro-alloy production	1 – 5	
Afterburner, cooler and fabric filter.	Copper industry (secondary)	1 – 5	

Table 2.14: Measured performance of dust removal systems when using various dust abatement techniques with suitable dusts

The measured levels are quoted as ranges. They will vary with time depending on the condition of the equipment, its maintenance and the process control of the abatement plant. The operation of the source process will also influence dust removal performance, as there are likely to be variations in temperature, gas volume and even the characteristics of the dust throughout a process or batch. The achievable emissions are therefore only a basis from which actual plant performance can be judged and the achievable and associated emissions discussed in the metal specific chapters take account of the suitability of the dusts encountered and the cost/benefits of the particular application of the technique. Process dynamics and other site specific issues need to be taken into account at a local level.

2.8.3.3 Gas scrubbing systems

The use of prevention and reduction techniques should be considered first. Reduction of these gases is often possible by good process control, raw material selection (e.g. to exclude organic contamination), use of recovery loops or fixing the material in a slag or matte. The use of low NO_x burners and staged combustion air for furnaces and other combustion plant can prevent the formation of these gases. Values less than 100 mg/Nm^3 NO_x have been reported [tm 160, Winter Cu 1999].

2.8.3.3.1 Wet scrubbers

Scrubbers that are correctly designed, constructed and sized for the application are techniques to consider to remove low concentrations of sulphur dioxide (less than 2%) and other acid gases such as HF and HCl that may be produced [tm 79, Soud 1995].

- Wet Scrubbers should incorporate a monitoring system if possible for pressure drop, liquor flow and pH.
- The scrubbed gases should exit the scrubber to a mist eliminator.
- Weak acid liquors produced by scrubbers should be re-used if possible.

These features can also be applied to most existing scrubber installations.

2.8.3.3.2 Dry or semidry scrubbers

Scrubbers using the correct reagent that are correctly designed, constructed and sized for the application are techniques to consider to remove low concentrations of sulphur dioxide (less than 2%) and other acid gases such as HF and HCl that may be produced [tm 79, Soud 1995; tm 224, VDI 3927 1998]. Dry scrubbers using activated carbon are techniques to consider to remove organic matter such as dioxins or to remove mercury.

- Dry and semidry scrubbers should incorporate suitable mixing and reaction chambers.
- Particles generated in the reaction chamber can be removed in a fabric filter or EP.
- Partially reacted scrubbing medium can be recycled to the reactor.
- Spent scrubbing medium should be used in the main process if possible. For example alumina and zinc oxide can be used in their respective processes.
- Semidry scrubbers should incorporate a mist eliminator if mists are produced.

These features can also be applied to most existing installations.

2.8.3.4 Gas recovery systems

Systems that are correctly designed, constructed and sized for the application are techniques to consider for the removal of varying concentrations of gaseous components.

2.8.3.5 Sulphur capture

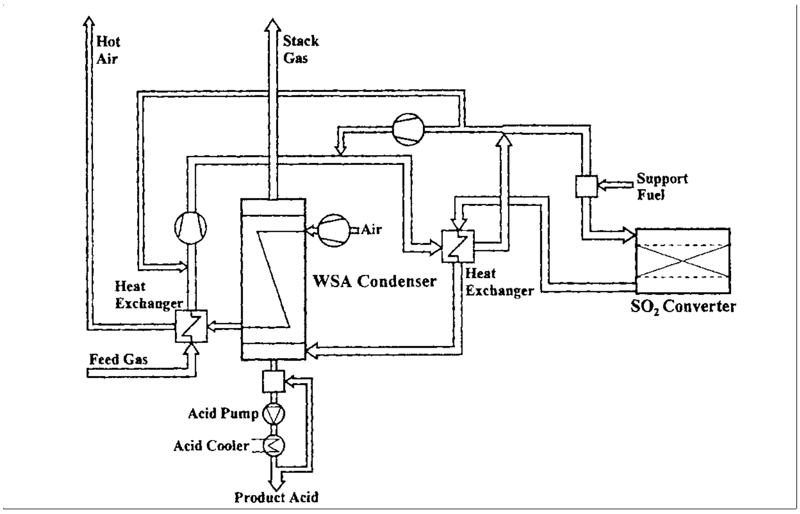
The techniques that are currently proven are the production of sulphuric acid and the absorption of sulphur dioxide in cold freshwater or seawater followed by vacuum stripping and recovery as liquid sulphur dioxide. Recovery as sulphur dioxide depends on a local market for the material.

Double contact sulphuric acid plants operate with a higher conversion efficiency than single contact plants. Conversion to double contact is complex and expensive but the use of a single contact plant with tail gas de-sulphurisation to produce gypsum for sale can allow energy savings and lower waste generation.

The following installations are examples of good, current practice: -

EXAMPLE 2.01 WET GAS SULPHURIC ACID (WSA) PROCESS FOR THE PRODUCTION OF SULPHURIC ACID FROM OFF-GASES WITH A LOW SO_2 CONTENT

Description: - The process is especially well suited the production of sulphuric acid from off-gases where the SO_2 content is low. In the process, up to 99.3% of the SO_2 is converted catalytically into SO_3, which reacts with water in the gas, hereby forming gaseous sulphuric acid. The acid is condensed in a WSA condenser. According to the heat economy and little sensitivity to the water balance, no extra sulphur burning is required at any SO_2 concentration. A typical flow sheet of a WSA plant for molybdenite roasting is shown in the figure below.



The catalyst used in the WSA technology is a potassium and sodium promoted vanadium catalyst in 10 and 20 mm extruded rings.

Main environmental benefits: - The conversion of SO_2 into sulphuric acid reduces the SO_2 emission and subsequently the effect of acid rain.

Operational data: - Typical performance data of a WSA plant is presented in the next table.

	Lead sintering
Flow Nm^3/h	100000
T_{inlet} °C	30 - 35
T_{outlet} °C	105
H_2O inlet, vol.%	5.5
O_2 inlet, vol.%	14.2
SO_2 content, vol.%	2.0 - 3.5
Conversion%	> 99
SO_3 in clean gas mg/Nm^3	< 28
H_2SO_4 product, wt%	> 97.5
Temp. of product °C	21
Acid production [t/d]	~290
Energy consumption (electricity & fuel) kW	850 (at 2.7% SO_2)
Cooling water consumption Gcal/h/tonne acid	0.25 ($\Delta T = 5$ °C)

Cross media effects: - The WSA process itself does not generate any waste products (except the spent catalyst) or wastewater and does not use any absorbents or other chemicals. If the WSA plant is used for converting SO_2 from a molybdenite roaster into sulphuric acid, the off-gas need first to be cleaned. The cleaning can be done by using a wet EP or wet scrubber where then the dust respectively the sludge is generated as a process residue.

Economics: - Not available

Applicability: - The WSA process is applicable to all new and existing plants especially for molybdenite and lead rosters where the SO2 content is lower than 5 - 6%.

Reference literature: - [tm 165, Bendixen, Haldor Topsøe, 1996], [tm 166, Bendixen, Haldor Topsøe, 1996], [tm 167, Bendixen, Haldor Topsøe, 1997], [tm 205, SADACI 1999]

EXAMPLE 2.02 SULPHURIC ACID PLANT OPERATING UNDER VARYING GAS CONDITIONS

Description: - Gas cleaning and washing section. Double contact sulphuric acid plant, 4 - 5 passes, modern catalyst. Weak acid to neutralisation ~ 12 – 15 m³/h with 5% H_2SO_4 as well as thermal decomposition of acid bleed with higher (~50%) acid concentration.

Main environmental benefits: - High conversion rate for sulphur dioxide. More than 99.6% achieved with a recent installation.

Operational data: -

Component	Measured Values	
Off-gas volume:	320000	Nm^3/h
SO_x	100 – 1100	mg/Nm^3
SO_3	20 – 40	mg/Nm^3
NO_x (as NO_2)	20 – 45	mg/Nm^3
Cl^- (as HCl)	2 – 7	mg/Nm^3
F^- (as HF)	1 – 4	mg/Nm^3
Average – residual dust:	< 2	mg/Nm^3
Range – residual dust :	1 – 7	mg/Nm^3
Range – components:		
Cd	< 0.01 – 0.02	mg/Nm^3
Hg	< 0.01 – 0.07	mg/Nm^3
Tl	< 0.01 – 0.02	mg/Nm^3
As	< 0.01 – 0.1	mg/Nm^3
Se	< 0.01 – 0.02	mg/Nm^3
Sb	< 0.01 – 0.03	mg/Nm^3
Pb	< 0.01 – 0.15	mg/Nm^3
Cu	< 0.01 – 0.09	mg/Nm^3
PCDD/PCDF	0.001 – 0.01	ng ITE/Nm^3

Cross media effects: - Positive effect – Reduction of main emissions of sulphur dioxide by conversion to sulphuric acid, recovery of the heat from the gases and evolved during conversion.

Economics: - See appendix on cost

Applicability: - Off gases from primary smelter (SO_x concentration > 6%; combination with off gases from secondary smelter is possible). These features can also be applied to most existing installations.

Example plants: - Germany

Reference literature : - [tm 124, DFIU Cu 1999]

EXAMPLE 2.03 MODERN SULPHURIC ACID PLANT OPERATING UNDER IDEAL CONDITIONS

Description: - Double contact sulphuric acid plant, 4 passes with intermediate absorption after 3rd pass, modern catalyst designed by Monsanto, heat recovery system (steam) after 1st pass treating the off-gas from an Outokumpu flash smelting and flash converting furnace with 30 - 40% SO_2.

Main environmental benefits: - Maximum conversion of sulphur dioxide.

Operational data: - Dilution to 14% SO_2 at drying tower inlet, annual average flow 171300 Nm^3/h. Up to 99.9% conversion achieved with a recent installation. ~ 150mg/Nm^3 SO_2 in tail gas as annual average. Plant relies on a high, constant sulphur dioxide feed and uses Cs doped catalyst.

Cross media effects: - Positive effect - Reduction of main emissions of sulphur dioxide.

Economics: - Not assessed.

Applicability: - Specific case for ideal feed gas conditions.

Example plants: - USA.

Reference literature : - [tm 140, Finland Cu 1998]

The emission of sulphur dioxide from sulphuric acid plants is proportional to the sulphur dioxide content of the feed gas and the conversion rate. A 99.8% conversion of a feed gas that contains 15% SO_2 results in the emission of approximately 900 mg/Nm^3 SO_2. These processes therefore use tall chimneys to assist the dispersion of the gases, the chimney height also takes into account the likely emissions during start up and shut down of the plant when full efficiency is not attained. Local, site specific factors are involved in these issues. The use of candle filters before the final stack is a technique to consider if an acid mist is produced.

Further sulphur dioxide removal from the final exit gas using a wet or semi-dry scrubber should be considered if specific environmental requirements are to be met.

2.8.3.6 Dioxins

This is covered under the relevant heading above in the above section on applied techniques. The techniques discussed in that section are all techniques to be considered in the determination of BAT depending on the source of material and the potential for de-novo synthesis.

2.8.3.7 The removal of other impurities

This is covered under the relevant heading above in the above section on applied techniques. The techniques discussed will be applicable in specific areas. Further discussion will be made under the relevant metal chapters.

2.8.3.8 The use of oxygen in combustion systems

This is a technique to consider and can be applied to most of the combustion and pyrometallurgical processes in use [tm 125, ETSU 1994]. The use of oxygen can give both financial and environmental benefits provided that the plant can accommodate the extra heat released. There is a possibility that higher concentrations of nitrogen oxides can be produced with oxygen enrichment but the associated reduction in gas volume usually means that the mass is reduced. Further discussion will be made under the relevant metal chapters.

2.8.3.9 The process control techniques for collection and abatement plant

The techniques covered under the heading above can be readily applied to existing processes. There are a number of cases (e.g. blast furnaces) where the development and use of modern process control is needed. More work is needed to identify the relevant control parameters and systems.

2.9 Effluent Treatment and Water Reuse

2.9.1 Main sources of liquid effluent arisings

This section gives an overview about the generation of liquid effluents in a common process. The ways to reduce the volume of wastewater, the practice of recycling water and the effluent treatment in a local or central wastewater treatment plant are discussed to give an understanding of some of the concepts that may be transferred between the metal groups [tm 28, WRC 1993].

The production of non-ferrous metals by pyrometallurgical and hydrometallurgical methods is associated with the generation of different liquid effluent arisings. The main sources of the most important effluent streams can be classified as shown in the following table.

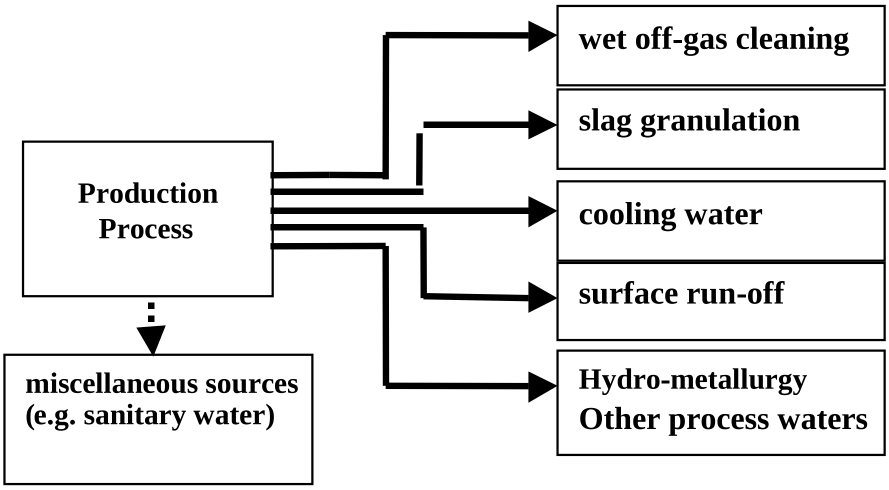


Figure 2.38: Effluent Classification

The above wastewater streams can be contaminated by metal compounds from the production processes and may have a high environmental impact. Even at low concentrations some metals like mercury and cadmium are very toxic. This can be illustrated by the fact that mercury and cadmium head the list of priority hazardous substances drawn up by the North Sea Conference of 1984, which calls for a 50% reduction of emissions into the North Sea. The toxic effect of some metal compounds is also due to the fact that under the correct chemical conditions metals can easily enter natural watercourses as soluble species and be quickly and irreversibly assimilated into the food chain [tm 169, J.H. Clark 1995].

This section first presents an overview about the different sources of effluents that can be found in a non-ferrous metal producing plant. The second part of the section reflects the techniques that are normally used to treat the contaminated wastewater streams.

2.9.1.1 Effluents from off-gas cleaning

Wet air pollution control equipment is gradually being replaced by dry control techniques. Dry abatement techniques like bag filters have the advantage that no sludge and wastewater has to be treated and the collected dust can often be recycled directly to the main process, the cross media issues are therefore reduced in comparison to wet systems.

There are certain cases when wet air cleaning techniques e.g. wet scrubbers or wet electrostatic precipitators need to be applied. These are used especially when other abatement systems are not suitable, there is a risk of explosion or combustion from flammable particles and if gaseous substances (for example sulphur dioxide or trioxide) as well as particles have to be removed from the off-gas stream. Wet electrostatic precipitators are necessary when humid, saturated gases with a high particulate content have to be cleaned. For example, during the production of primary zinc and copper, the off-gas from the process, which contains dust and sulphur dioxide, is cleaned by using a scrubber and a wet electrostatic precipitator. Wet precipitators are also used to collect the tar mist in the waste gases from an electrode-baking furnace. In wet scrubbers, acceleration and deceleration of the gas stream and the atomised scrubbing liquid produces high turbulence between the gases, the dust and the droplets of liquid. The dust particles are very quickly wetted and chemical reactions are speeded up. A subsequent collector extracts the droplets of liquid and the wetted dust from the gas steam. The contaminated effluent can then be removed for further treatment. If there is no enrichment of soluble components in the washing liquor, removal of the suspended solids by a thickener makes it possible to reuse the washing water. However, in some cases precipitation of soluble components has to be carried out in order to reuse the washing liquid.

The liquid effluent generally requires further treatment, for instance by neutralisation and/or sedimentation for solid-liquid separation. Sometimes specific treatment measures like ion exchange are used to remove very harmful or valuable metal compounds. For example ion exchange is used to recover rhenium from the scrubber effluent that is generated by cleaning the off-gas from a molybdenite roaster. This process is used for both removing a metal compound from the wastewater and serves as the most important source for the production of rhenium metal.

The treated liquid can normally be sent back to the wet-cleaning system but a bleed is required to control the composition of the liquor. Weak acid from these processes can also be re-used in other processes if they are available.

It has been reported that in several cases the process water from the wet scrubbing system of a smelting furnace contains cyanides formed by the reaction of carbon with atmospheric nitrogen. The cyanide level can be reduced by using the scrubbing water for slag granulation, which leads to evaporation and oxidation of most of the cyanides.

Another main effluent stream arises from the removal of mercury from some roaster off-gases. The mercury-removal step involves a gas-liquid contact tank with a solution of mercury chloride ($HgCl_2$). This mercury chloride reacts with metallic mercury from the gas to form a solid Hg_2Cl_2-precipitate ("calomel"). The precipitated slurry is removed and oxidised with Cl_2 to form the $HgCl_2$ washing solution. Some of the slurry is de-watered by a filter press and sold as Hg_2Cl_2 for mercury recovery or disposed of as a special waste.

Effluents from the process are pre-treated locally for mercury-removal by reaction with zinc dust or by precipitation as HgS before processing in a final effluent treatment plant

2.9.1.2 Effluent from slag granulation and the production of metal shot and density separation

During the production of non-ferrous metals the slag and the produced metal will be tapped off the furnaces. The molten metal and the slag can be granulated separately by pouring into water, using a high-pressure water jet or other quench systems to form evenly sized particles. The granulated metal can then be sold as metal shot. The granulated slag may be used for other purposes. A typical granulation stage is shown in the next figure.

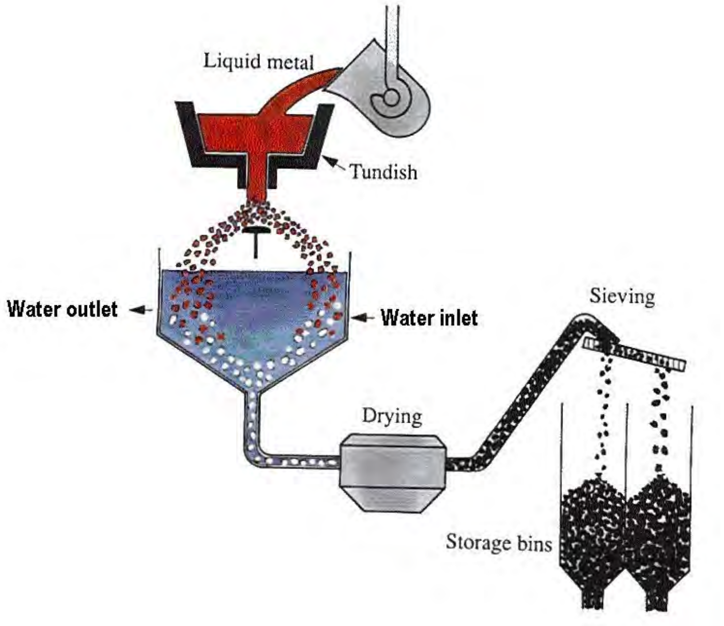


Figure 2.39: Granulation of molten metal
[tm 152, Schei, Tuset,Tveit, 1998]

The liquid effluent that arises from the granulation step is usually recycled in a closed circuit. To prevent a build up of suspended solids and metal compounds a blow-down has to be removed from the water circulation continuously. The blow-down effluent can be sent to a central wastewater treatment plant or be treated separately.

Density separation (sink and swim) is also used to separate metals and compounds from light contaminants for example the removal of plastic components after shredding. The liquid effluent that arises is usually recycled and floating material removed. To prevent a build up of suspended solids and metals a blow-down has to be removed from the water circulation continuously. The blow-down or effluent is usually sent to a central wastewater treatment plant.

2.9.1.3 Cooling water

Cooling water is used on a large scale for the different cooling requirements in metal producing industries. It can be divided into non-contact cooling water and direct contact cooling water.

- Non-contact cooling water is used for cooling furnaces, furnace hoods, casting machines etc. Depending of the location of the plant cooling can be achieved by a once through system or a re-circulation system with evaporative cooling towers. Water from a once through cooling system is normally discharged back to the natural source for instance a river or a cooling pond. In this case the increase of temperature should be regarded before the water is discharged to the natural water body. Non-contact cooling water may also be recycled via cooling towers.

- Direct contact cooling is used during some casting operations. This cooling water is normally contaminated with metals and suspended solids and often arises in large quantities. Due to the specific matrix and in order to avoid dilution effects, direct contact cooling water should principally be treated separately from other wastewater.

In order to minimise the impact of cooling on the environment as a whole the best available technique reference document for cooling system should be used.

2.9.1.4 Surface run-off water

Surface run-off water arises from contamination of rainwater that is collected from building roofs and paved areas at the production facility. Contamination of rainwater occurs when materials such as dust containing metals from storage, surface deposition etc or oils are washed into the drainage system. Contamination of surface water can be prevented or minimised by the use of good practise for the storage of raw materials as well as by a good maintenance and cleaning of the whole production plant.

Surface run-off may be collected separately. After a sedimentation step or chemical treatment it can be reused for other purposes in the production process, for instance as cooling water or for water sprays to prevent dust formation.

2.9.1.5 Effluents from the hydrometallurgical process

The main liquid effluent arisings from the hydrometallurgical production of non-ferrous metals are listed in the table below.

Process unit	Operation/source	Use options
Roasting gas cleaning	Wet cleaning of roast gases	Waste water treatment plant consisting of precipitation steps sometimes with a removal of heavy metals by using ion exchangers
Leaching	General operations including wet gas cleaning	Return to leaching.
Purification	General operations	Return to leaching or next process step.
Electrolysis	Cleaning of cells, anodes and cathodes. Spent electrolyte. Electrolyte bleed.	Return to leaching. Return to electrolysis after treatment.

Table 2.15: Potential sources of liquid effluents from electrolytic production of non-ferrous metals

The hydrometallurgical production process starts usually with a leaching operation. During leaching the desired metal and other elements will liberated from the mineral and go into solution.

Typical leaching reagents and reactions are shown below [tm 107, Ullmans 1996].

- water for water-soluble compounds (copper sulphate);
- sulphuric, hydrochloric, and nitric acids or sodium hydroxide for metal oxides;
- complexing agents e.g. cyanide (gold, silver) or ammonia (copper and nickel minerals);
- reduction of a mineral by a suitable gas or oxidation, for example, manganese dioxide by sulphur dioxide, and nickel matte by chlorine;
- acid-base reactions, e.g. recovery of tungsten complex from tungsten at high pH.

To increase the amount of the desired metal in the leach liquor a number of hydrometallurgical purification and enrichment techniques may be used. The target metal may be recovered from the purified solution by using different techniques such as cementation, gaseous reactions, selective precipitation, ion exchange, solvent extraction, crystallisation, evaporative

concentration or electrolysis. To ensure a correct balance in some of these processes it is normally necessary to remove constantly a part of the liquor.
During the production of zinc for instance, electrolyte may be bled to control the build up of magnesium that may have a detrimental impact on the operation of the electrolytic cells. The flows in the electrolytic cells belong to the same (closed) water circuit as the leaching and purification stages: the sulphuric acid formed during electrolysis is fed to the leaching process and the remaining liquid is purified and fed to the electrolysis.

The effluent bleed of the electrolytic-leaching-purification circuit is strongly acidic and contains high concentrations of zinc and suspended solids. The volume of the bleed depends strongly on the composition of the zinc concentrates that are used in the roasting. Components that tend to build up (i.e. are not sufficiently removed from the solution) in the circuit, especially magnesium, will determine the bleed flow.

Many facilities have already been demonstrated that effluents generated as electrolyte bleed may be recycled to the leaching operation depending on the contaminants that are present. Electrolyte bleed may also be recycled to electrolysis after the removal of contaminants or minor value elements.

2.9.1.6 Other process waters

There are few direct process effluents encountered during non-ferrous metal production that are not covered by the above headings. The most important are the liquors produced during the Bayer process to produce alumina and acidic wastewaters produced during lead acid battery processing or the processing of precious metals, weak sulphuric acid from sulphuric acid plants and wastewaters from the refining of germanium, gallium etc. These wastewaters are covered in more detail in the metal specific chapters but the processes used are sometimes capable of recycling the liquors back into the process or using the acid value in other processes.

Pickling operations are also sources of process waters and the following examples show how non acid pickling can be used and how the impact of acid pickling can be minimised.

a) Non acid pickling

This process operates in a sealed circuit. Rod can be pickled in an in-line system that consists of a compartmentalised horizontal steel pipe. A 2.5% to 3.5% solution of isopropanol alcohol (IPA) in water is used. In copper the process of converting the cuprous oxide scale in a vapour phase to form copper (left on the rod), is known as the Burns process [tm 92, Copper Expert Group 1998]. IPA is recovered from the spent solutions for reuse and metal containing sludges are recovered. Water from the IPA recovery stage is usually sent for wastewater treatment.

b) Acid pickling

Acid pickling uses a compartmentalised horizontal system [tm 92, Copper Expert Group 1998]. In a first stage the material is pickled with diluted sulphuric acid; then the residual acid is washed in several stages from the metal surface by water sprays followed by drying using compressed air. Surface pickling is usually performed with sulphuric acid but for some alloys and for metals such as titanium nitric acid, sometimes as a mixture with sulphuric, is used in continuous lines or automatic systems. Gas cleaning is used to recover or remove nitric acid fumes, the acid is changed from time to time. Spent acid is sent for treatment and recovery of metal. The pickling systems are vented for worker protection.

The products are rinsed and the rinse water is sent for treatment, sludges are recycled if possible. For surface degreasing of rolled products, detergents containing water are used. The spent water is cleaned by ultra filtration. If organic solvents are used for surface degreasing a vapour degreasing system is used. In this case chlorinated hydrocarbons may be present in any wastewater treatment sludge that is produced.

An alternative process is used for some copper rod production. After partial cooling in a long water-filled tube, the rod is formed into spirals corresponding to the diameter of the coil. These spirals are spread onto a roller table where the temperature is reduced to 20 ºC by water sprinklers. An acid-resistant alloy conveyor carries these spirals into the pickling tanks where the rod is pickled with a 20% sulphuric acid solution. The acid lay pickling system ensures a perfect removal of all oxides form the rod surface. The loops are then washed with rinsing water and finally protected by a wax solution.

Electro-winning can be used to recover the metal dissolved by the pickling acid. The wash solution also may be treated by ion exchange.

2.9.1.7 Miscellaneous sources

In an industrial plant for producing non-ferrous metals a great number of other sources are involved. Examples are liquid effluents from cleaning stations for trucks delivering raw material; sealing water from pumps; general operations, including cleaning of equipment, floors, etc. These liquid effluents are normally collected and treated. Water from the sanitary system is normally discharged to the public sewage system.

2.9.2 Applied treatment techniques

The applied treatment methods, which will be discussed in this part of the sector, are also techniques to be considered in the determination of BAT. In the case of wastewater treatment measures and treatment plants it is very difficult in this part of the document to define a BAT level. The treatment methods and consequently the achievable emission levels are very much dependent on the specific process and the metals involved [tm 211, Noyes 1993]. Due to this problem the techniques in this part will only be described in general by pointing out their advantages and disadvantages. For more detail information especially of achievable emission levels the specific chapters for the different non-ferrous metals should be used.

2.9.2.1 Process integrated measures

Techniques and methods for the reuse of water are already successfully used in the non-ferrous metal industry to minimise the amount of liquid effluent that has to be discharged as wastewater. The reduction of wastewater is sometimes also economically viable because as the amount of discharged wastewater is reduced, the amount of fresh water that has to be taken from the aquatic environment is also reduced. This has as well a beneficial effect on the cross media issues.

The following table demonstrates as an example for a few non-ferrous metals, the process steps from which the liquid effluents are already extensively recycled and reused.

Recycling and/or reuse of effluents in the Non-ferrous metal industry						
Source	**Production Process**					
	Primary copper	**Secondary copper**	**Primary lead**	**Secondary lead**	**Primary Zinc**	**Ferro-alloys**
Slag granulation	■	■	■		■	■
Wet air pollution control	■	■	■	■	■	■
Roasting gas washing Effluent	■		■		■	
Cooling water	■	■	■	■	■	■
Anode and cathode rinse water	■	■			■	n.r
Spent electrolyte	■	■			■	n.r.
Battery breaking				■		
Battery classification				■		
Lead paste de-sulphurisation				■		

Table 2.16: Overview of Recycling and Reuse

Recycling and reuse techniques are process-integrated measures. Recycling involves re-circulation of the liquid to the process where it has been generated. Reuse of an effluent means the re-circulation of one source of water for another purpose, e.g. surface run-off may be reused as cooling water.

Normally a recycling system needs a basic treatment technique or a blow-down of approximately 10% of the circulating liquid, to prevent a build up of suspended solids, metals and salts in the recirculation system. For instance cooling water is normally recycled and led in a recirculation system as shown below. Biocide input has to betaken.

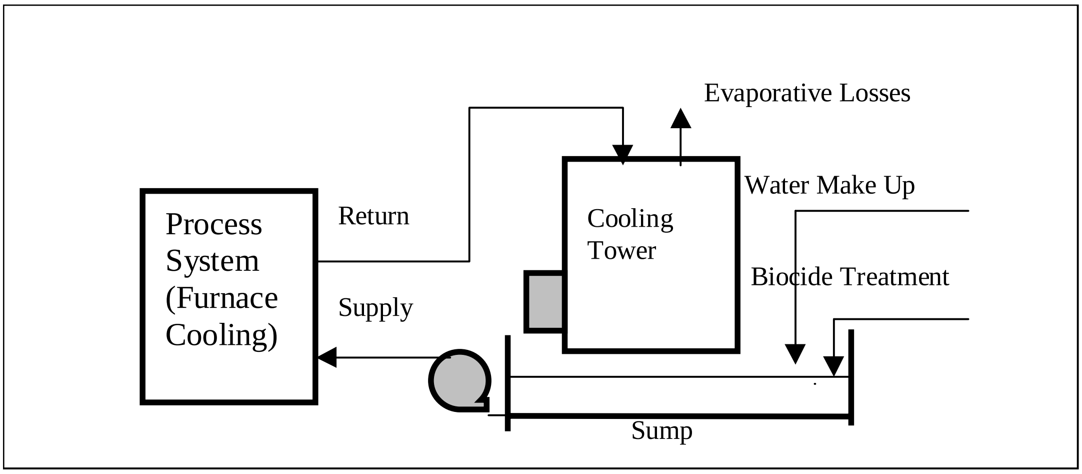


Figure 2.40: Example of a Cooling Water Re-circulation System

If large quantities of water are available, for example in a coastal site, a flowing cooling water system can be used provided the environmental impact is negligible. Nevertheless effects to the marine environment in the suction area of the flowing cooling water system needs to be considered. The case for this approach needs to be made on a site by site basis as the energy costs of pumping and cooling systems needs to be balanced.

The minimisation of wastewater can also be supported by good housekeeping, which may advantageously be based on a water management plan.

2.9.2.2 End of pipe techniques

Any non-recyclable or non-reusable amounts of water have to be treated in order to minimise the concentration of pollutants like heavy metals, acidic substances and solid particles in the final effluents discharged to the aquatic environment. To reduce the concentration of water pollutants, end off pipe techniques e.g. chemical precipitation, sedimentation or flotation and filtration may be used. These techniques are normally used together in a final or central on site wastewater treatment plant but opportunities can also be taken to precipitate metals before the process stream is mixed with other effluents.

2.9.2.2.1 Chemical precipitation

Chemical precipitation is used primarily to remove the soluble metal ions from the liquid effluent. The soluble metals can be precipitated from the wastewater by the adjustment of the pH-value. A reagent, such as lime, sodium hydroxide, sodium sulphide or a combination of reagents is added to the effluent and forms an insoluble compound with the metal to form a precipitate. These insoluble compounds can than be removed from the water by filtration and sedimentation. The addition of a coagulant or flocculant that helps to form larger flocs that can be separated more easily is often used to improve the performance of the system.

Precipitation is usually used to remove heavy metals from a wastewater stream such as the removal of iron, lead, zinc, chromium, manganese, molybdenum etc. The hydroxides of heavy metals are usually insoluble, so lime is commonly used for precipitating them. Similarly metal sulphides are also insoluble and reagents such as sodium sulphide, sodium hydrogen sulphide and tri-mercapto-sulpho-triazine (TMS) are used in alkaline conditions. Ferric sulphate can be added after precipitation to remove the excess sulphide. Sulphide precipitation can result in much lower concentrations in the cleaned effluent for certain metals depending on the pH and temperature. In some cases, precipitation of a mixture of metals can be carried in two stages; firstly with hydroxide followed by a sulphide precipitation [tm 171, Steil&Hahre 1999].

In order to maximise the efficiency of metal removal the process has to be treated at different pH-values with different reactants. The choice of reactant and the pH value is the main consideration for the precipitation of heavy metals. Solubility is also affected by temperature and this should be taken into account.

Another important factor is the valance-state of the metal in the water. For example chromium, whose hexavalent form, chromate is considerably more soluble than the trivalent form. In this case chromate must be reduced, usually with SO_2 at a low pH, for removal of chromium by a precipitation process.

The final aspect is the possible formation of complex ions, which are generally more soluble. This is common when dealing with wastewater containing ammonia, chloride, fluoride or cyanides along with the heavy metals [tm 149, Kemmer 1987].

In many plants where heavy metals are being removed, one of the principal problems in reaching the desired effluent limits is the colloidal state of the precipitated materials. This can result from improper neutralisation and flocculation. Various flocculants or coagulants can be used to improve the condition of the precipitated material and suppliers of these materials are able to test the precipitates and specify the correct coagulant.

The efficiency of the wastewater cleaning by using chemical precipitation is mainly influenced by the following factors: -

- the choice of chemical precipitant;
- the amount of precipitant added;
- the efficiency with that the precipitated metal is removed from the solution;
- the maintenance of the correct pH throughout the treatment process;
- the use of iron salts to remove specific metals;
- the use of flocculating or coagulating reagents.

Component	**Primary and secondary copper process water after lime and iron sulphate treatment and settlement**	**Secondary copper process and surface water after NaHS treatment, settlement and sand filtration**
pH	9.5	
Cu mg/l	0.2 – 0.5	0.04
Pb mg/l	0.2	0.04
Ni mg/l	0.5	0.07
Zn mg/l		0.13
As mg/l	0.1	< 0.01
Cd mg/l	0.1	0.004
Hg mg/l	0.05	
Variations in effluent composition are taken into account.		

Table 2.17: Concentration of some metals after wastewater treatment with lime or with NaHS

To ensure the maximum removal efficiency of heavy metals the most important factor is the maintenance of the choice of precipitant, the table above shows that the use of sulphide based reagents can achieve lower concentrations of some metals. Correct pH throughout the effluent treatment process is also of primary importance because some of the metal salts are insoluble only over a very short range of pH-values. Outside these ranges the efficiency of metal removal is decreasing rapidly, for example zinc will form a soluble anion, zincate, at high pH-values [tm 12, HMIP Zn 1993].

2.9.2.2.2 Sedimentation

Sedimentation is a solid liquid separation technique that utilises gravity to separate the insoluble metal complexes and solid particles from the liquid effluent. Sedimentation can take place in a variety of different settling vessels like sedimentation basins, lagoons or specialised sedimentation tanks (thickeners, clarifiers) with a sludge removal device on the bottom of the tank. Sedimentation basins, which are commonly used, are rectangular, square or circular in plan area. The sludge that is removed from the sedimentation step can be de-watered, by using e.g. a vacuum filter press. The filtrate that is generated may be sent back to the beginning of the effluent treatment process or to the process step where it has been generated depending on the treatment process. Sedimentation can be used to separate solid particles from wastewater that has been used for the granulation of slag or the production of metal shot.

An alternative to sedimentation may be flotation. Flotation techniques are used to separate large flocs or floating particles like plastic parts from the effluent by bringing them to the surface of the suspension. Flotation can be achieved by dissolved air flotation (DAF). Air is dissolved in the suspending medium under pressure and comes out of solution when the pressure is released as minute air bubbles attached to suspended particles. This causes the particles to float to the surface and the flocs can then easily be taken away from the surface of the liquid.

2.9.2.2.3 Filtration

Filtration techniques are normally used for solid/liquid separation and as a final clarification step in a wastewater treatment process. The filtration unit is usually located between the sedimentation step and the final control to remove solids carried over from the previous cleaning step. Filtration can take place in a variety of different filter systems depending on the solid particles that have to be removed.

The normal filter unit consists of a bed of material or materials through which the liquid effluent flows. The fine particles that can't pass through the filter medium form a filter cake that has to be removed either continuously or from time to time for example by back washing in order to keep the pressure loss low. If the pressure loss is low it enables the filtration to be fed with the wastewater flow via gravity flow.

Sand filters are designed for the mechanical removal of suspended solids or semi-solid materials e.g. sediments or metal hydroxides. The purification of wastewater by using sand filtration is due to the combined effects of filtration, chemical sorption and assimilation. Sand filters are sometimes operated as pressure vessels filled with layered sand, which increases in grade with depth. Initially the filter cake can lead to an enhancement of the filtration efficiency particularly for smaller particles. After a period of time the sand bed needs to be back washed. Sand filters are often used for polishing a bleed from a closed water cycle or to allow the effluent to be used as process water.

Hyper-filtration or reverse osmosis is used to obtain the desired result with very fine particles. Hyper-filtration allows passage of particles with a molecular mass of about 100 to 500, whereas ultra-filtration is used in the range of 500 up to 100000.

Ultra-filtration is a simple and effective method of wastewater treatment but has a high energy requirement. The effluent is placed in contact with an ultra-filtration membrane. This membrane, which contains small pores allows the passage of molecular particles like water and hinders larger molecular particles. With a very fine membrane it is even possible to filter solutes as small as metals. the filtration processes based on membranes produce a clean permeate and a concentrate that may require further treatment.

2.9.2.2.4 Electrolysis

Electrolytic techniques are used to remove metals such as copper, precious metals, chromium, manganese, cadmium etc. from process water streams. Because the metal concentrations are usually low, electrolysis is most effective for waste streams before they are diluted with other effluents. Special electrodes such as fluidised bed electrodes or three-dimensional electrodes can be used to improve efficiency [tm 148, EA Technology 1998]. Maximum efficiency of the cell is achieved when the current density changes with solute concentration and the mass transfer takes place close to the limiting current density. In other words the cathode must always have a fresh supply of ions to reduce.

An alternative, and very successful, use of electrochemical methods for metal clean up is to oxidise metals in effluents so that they can be recycled. One example is the treatment of chromium (III) containing effluents. The largest use of chromium is as an oxidising agent where chromium is in its (VI) oxidation state. The by-product from the oxidation is chromium (III), which is normally released with waste. Anodic oxidation of chromium (III) effluent has been used to regenerate chromium (VI), which can be reused [tm 169, J.H. Clark 1995].

The difference in the relative position in the electrochemical series or the redox potential of the elements can also be exploited by controlling the current and voltage of an electrolytic cell to recover the more noble metals. These properties can also be exploited by using cementation where for example, copper can be precipitated by adding iron.

Another electrochemical treatment method is electro-dialysis. The electro-dialysis cell consists of two electrodes separated by an ion exchange membrane. The theory is fairly straightforward. Cations under the influence of an electrode potential migrate through a cationic exchange-membrane where they are exchanged for less toxic cations (for example exchanging cadmium for sodium). This method aims to combine the advantages of ion exchange with the advantages of electrochemical treatment [tm 169, J.H. Clark 1995].

2.9.2.2.5 Reverse osmosis

Reverse osmosis is extensively used for the removal of dissolved metals, especially in the electroplating industry. Osmosis is natural diffusion of a solvent such as water caused by a difference in the concentration of two solutions separated by a membrane. The solvent flows in the direction that will reduce the concentration of the stronger solution. In reverse osmosis a driving force is applied to reverse the solvent flow. A pressure difference applied between the compartments separated by the membrane causes water to flow from the stronger solution to the weaker. The pressure required must exceed the osmotic pressure. Typical data of the passage of ions across the reverse osmosis membrane are presented in the following table. Reverse osmosis is sometimes used in the recovery of precious metals in the metal plating industry.

Ions	% passage	% rejection
Ammonium	8	92
Sodium	5	95
Potassium	5	95
Magnesium	3	97
Strontium	3	97
Calcium	2	98
Nitrate	15	85
Bi-silicate	10	90
Chloride	5	95
Fluoride	5	95
Bicarbonate	5	95
Sulphate	3	97
Phosphate	1	99

Table 2.18: Typical passage of ions across the reverse osmosis membrane
[tm 149, Kemmer 1987]

2.9.2.2.6 Ion exchange

Ion exchange is sometimes used as a final cleaning step in the removal of heavy metals from a process wastewater. By using ion exchange unwanted metal ions can be removed from a wastewater stream by transferring them to a solid matrix while giving back an equivalent number of other ions stored on the ion exchanger skeleton. The ion exchange process usually is used if the metal concentration is below 500 mg/l.

The ion exchange process takes normally place in a column that is packed with beads of the ion exchange resin. The exchange starts first at the top of the column and then passes through the column in order to keep the equilibrium exchange conditions. Depending on the amount of ions stored on the skeleton the capacity of the ion exchanger is limited. The ion exchanger should therefore be regenerated with hydrochloric acid or caustic soda. In some cases such as the removal of selenium and rhenium from the off-gas of a molybdenite roaster, the ion exchangers are replaced periodically so that the metal can be recovered by themselves or specialised plants.

Some specified ion exchangers are being able to remove specific metals from the wastewater. This selective ion exchange process is much more efficient in removing toxic metals form the effluent. Furthermore, the column is capable of a very high level of clean up, which is as well be able to operate efficiently in mixed content effluents.

2.9.2.2.7 Activated carbon

Activated carbon, a highly porous carbonaceous substance, is usually used to remove organic materials from wastewater but also has applications in the removal of mercury and precious metals. These filters are normally used in the form of beds or cartridges operated in multiples so that breakthrough from one filter is treated by a second one. The spent filter is then replaced and becomes the downstream filter. This operation depends on an adequate method to detect breakthrough from the filters.

2.9.2.3 Process control techniques for effluent treatment

Process operation and control has developed recently in this sector. The following techniques are used [tm 106, Farrell F 1998]: -

- Reagent metering systems are used extensively.
- Microprocessor control of reagent feed and plant performance is used. On-line monitoring of temperature, turbidity, pH, conductivity, REDOX, TOC, individual metals and flow is used.
- Operators are trained and assessed in the use of operating instructions and the use of the modern control techniques described.
- Levels of supervision are optimised to take advantage of the above and to maintain operator responsibility.
- Environmental management and quality systems are used.
- Robust maintenance systems are used. There is growing use of dedicated maintenance staff forming part of the operator teams.

2.9.3 Present consumption and emission levels

The composition of the liquid effluents from pyrometallurgical as well as from hydrometallurgical methods depends very much of the metal being produced, the production process and the raw material that is used. However, the liquid effluents from a non-ferrous metal production plant normally contain heavy metals, e.g. copper, lead, zinc, tin, nickel, cadmium, chromium, arsenic, molybdenum and mercury, and suspended solids.

The following tables give some examples of clean up rates for different wastewater streams and production processes. The consumption of water, the amount and composition of the liquid effluent and the achievable emission values will be discussed in more detail in the chapter for the individual non-ferrous metal.

Source	**Main Component [mg/l]**					
	Cu	**Pb**	**As**	**Ni**	**Cd**	**Zn**
Process water ($100000 m^3/a$) Before treatment After treatment	 2000 0.01-0.2	 500 0.001-0.04	 10000 001-0.1	 1000 0.004-0.15	 500 0.0001-0.1	 1000 0.01-0.2
Precipitation water Before treatment After treatment	 15 – 30 0.01-0.4	 < 5 0.005-0.2	 < 2 0.003-0.007	 < 2 0.002-0.4	 < 0.5 0.0002-0.1	 < 2 0.03-0.4
Direct cooling water ($16000000 m^3/a$) Before treatment After treatment	 < 3 0.01-0.25	 < 0.5 0.001-0.1	 < 0.1 0.001-0.1	 < 0.1 0.002-0.6	 < 0.05 0.0001-0.003	 < 0.5 0.02–0.5
Overall pollutant rate (g/t of Cu produced)	2.3	0.3	0.23	0.1	0.05	0.8

Table 2.19: Example of the metal content in waste waters before and after treatment relevant to a copper smelter/refinery complex
[tm 124, DFIU Cu 1999]

Component	Source and treatment method						
	Primary + secondary copper process water. Lime and iron sulphate treatment, settlement	Secondary copper process and surface water after NaHS treatment, settlement and sand filtration	Direct cooling water after pH adjustment and settlement	Surface run off water after pH adjustment and settlement	Copper wire-rod process water after treatment	Copper semis process water after treatment	Copper alloy semis process water after treatment
pH	9.5		8.5 – 9.5	6.5 – 8.5	6.5 – 95	6.5 - 9.5	6.5 - 9.5
Cu mg/l	0.2 – 0.5	0.04	0.01 – 0.25	0.01 – 0.4	0.2 – 0.3	0.3 - 0.4	0.2 - 0.4
Pb mg/l	0.2	0.04	0.001 – 0.1	0.005 – 0.2		0.02 – 0.03	0.2 - 0.3
Ni mg/l	0.5	0.07	0.002 – 0.06	0.002 – 0.4		0.09 – 0.1	0.3 - 0.4
Zn mg/l		0.13	0.02 – 0.5	0.03 – 0.4		0.7 – 0.8	0.8 - 1.0
As mg/l	0.1	< 0.01	0.001 – 0.1	0.003 – 0.07		0.01 - 0.03	< 0.1
Cd mg/l	0.1	0.004	0.0001 – 0.003	0.0002 – 0.1		0.001	< 0.2
Hg mg/l	0.05						< 0.05
Oil or hydrocarbon mg/l					< 10	< 10	< 10
Suspended solids mg/l					< 5	< 100	< 100
Indications take variations in effluent composition into account.							

Table 2.20: The treatment of some copper waste-streams

An overview of some sources of wastewater and the minimisation and treatment methods is given below.

Source of wastewater	Associated metals produced	Minimisation methods	Treatment Methods
Process water	• Alumina production, • Lead-acid battery breaking. • Pickling.	• Return to process as far as possible.	• Neutralisation and precipitation. • Electrolysis.
Indirect cooling water	• Furnace cooling for most metals. • Electrolyte cooling for Zn	• Use of sealed cooling system. • System monitoring to detect leaks.	• Settlement.
Direct cooling water	• Cu & Al castings. • Carbon electrodes. • Ferro-alloys • Chromium metal	• Settlement or other treatment. • Closed cooling system.	• Settlement. • Precipitation if needed.
Slag granulation	• Cu, Ni, Pb, Precious metals, ferro alloys	• Reuse in a sealed system.	• Settlement. • Precipitation if needed.
Electrolysis	• Cu, Ni, Zn Mg	• Sealed system. • Electro-winning of electrolyte bleed.	• Neutralisation and precipitation.
Hydro-metallurgy (blow-down)	• Zn, Cd	• Sealed system. • Blow-down treatment.	• Settlement. • Precipitation if needed.
Abatement system (blow-down)	• Wet scrubbers. • Wet EPs and scrubbers for acid plants.	• Blow-down treatment reuse of weak acid streams if possible.	• Settlement. • Precipitation if needed.
Surface water	• All	• Good raw materials storage	• Settlement. • Precipitation if needed. • Filtration.

Table 2.21: Overview of wastewater streams

2.9.4 Techniques to consider in the determination of BAT

As already explained all the wastewater treatment methods are also techniques to be considered in the determination of BAT. The best available treatment technique or a combination of the different treatment methods can only be chosen on a site by site basis by taking into account the site specific factors. The most important factors to decide, which in a specific case would be the best solution in order to minimise the amount of wastewater and the concentration of the pollutants are:

- The process where the wastewater is generated,
- The amount of water,
- The pollutants and their concentrations,
- The level of clean up required, i.e. local or regional water quality standards,
- The availability of water resources.

The following table presents the advantages and disadvantages of the most common treatment techniques [tm 169, J.H.Clark, 1995].

Treatment Technique	Advantages	Disadvantages
Precipitation	• Cheap and simple technique • Long history of successful use • Does not require large expenditure in a new plant • Capable of treating a wide range of metal contaminants particularly if two stage precipitation with hydroxide and then sulphide reagents is used • Under the correct conditions can give excellent removal of metals • Specified precipitants are commercially available • Allows absorptive precipitation • Precipitates can often be returned to the feed.	• Acid effluents can be difficult to treat • Non selective: it gives a high water content sludge containing a cocktail of toxic and non toxic metals • The sludge may have to be landfilled at sometimes large cost • The presence of other salts, organic complexing agents and solvents can severely compromise the precipitation efficiency • Cannot always be used to treat low concentrations of metals • Some hydroxides inefficiently precipitated
Sedimentation	• Cheap and simple technique • Long history of successful use	• Can only remove solid particles • For particles with a small density difference to water sedimentation takes long and large basins are required
Filtration	• Cheap and simple technique • Long history of successful use • Filtration e.g. sand filters are best used for a known particulate matter	• Can only remove solid particles • The filtration efficiency decreases if the particles are very small • Filtration efficiency decreases with increased velocity
Flotation	• Cheap and simple technique • Long history of successful use	• Can only remove solid particle complexes that are floatable • Air needs first to be dissolved in pressurised water to be dispersed in the water.
Ultrafiltration	• Simple technique • Very fine particles, even molecules can be removed from the wastewater • Very fine membranes will also filter solutes as small as metals • Virtually zero particulate emissions	• Limited flow rate and filtration velocity • Membranes can quickly decompose in corrosive effluents • No separation of metals • Old membranes can leak • Membranes can be easily fouled
Electrolysis	• Can be used to recover and recycle metals • Can be used to treat concentrated metal effluents (ca. 2 g/l) in a single step • Technology most available • Tried and tested with good track record in electroplating industries • Can be used to clean up organic contaminants simultaneously • Can be used in batch or continuos flow modes	• Better than ppm level of clean up is difficult • Ineffective cells are expensive to maintain and operate • High electric potentials are safety hazards • Electrolysis not selective • Needs constant monitoring • Poor at treating variable content, high volume effluents
	•	•

Table 2.22: a) Summary of advantages and disadvantages of common wastewater treatment techniques

Treatment Technique	Advantages	Disadvantages
Electro-dialysis	• Can be used to recover and recycle metals • Electro-dialysis can be selective • Electro-dialysis already used in desalination and electroplating industries • Electro-dialysis capable of sub ppm level of clean up	• Electro-dialysis suffers from the same disadvantages as ion-exchange methods (for example, membrane fouling) • Needs constant monitoring • Poor at treating variable content, high volume effluents
Reverse osmosis	• Virtually zero emission • Technology exits and equipment is commercially available • Can be used for recycling metals • Can be operated in continuous flow or batch mode • Can deal with a large range of metal concentrations • Can be used to remove organics in effluent • Efficacy is not strongly dependent on the concentration of non-corrosive contaminants in effluent	• Limited flow rate and filtration velocity • Membranes can quickly decompose in corrosive effluents • No separation of metals • Old membranes can leak • Membranes can easily fouled • Membranes need frequent monitoring and replacement • Equipment is specialised and expensive • Reverse osmosis uses high pressure • Restriction of a minimum flow rate of ca. 200 l/min
Ion exchange	• Relative in expensive • Commercial products available • Tried and tested in industrial applications (e.g. rhenium and selenium removal and recovery) • Capable of clean up to ppb level (selective ion exchange capable of ppt level) • Can be easily used in conjunction with other techniques (for example precipitation) as part of an integrated wastewater treatment • Can be selective for heavy metals • Can be applied to many flow types: intermittent, continuos, relatively large volume • Selective ion exchange has been used in isolated cases, such as treatment of nuclear industry effluents	• Cannot handle large concentrations of metal • Matrix easily fouled be solids and some organics • Traditional ion exchange is nit selective • Exhausted exchanger must usually be disposed of as toxic waste • Matrices can decompose over time • Performance is sensitive to effluent pH • Large volume effluents require very large ion exchange columns • Selective ion exchange does not have extensive industrial use to date • Regeneration of selective ion exchange columns is time-consuming • Long contact times with effluent may be needed
Activated carbon	• Can be used for a wide range of applications (e.g. removal of mercury or dioxin from effluent • Can be added after coagulation and sedimentation as a layer in sand filters • Technology exits and equipment is commercially available	• Activated carbon is expensive • Activated carbon can become a breeding ground for micro-organisms • High emissions of SO_2 generated from the heating process in manufacturing carbon from coal

Table 2.23: b) Summary of advantages and disadvantages of common wastewater treatment techniques

2.10 Waste Minimisation and Handling

2.10.1 Residues and waste from non ferrous metal production

The production of non-ferrous metals from primary and secondary raw material is related to the generation of a wide variety of by-products, intermediate products and residues. These residues arise from different stages of the production process such as from the metallurgical operations, the smelting process as well as from the off gas and waste water treatment [tm 85, MURL Düsseldorf 1997]. The content and value of the elements contained in the residue influences its potential for reuse e.g. anode slime is a viable raw material for the recovery of precious metals. Any designation of a residue as waste for disposal takes this into account. Also some filter dust such as silica fume that arises from the smelting process of ferro-silicon and silicon metal is today recommended as a by-product.

According to the current EU legislation, many of these residues are regarded as wastes. However the non-ferrous metal industry has for many decades used many residues as raw materials for other processes and an extensive network of metallurgical operators has been established for many years to increase the recovery of metals and reduce the quantities of waste for landfill. It has been reported that some legislative measures to control waste movements are inhibiting the recycling of residues from metallurgical operations [tm 99, Bontoux 1997]. It is also well known that the metal producing industries obtain one of the highest recycling rates in all industrial sections. This helps to reduce Cross Media Issues to a minimum. Nevertheless the problem of residues from production facilities and the designation of some of these materials will also play an important role in future permits and the techniques tend to concentrate on this aspect.

The following table offers examples of the potential wastes according to the European Waste Catalogue (Council Decision 94/3/EEC)[1] and the Hazardous Waste List (Council Decision 94/904/EEC). Waste in general terms is defined by the framework directive on waste (Directive 75/442 EEC amended by Directive 91/156/EEC) as “any substances or objects in the categories set in Annex I which the holder discards or intends or is required to discard”. A second definition of waste co-exists with the definition presented above. It is that from the Basel Convention, adopted by the European Union in 1993: “Wastes are substances or objects which are disposed of or are intended to be disposed of or required to be disposed of by provisions of national law” [tm 99, Bontoux 1997].

Waste from the production of non ferrous metals

EWC-Code	Description	Hazardous Waste	Origin
01 03 03	Red mud from alumina production		Bauxite process
10 03 00	Wastes from aluminium thermal metallurgy		
10 03 01	Tars and other carbon-containing wastes from anode manufacture	•	Anode baking plant
10 03 02	Anode scraps		Pot room
10 03 03	Skimmings	•	Smelting
10 03 04	Primary smelting slag/white drosses	•	Smelting
10 03 05	Alumina dust		Smelting
10 03 06	Used carbon strips and fire proof materials from anode manufacture		Anode baking plant
10 03 07	Spent pot linings	•	Pot room
10 03 08	Salt slag from secondary smelting	•	Smelting

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[1] The EWC is a harmonised, non-exhaustive list of wastes, that is to say, a list, which will be periodically reviewed and if necessary revised in accordance with the committee procedure. However, the inclusion of a material in the EWC does not means that the material is a waste in all circumstances. The entry is only relevant when the definition of waste has been satisfied [tm 99, Definition of Waste 1997].

Waste from the production of non ferrous metals			
EWC-Code	Description	Hazardous Waste	Origin
10.03 09	Black drosses from secondary smelting	•	Smelting
10 03 10	Waste from treatment of salt slag and black drosses treatment	•	Salt slag recovery plant
10 03 11	Flue gas dust		Abatement system
10 03 12	Other particulates and dust (including ball mill dust)		Milling, storage
10 03 13	Solid waste from gas treatment		Abatement system
10 03 14	Sludges from gas treatment		Abatement system
10 03 99	Wastes not otherwise specified		
10 04 00	Wastes from lead thermal metallurgy		
10 04 01	Slags (first and second smelting)	•	Smelting
10 04 02	Dross and skimmings (fist and second smelting)	•	Smelting
10 04 03	Calcium arsenate	•	Abatement system
10 04 04	Flue gas dust	•	Abatement system
10 04 05	Other particulates and dust	•	Storage, handling
10 04 06	Solid waste from gas treatment	•	Abatement system
10 04 07	Sludges from gas treatment	•	Abatement system
10 04 08	Spent linings and refractories		Furnace
10 04 99	Wastes not otherwise specified		
10 05 00	Wastes from zinc thermal metallurgy		
10 05 01	Slags (first and second smelting)	•	Smelting
10 05 02	Dross and skimmings (fist and second smelting)	•	Smelting
10 05 03	flue gas dust	•	Abatement system
10 05 04	Other particulates and dust		Storage, handling
10 05 05	Solid waste form gas treatment	•	Abatement system
10 05 06	Sludges from gas treatment	•	Abatement system
10 05 07	Spent linings and refractories		Furnace
10 05 99	Wastes not otherwise specified		
10 06 00	Wastes from copper thermal metallurgy		
10 06 01	Slags (first and second smelting)		Smelting
10 06 02	Dross and skimmings (fist and second smelting)		Smelting
10 06 03	flue gas dust	•	Abatement system
10 06 04	Other particulates and dust		Storage, handling
10 06 05	Waste from electrolytic refining	•	Tank house
10 06 06	Solid waste from gas treatment	•	Abatement system
10 06 07	Sludges from gas treatment	•	Abatement system
10 06 08	Spent linings and refractories		Furnace
10 06 99	Wastes not otherwise specified		
10 07 00	Wastes from silver, gold an platinum thermal metallurgy		
10 07 01	Slags (first and second smelting)		Smelting
10 07 02	Dross and skimmings (first and second smelting)		Smelting
10 07 03	Solid waste from gas treatment		Abatement system
10 07 04	Other particulates and dust		Storage, handling
10 07 05	Sludges from gas treatment		Abatement system
10 07 06	Spent linings and refractories		Furnace
10 07 99	Wastes not otherwise specified		
10 08 00	Wastes from other non ferrous thermal metallurgy		
10 08 01	Slags (first and second smelting)		Smelting
10 08 02	Dross and skimmings (first and second smelting)		Smelting
10 08 03	Solid waste from gas treatment		Abatement system
10 08 04	Other particulates and dust		Storage, handling, powder metal process
10 08 05	Sludges from gas treatment		Abatement system

Waste from the production of non ferrous metals

EWC-Code	Description	Hazardous Waste	Origin
10 08 06	Spent linings and refractories		Furnace
10 08 99	Wastes not otherwise specified		
11 02 00	Wastes and sludges from non ferrous hydrometallurgical processes		
06 05 01	Sludge from wastewater treatment on side		Wastewater treatment
11 02 01	Sludges from copper hydro-metallurgy		Leaching process
11 02 02	Sludges from zinc hydro-metallurgy (including jarosite, goethite)	•	Leaching process
11 02 03	Wastes from the production of anodes for aqueous electrolytic processes		Anode production plant
11 02 04	Sludges not otherwise specified		
13 01 00	Waste hydraulic oils and break fluids		
13 01 01	Waste hydraulic oils, containing PCPs or PCTs	•	Transformer
13 01 02	Other chlorinated hydraulic oils (not emulsions)	•	Transformer
13 01 03	non chlorinated hydraulic oils (not emulsions)	•	Transformer
13 01 06	Hydraulic oils containing only mineral oil	•	Transformer
13 03 00	Waste insulating and heat transmission oils and other liquids		
13 03 01	Insulating or heat transmission oils and other liquids	•	Transformer
13 03 02	Other chlorinated insulating oils and other liquids containing PCBs or PCTs		Transformer
13 03 03	non-chlorinated insulating and heat transmission oils and other liquids	•	Transformer
13 03 04	Synthetic insulating and heat transmission oils and liquids	•	Transformer
13 03 05	Mineral insulating and heat transmission oils	•	Transformer
15 02 00	Absorbents, filter materials, wiping clothes and protective clothing		
15 02 01	Absorbents, filter materials, wiping clothes, protective clothes		Abatement system (dry de-dusting)

Table 2.24: Materials from non-ferrous metal production

Most of the materials listed above are recycled or reused within the non-ferrous metal industry itself as well as in other industries, for example in the cement, abrasives manufacturing and construction industries. It is not the intention to discard or dispose them. They are the result of metal separation that is necessary for their recovery and the production of pure metals from complex sources. Some examples are given below.

2.10.2 Applied process and techniques

2.10.2.1 Residues from the smelting process

The main residues arising from the smelting of non-ferrous metals are slag, drosses and skimmings removed during the pyrometallurgical processes. Slag is generated by the reaction of slag forming accompanying elements (e.g. Fe) with added fluxes. In the smelting process the slag is liquid and has a different density to the melted metal and can therefore be tapped off separately.

Most of the slag generated by down-stream or refining operations in the non-ferrous metal production processes can usually be recycled or used for further metal recovery. The following figure shows the internal recycling of the slag produced during the production of primary copper. In this example, molten slag obtained from the converter, which has a high copper content, is returned to the smelter. The slag leaving the smelter is de-copperised in an electric slag-cleaning furnace. This furnace is operated continuously with an almost continuous flow of slag. Depending on local facilities the resulting clean slag is either granulated to produce abrasives or cooled slowly and broken into lumps for filling or construction material.

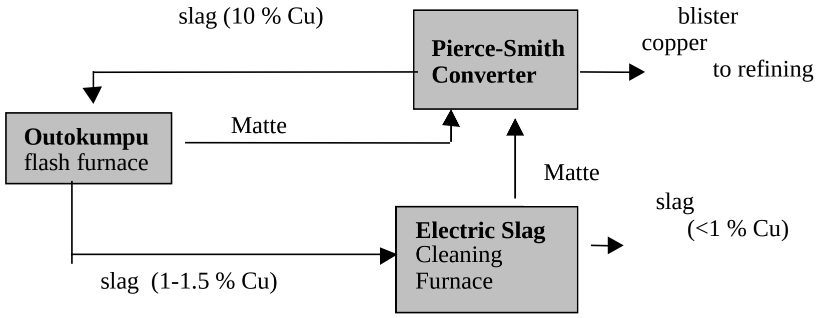


Figure 2.41: Electric furnace cleaning of copper slags

There is a distinction between slag with a high metal content, which is recycled within the process and final slag with a low metal content. Several facilities in the non-ferrous metal industries have demonstrated that there is a market in which they are able to sell slag for further beneficial use. The use of slag as a construction material is only possible if the amount of the leachable metal compounds is low. There are various tests to demonstrate this. Slag that cannot be used as abrasive or in civil engineering and construction is sent for ultimate disposal to a landfill.

Salt slag is generated by melting light metals (aluminium, magnesium). The use of a salt flux prevents the melted metal from oxidation and binds the impurities from the process. There are different ways to minimise the amount of salt flux used as well as different treatment techniques for salt and metal recovery that are available and they are discussed in more detail in Chapter 4 of this document.

Drosses and skimmings are generated by oxidation of metals at the bath surface or by reactions with fireproof material used as furnace linings. The metal content of skimmings is relatively high (between 20 and 80%), therefore they can normally be recycled to the main process or supplied as secondary raw material to other non-ferrous metal plants.

Another source of residues is spent linings and refractories. These arise when refractory material falls out of the furnace linings or when the furnace lining has to be renewed completely. The durability of a furnace lining lies between a few weeks and several years depending on the process and metal (e.g. for the Outokumpu flash furnace in the primary copper production 6 to 10 years are possible). The amount of furnace lining material could rise up to 5 kg/t of metal produced according to the melted metal [tm 85, MURL Düsseldorf 1997]. The following practices are used for furnace linings: - Treatment in a smelter to form an inert slag, e.g. linings from a brass melting process are sent directly to a local secondary copper smelter; use as a component in the tap-hole mass; landfill of inert linings. The following table gives an overview of the amount of recycled, reused and discharged residues from some non-ferrous metal smelting furnaces in Germany. In this sense recycling means that the residue is returned to the process from where it has been produced. Reuse means that the residue is used for another purpose e.g. slag may be reused as a construction material.

Residue	Amount of residue reported in tonnes for 1996		
	Recycled or reused	Discharged to a landfill	Total amount
Refractory waste (Silicon dioxide)	21	188	209
Refractory waste	1655	1145	2800
Refractory waste with harmful components	637	728	1365
Slag	16869	3	16871
Drosses from lead smelting	1903	0	1903
Aluminium containing skimmings	45904	927	46831
Magnesium containing drosses	615	81	696
Salt slag from aluminium smelting	112438	0	112438
Other residues	348	0	348

Table 2.25: Amount of recycled, reused and discharged residues that have been reported in 1996 for some non-ferrous metal plants in North-Rhine Westphalia
[tm 83, MURL Düsseldorf 1999]

2.10.2.2 Residues from the abatement system

The abatement system is another major source of solid materials. These are flue gas dust and sludge recovered from the air pollution control equipment as well as other solid waste like spent filter material.

Dust from the storage and handling of raw material or from pre-processing unit operations is collected by the de-dusting system (usually a bag filter) and sent back to the main process or another smelter. In some cases the dust needs to be agglomerated before it can be recycled to the raw material storage and handling station.

Dust-laden off-gas from the smelting and refining facilities can be cleaned (as described in section 2.8) by using different abatement techniques. The material collected as dust by the off-gas cleaning can be agglomerated and sent back to the smelter or supplied as a raw material for further metal recovery in other facilities. An example is the zinc rich dust from a converter or an electric slag-cleaning furnace in the primary copper smelting process which can be treated as a by-product and reused as a raw material in a zinc recovery plant [tm 92, Copper Expert Group 1998]. Another example is the use of silica fume (micro silica), which is collected in the bag filter by smelting silicon-metal or ferro-silicon and sold as a valuable by-product to the construction industry.

The metal containing sludge from a scrubber is normally drained for instance in a chamber filter press and sent back to the smelter.

When off-gas cleaning takes place in a dry de-dusting system, the filter material occasionally needs to be replaced. The filters contain metal compounds and particles from the process. There are a number of examples where filter material is used in the pyrometallurgical process. If this is not possible they are sent for ultimate disposal to an incinerator or landfill. The following table gives some information about the amount of recycled, reused and discharged residues from the abatement system in some non-ferrous metal plants in Germany.

Residue	Amount of residue reported in tonnes for 1996		
	Recycled or reused	Discharged to a landfill	Total amount
Non-ferrous metal containing dust	6550	1886	8436
Dust	201	13	214
Mineral residues from the abatement system	2638	1752	4390
Sludge	508	4	511
Aluminium containing dust	1477	66	1543

Table 2.26: Amount of recycled, reused and discharged residues that have been reported in 1996 for some non-ferrous metal plants in North-Rhine Westphalia
[tm 84, MURL Düsseldorf 1999]

2.10.2.3 Residues from liquid effluent treatment

Pyrometallurgical processes for the production of non-ferrous metals normally do not produce harmful wastewater. The water is used for direct or indirect cooling of furnaces, blowing lances and casting machines e. g. for copper-anode or continuous casting. This water is warmed up by cooling the equipment but is normally not polluted with chemical impurities or metal particles. Therefore cooling water is usually discharged directly after settlement or another treatment step back into the receiving source. Solid material that is removed is returned to the smelter

If a wet scrubber is used for cleaning the process off-gas, wastewater is generated. This stream of wastewater has to be treated to reduce the amount of metal compounds. From this treatment, sludge is produced that may be rich in metal and can sometimes be recycled to the process if the metal content is high enough.

Process water arises from hydrometallurgical operations and presents a high risk of water pollution. It has therefore to be cleaned in a wastewater treatment plant. The cleaning takes place by neutralisation or precipitation of specific ions. The main residue from these effluent treatment systems is gypsum ($CaSO_4$) and metal hydroxides and sulphides. The sludge sometimes is recycled back to the main production process when neutralisation does not present a bled for minor elements but more usually it is disposed.

2.10.2.4 Residues from the non-ferrous metal hydrometallurgical processes

The production of non-ferrous metals by hydrometallurgical processes is another significant source of solid residue. The leaching process can generate relatively large quantities of sludge (e.g. approximately 0.3 to 0.5 tonnes iron based solids per tonne of zinc depending on the quality of the concentrate). These residues are normally disposed in specially sealed lagoons.

The leaching and purification process and the electrolysis processes also generate other metal rich solids. They are usually rich in a specific metal and can sometimes be recycled to the production process or sent for metal recovery to other non-ferrous metals facilities (e.g. for the production of precious metals, lead, copper and cadmium). The anode slime from the copper tank house for instance is one of the most important raw materials of the recovery of precious metals and is therefore considered as a valuable by-product of the copper production. These issues are discussed in the chapters dealing with the individual metal groups.

2.10.2.5 Other residues from the production of non-ferrous metals

There are several other kinds of residue like hydraulic and heat transmission oils that result from regular maintenance of the equipment, for example the transformer for the electric furnaces. This is usually supplied to a used oil refinery (or in some Countries e.g. Italy, to a compulsory consortium or agency). In some circumstances they can be used as a source of energy on site.

2.10.3 Techniques to consider in the determination of BAT

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau.

2.10.3.1 Minimisation of residues from the metallurgical process

As mentioned in section 2.10.2.1, the amount of slag and skimmings that is produced by smelting metals is mainly influenced by the impurities of the raw material, so that cleaner materials lead to reduced generation of these solids. In some cases this can be ensured by the selection of the raw material that will be used. For example some zinc concentrates can contain lower quantities of iron [tm 101,NL Zn 1998], and the processes developed to used these concentrates can minimise the production of iron based residues. The limited availability and higher cost of these concentrates means that this is not a global solution. For secondary aluminium the pre treatment of scrap or the use of cleaner materials results in the reduction or elimination of salt flux used depending on the furnace used. The economics of pre-treatment need to be balanced.

On the other hand inappropriate storage and handling may lead to the wetting of materials. For example in a re-melting process for aluminium the water is vaporised with the consequence of explosion.

The generation of skimmings can be minimised by optimising operation of the furnace e.g. decreasing the burn-up by avoidance the overheating of melt. Modern process control techniques are used to ensure optimised operation conditions.

To avoid oxidising the bath surface of a melt, a closed furnace operation could be used. For example by melting aluminium under a reducing atmosphere (rinsing the furnace with inert gas) reduces the amount of skimmings that will be generated. Similarly the use of a pumping system and a side well is another measure which can reduce oxidation.

As it has been demonstrated that lead ashes and a large amount of the slag that is generated by the smelting process can be recycled or reused to a large extent.

Spent linings and refractories cannot be completely be avoided, but a decrease of the quantity can be obtained by the following measures:

- Careful construction of the brick lining of the furnace
- Continuous use of the furnace and thus minimisation of the variations in temperature
- Short impact time of the fluxing agents

- Avoidance of aggressive fluxing agents
- Careful cleaning of furnaces and crucibles
- Reduction of furnace agitation (rotation)

Under certain conditions, depending on the composition of the spent linings and refractories, reuse is possible. For example refractories are reused in primary and secondary copper smelting after grinding as cast-able or tapping mass or as a flux to adjust slag composition. Alternatively the metal content can be separated from the material by milling and grinding and the spent linings and refractories can be reused for construction purposes. The metal content can be recycled to the smelter or supplied to other non-ferrous metal facilities.

2.10.3.2 Minimisation of residues arising from the abatement system

As described above, the main source of residue generated by the abatement system is flue gas dust and sludge depending on the abatement technology. The volume of process gases that has to be cleaned is largely dependent on the furnace type. For example a totally sealed furnace develops far less flue dust than a semi closed or an open furnace.

As already mentioned the metal laden dust can normally be recycled to the smelter or sold for further beneficial use to other non-ferrous metal facilities. The direct reuse of dust as a raw material often requires an agglomeration step as a pre-treatment process. Flue dust and sludge may be processed in a variety of pyrometallurgical or hydrometallurgical processes.

Drying of the smelter feed can lead to a release of SO_2, especially when sulphidic ores or concentrates are used as raw material (the other source is the sulphur content of the fuel). The gypsum ($CaSO_4$) produced in the SO_2 scrubber can sometimes be recycled to the dryer as part of the furnace flux feed depending on the process used.

The quantity of spent filter bags may be decreased be using modern filter materials that are more robust. Bag filters are characterised as an abatement technique that does not need very much maintenance. In the case of bag damage the appropriate filter compartment can be isolated with cover plates until repairs can be carried out safely. A filter change is normally only necessary if 10 to 20% of the filter compartments were taken out of service.

The replacement of filter bags with modern, reliable fabrics is often easy but the technical requirements and the related investment costs of individual cases needs to be considered. Used filter bags can be recycled into the smelter. In the case of a conversion or renewal of the filter system, the service life and the filter susceptibility can generate fewer bags. If this result in additional installation costs they usually can be compensated by the decrease in the number of bag failures.

2.10.3.3 Reduction of residue generated by the effluent treatment

The avoidance of thermally loaded cooling water to the environment can be reduced by the use of different kinds of cooling systems, such as closed cooling systems, quasi closed systems and open cycle cooling techniques (cooling towers). If a closed cooling cycle (e.g. air-coolers) is used the release of cooling water can be minimised, some blow down may be required to avoid salt build up. It should be noted that the choice of the best cooling system depends on a variety of site specific parameters. In order to minimise the impact of cooling on the environment as a whole the BAT Reference Document for Cooling Systems should be consulted.

The amount of wastewater that is generated by a wet scrubber can be reduced if the treated water is recycled back to the scrubber. To avoid an increasing content of salts in the washing water cycle a small quantity of water has to be bled continuously from the system and replaced by fresh water.

2.10.3.4 Reduction of other residues arising from the production of non-ferrous metals

All machinery that is operated in an industrial installation uses oil as a lubricant. This has to be changed, due to metal pick-up and chemical reactions in the oil. Regular maintenance, repairs and preventive maintenance can minimise oil loss by leakage and increases the intervals between the oil change. A reduction of the quantity of used oil is reached also by the use of filtration, which gives an extension of the service life. For example by-pass filters may be installed to continuously clean a small part of the oil. These measures cause result in an extension of the service life up to the factor of 10 depending on the specific filter system. If used oil filters are collected separately they can be crushed in a shredder. The metal can be reused in a smelter as secondary raw material, the oil can be centrifuged and then sent to a used oil refinery.

2.10.3.5 Recycling and reuse of residues form non-ferrous metal smelting processes

As already shown in this section, residues from the production of non-ferrous metals can be recycled and reused to a large extent. The following table summarises the different possibilities of recycling and reuse of these residues.

Source of the residues	Associated Metals	Intermediate product or Residue	Options for recycling or reuse
Raw materials handling etc.	All metals	Dust, sweepings	• Feed for the main process
Smelting furnace	All metals	Slag	• Return to smelting • Construction material after slag treatment • Abrasive industry • Parts of slag may be used as refractory material e.g. slag from the production of chromium metal
	Ferro-alloys	Rich slag	• Raw material for other ferro-alloy processes
Converting furnace	Cu	Slag	• Recycle to smelter
Refining furnaces	Cu	Slag	• Recycle to smelter
	Pb	Skimmings	• Recovery of other valuable metals
	Precious metals (PMs)	Skimmings and slag	• Internal recycle
Slag treatment	Cu and Ni	Cleaned slag	• Construction material
		Matte	• Metal recovery
Melting furnace	All metals	Skimmings	• Return to process after treatment.
		Slag	• Metal recovery
	Secondary Al	Salt slag	• Metal, salt and oxide recovery
Electro-refining	Cu	Electrolyte bleed	• Recovery of Ni.
		Anode remnants	• Return to converter
		Anode slime	• Recovery of precious metals
Electro-winning	Zn, Ni, Co, PMs	Spent electrolyte	• Reuse in leaching process
Fused salt electrolysis	Al	SPL	• Carburant or disposal
		Excess bath	• Sale as electrolyte
		Anode stubs	• Recovery
	Na and Li	Cell material	• Scrap iron after cleaning
Distillation	Hg	Residues	• Reuse as process feed
	Zn, Cd	Residues	• Return to ISF
Leaching	Zn	Ferrite residues	• Disposal, reuse of liquor
	Cu	Residues	• Disposal
	Ni	Cu/Fe residues	• Recovery, disposal
Sulphuric acid plant		Catalyst	• Regeneration
		Acid sludges	• Disposal
		Weak acid	• Leaching, decomposition, neutralisation
Furnace linings	All metals	Refractory	• Use as slagging agent, disposal
Milling, Grinding	Carbon	Carbon and graphite dusts	• Use as raw material in other processes
Pickling	Cu ,Ti	Spent acid	• Recovery
Dry abatement systems	Most - using fabric filters or EPs	Filter dust	• Return to process • Recovery of other metals
Wet abatement systems	Most - scrubbers or wet EPs	Filter sludge	• Return to process or recovery of other metals (e.g. Hg). Disposal
Wastewater treatment sludge	Most	Hydroxide or sulphide sludges.	• Disposal, reuse • Reuse
Digestion	Alumina	Red mud	• Disposal, reuse of liquor

Table 2.27: Residues and potential uses

According to a research project on the avoidance and recycling of waste from a large number of non-ferrous metal smelting plants in North-Rhine Westphalia the following breakdown can be presented to demonstrate the importance of the different recycling routes [tm 83, MURL Düsseldorf 1999] [tm 168, W. Neuhaus 1999].

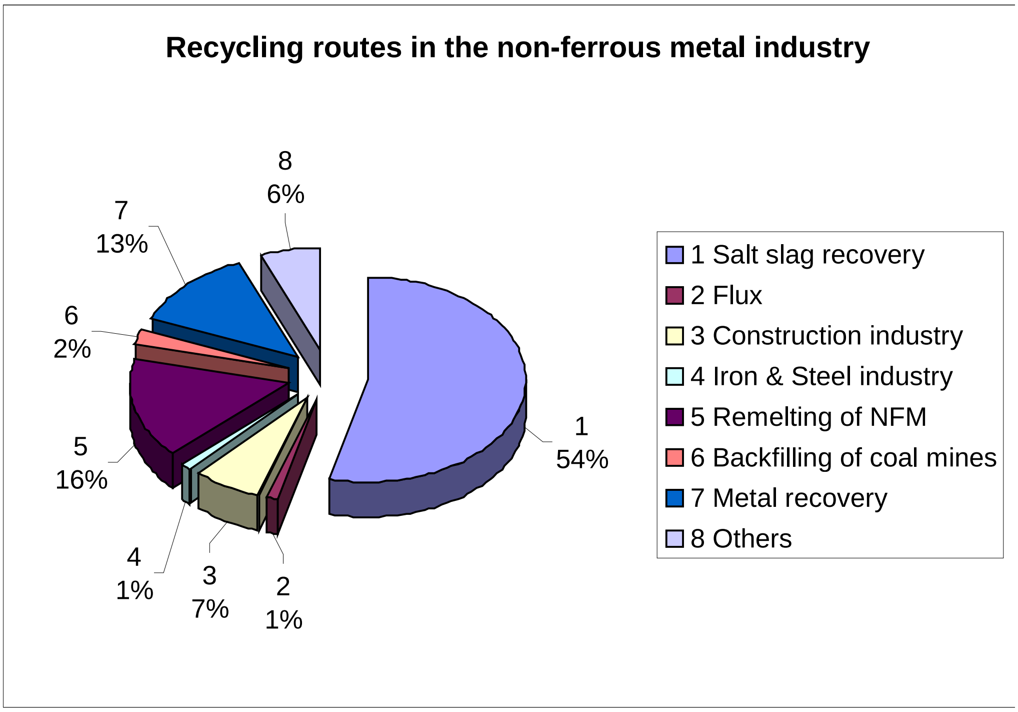


Figure 2.42: Different recycling routes according to the amount of residues generated by some non ferrous metals producing plants in North-Rhine Westpfalia

To achieve effective waste minimisation and recycling the following can be considered:

- Waste minimisation audits can be conducted periodically according to a programme.
- The active participation of staff can be encouraged in these initiatives.
- Active monitoring of materials throughput, and appropriate mass balances should be available. Monitoring should include water, power, and heat.
- There should be a good understanding of the costs associated with waste production within the process. This can be achieved by using accounting practices that ensure that waste disposal and other significant environmental costs are attributed to the processes involved and are not treated simply as a site overhead.

2.11 Energy Recovery

Article 3(d) of the IPPC Directive requires that energy is used efficiently and this note includes comment on energy use and it's place in the assessment of BAT under each of the metal production chapters. Energy use in the non-ferrous metal industry is covered by a series of reports prepared by the Centre for the Analysis and Dissemination of Demonstrates Energy Technologies (CADDET). These reports have been used extensively in comparing techniques.

2.11.1 Applied techniques

Energy and heat recovery is practised extensively during the production and casting of non-ferrous metals. Pyrometallurgical processes are highly heat intensive and the process gases contain a lot of heat energy. As a consequence recuperative burners, heat exchangers and boilers are used to recover this heat. Steam or electricity can be generated for use on or off site and process or fuel gases can be pre-heated [tm 118, ETSU 1996]. The technique used to recover heat varies from site to site. It is governed by a number of factors such as the potential uses for heat and energy on or near the site, the scale of operation and the potential for gases or their constituents to foul or coat heat exchangers.

The following examples are typical and constitute techniques to consider for use in the processes to produce non-ferrous metals [tm 118, ETSU 1996]. The techniques described can be incorporated into many existing processes:

- The hot gases produced during the smelting or roasting of sulphide ores are almost always passed through steam raising boilers. The steam produced can be used to produce electricity and/or for heating requirements. An example of this in where a copper smelter produces 25% of its electrical requirements (10.5 MVA) from the steam produced by the waste heat boiler of a flash furnace. In addition to electricity generation, steam is used as process steam, in the concentrate dryer and residual waste heat is used to pre-heat the combustion air.

- Other pyrometallurgical processes are also strongly exothermic, particularly when oxygen enrichment of combustion air is used. Many processes use the excess heat that is produced during the smelting or conversion stages to melt secondary materials without the use of additional fuel. For example the heat given off in the Pierce-Smith converter is used to melt anode scrap. In this case the scrap material is used for process cooling and the additions are carefully controlled, this avoids the need for cooling the converter by other means at various times of the cycle. Many other converters can use scrap additions for cooling and those that are not able are subject to process developments to allow it.

- The use of oxygen enriched air or oxygen in the burners reduces energy consumption by allowing autogenic smelting or the complete combustion of carbonaceous material. Waste gas volumes are significantly reduced allowing smaller fans etc to be used.

- Furnace lining material can also influence the energy balance of a melting operation. In this case Low Mass refractories are reported to have a beneficial effect by reducing the thermal conductivity and storage in an installation. [tm 106, Farrell 1998]. This factor must be balanced with the durability of the furnace lining and metal infiltration into the lining and may not be applicable in all cases.

- Separate drying of concentrates at low temperatures reduces the energy requirements. This is due to the energy required to super heat the steam within a smelter and the significant increase in the overall gas volume, which increases fan size.

- The production of sulphuric acid from the sulphur dioxide emitted from roasting and smelting stages is an exothermic process and involves a number of gas cooling stages. The heat generated in the gases during conversion and the heat contained in the acid produced can be used to generate steam and /or hot water.

- Heat is recovered by using the hot gases from melting stages to pre-heat the furnace charge. In a similar way the fuel gas and combustion air can be pre-heated or a recuperative burner used in the furnace. Thermal efficiency is improved in these cases. For example, nearly all cathode/copper scrap melting shaft furnaces are natural gas fired, the design offers an thermal efficiency (fuel utilisation) of 58% to 60%, depending on diameter and height of the furnace. Gas consumption is approximately 330 kWh/tonne of metal. The efficiency of a shaft furnace is high, principally because of charge preheating within the furnace. There can be sufficient residual heat in the off-gas to be recovered and re-used to heat combustion air and gas. The heat recovery arrangement requires the diversion of the furnace stack gases through a suitably sized heat exchanger, transfer fan and ductwork. The heat recovered is approximately 4% to 6% of the furnace fuel consumption.

- Cooling prior to a bag filter installation is an important technique as it provides temperature protection for the filter and allows a wider choice of fabric. It is sometimes possible to recover heat at this stage. For example in a typical arrangement used by a shaft furnace to melt metal, gases from the top of the furnace are ducted to the first of two heat exchangers that produces preheated furnace combustion air. The temperature of the gases after this heat exchanger can be between 200 and 450 ºC. The second heat exchanger reduces the gas temperature to 130 ºC before the bag filter. The heat exchangers are normally followed by a cyclone, which removes larger particles and acts as a spark arrester.

- Carbon monoxide produced in an electric or blast furnace is collected and burnt as a fuel for several different processes or to produce steam or other energy. Significant quantities of the gas can be produced and examples exist where a major proportion of the energy used by an installation is produced from the CO collected from an electric arc furnace installation. In other cases the CO formed in an electric furnace burns in the furnace and provides part of the heat required for the melting process.

- The re-circulation of contaminated waste gas back through an oxy-fuel burner has resulted in significant energy savings. The burner recovers the waste heat in the gas, uses the energy content of the contaminants and removes them [tm 116, Alfed 1998]. Such a process can also reduce nitrogen oxides.

- The use of the heat content of process gases or steam to raise the temperature of leaching liquors is practised frequently. In some cases a portion of the gas flow can be diverted to a scrubber to recover heat into the water, which is then used for leaching purposes. The cooled gas is then returned to the main flow for further abatement.

- During the smelting of electronic scrap or battery scrap in metallurgical vessels the heat content of the plastic content is used to melt the metal content and other additional scrap and slag forming components.

The advantage of preheating the combustion air used in burners is well documented. If an air preheat of 400 °C is used there is an increase in flame temperature of 200 °C, while if the preheat is 500 °C the flame temperature increases by 300 °C. This increase in flame temperature results in a higher melting efficiency and a reduction in energy consumption.

The alternative to preheating the combustion air is to preheat the material charged to the furnace. Theory shows that 8% energy savings can be obtained for every 100 °C preheat and in practice it is claimed that preheating to 400 °C leads to 25% energy savings while a preheat of 500 °C leads to a 30% energy savings. Pre-heating is practised in a variety processes for example the pre-heating of the furnace charge using the hot furnace off-gases during the production of ferro-chrome.

The following figure illustrates the energy balance of the Contimelt process, which uses the rising, hot gases in a shaft furnace to pre-heat the charge.

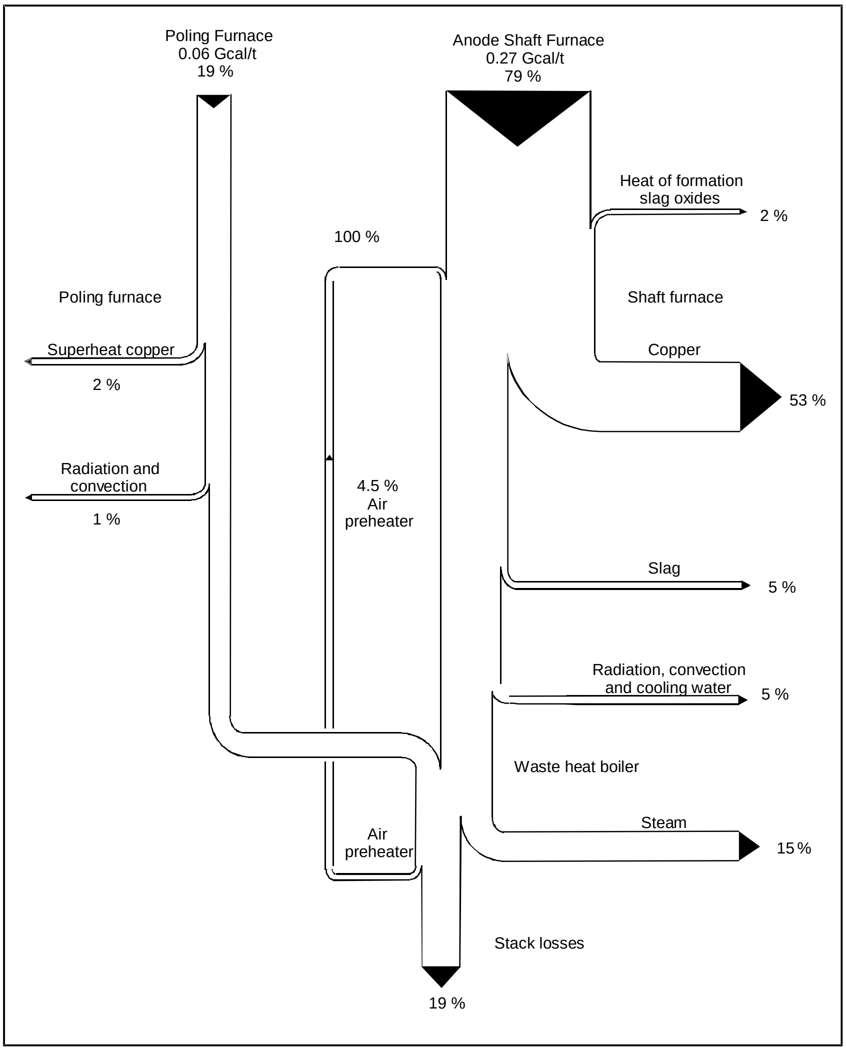


Figure 2.43: Energy balance of the Contimelt process
[tm 124, DFIU Cu 1999]

Heat and energy recovery is therefore an important factor in this industry and reflects the high proportion of costs that energy represents. Many techniques for energy recovery are relatively easy to retrofit [tm 118, ETSU 1996] but there are occasionally some problems of deposition of metal compounds in heat exchangers. Good design is based on a sound knowledge of the compounds released and their behaviour at various temperatures. Heat exchanger cleaning mechanisms are also used to maintain thermal efficiency.

Whilst these savings are examples of individual components of installations they are critically dependant upon the site and process specific conditions including economics.

2.12 Cross Media Issues

Cross media issues result from the abatement of emissions from one environmental medium producing emissions to another environmental medium. IPPC encourages the prevention of emissions by process design and good operation and maintenance. This factor will minimise the overall environmental impact on all environmental media. Few processes can be operated with zero emissions but some “Clean Technologies” are suggested as techniques to consider when determining BAT. The principles of the minimisation and reuse of residues and water and the energy recovery techniques discussed above are prime examples of this.

In a similar way the use of oxygen, the minimisation of the transfer of molten material in ladles and the collection and re-circulation or conversion of gases are also significant factors in minimising cross media issues. Common examples are the collection of chlorine from electrolysis with re-use in a leaching stage and the recovery of sulphur dioxide.

The choice of abatement process is also a significant factor and a prime example is a comparison of a wet scrubber with a fabric filter. The wet scrubber will generate an effluent from the liquor bleed and will also generate a wet sludge. Wet sludges may be more difficult to re-use and may cause problems at a disposal site but they will not form a dust during storage. On this basis a wet scrubber is less attractive than a fabric filter and also suffers from inferior particle removal in most installations. The wet scrubber however does have an application where the dust to be removed is very abrasive and dense or is very hygroscopic. In these cases rapid wear or bag blinding can make a fabric filter very difficult to operate and can result in significant emissions during breakdown. pH controlled wet scrubbing is very efficient in SO_2 absorption from gases with low SO_2 concentrations. These factors need to be considered and balance on a site-specific basis.

The environmental cost of producing the energy required for processes and abatement is another important cross-media effect. This factor is taken into account in the examples used in this document. There are difficulties however in making direct comparisons and issues such as the source of the energy for a particular site can make this a complicated assessment.

The assessment of Cross Media Issues is a significant factor and is identified under the metal specific chapters where site and technique specific aspects are illustrated.

2.13 Noise and Vibration

Noise and vibration are common issues in the sector and the sources are encountered in all sections of the Industry. Process noise emitted from an installation into the surrounding environment is a factor that has caused many complaints in the past and some information about causes and approaches to prevent and minimise noise and vibration have been received. The effect of noise on operators within an installation is not within the scope of this note.

The significant sources are transport and handling of raw materials and products; the production processes involving pyro-metallurgy, grinding and milling operations; the use of pumps and fans; the venting of steam and the existence of unattended alarm systems. Noise and vibration can be measured in a number of ways but generally the detail is site specific and takes account of the frequency of the sound and the location of population centres.

New plant can be specified with low noise and vibration levels. Good maintenance can prevent equipment such as fans and pumps from becoming un-balanced. The interconnections between equipment can be designed to prevent or minimise the transmission of noise. Common noise abatement techniques are: -

- the use of embankments to screen the source of noise;
- the enclosure of noisy plant or components in sound absorbing structures;
- the use of anti-vibration supports and interconnections for equipment;
- the orientation of noise emitting machinery and
- the change of the frequency of the sound.

2.14 Odour

There are several potential sources of odour in the non-ferrous metal industry. The most significant are metal fume, organic oils and solvents, sulphides from slag cooling and wastewater treatment, chemical reagents used in hydro-metallurgical and effluent treatment processes (e.g. ammonia) and acid gases. Odours can be prevented by careful design, choice of reagents and by correct material handling. For example production of ammonia from aluminium skimmings can be prevented by keeping the material dry.

The abatement techniques described earlier in this chapter will all contribute to the prevention and elimination of odours. The general principles of "Good House-keeping" and good maintenance practice also have a major contribution to prevention and control.

The basic hierarchy of the principles of odour control are: -

- to prevent or minimise the use of malodorous materials;

- to contain and extract odorous materials and gases before they are dispersed and diluted;

- to treat them possibly by after burning or filtration.

The use of biological media such peat or similar material that acts as a substrate for suitable biological species has been successful in removing odours [tm 159, VDI 1996]. The removal of odours can be a very complex and expensive process if strongly odorous materials are diluted. The treatment of very large gas volumes with low concentrations of odorous materials requires major process plant.

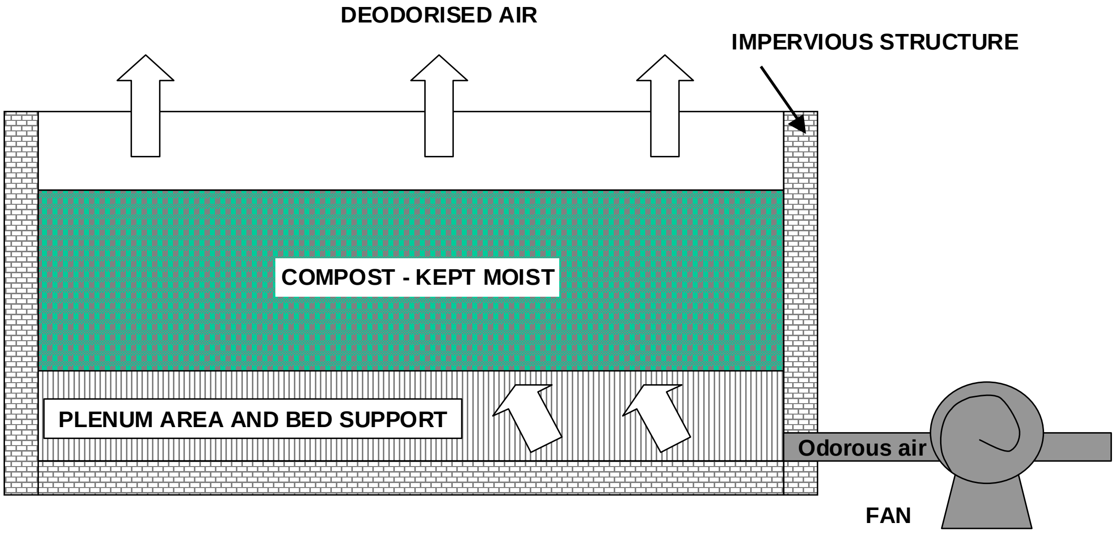


Figure 2.44: Arrangement of a simple Bio-filter

2.15 Safety Aspects

The general policy for the prevention of, the preparation for and the response to industrial accidents is based on the following principles: -

2.15.1 Prevention principle

- The plant construction and operation in such a way as to prevent the uncontrolled development of abnormal operation.
- the plant construction and operation in such a way that the consequences of accidents are reduced.
- the plant construction and operation according to the best available safety techniques (state of the art safety technology).

2.15.2 Consideration of complex systems in process industries

Complex systems can only be examined sufficiently by means of systematic, logical methods. This is taken into account by applying: -

- systematic analytical investigation methods such as Hazard and Operability studies (HAZOP),
- detailed safety analysis considering the conditions of the individual case.

2.15.3 Appropriateness of means

Safety requirements are graded according to "type and scope of hazards to be expected". To this end, rules within Member States are usually set up for:

- substances relevant to accidents (substance criteria, list of substances),
- industrial activities relevant to accidents (list of plants).

The objective dependence of the disaster potential upon the quantity of hazardous substances is considered by a quantity threshold concept that defines staged safety requirements as a function of quantity.

2.16 Plant operation and decommissioning

Article 3(f) of the IPPC Directive requires that the necessary measures are taken upon definitive cessation of activities to avoid any pollution risk and return the site of operation to a satisfactory state. Soil and water protection are of major importance and re-suspension of soil and dust to air needs to be prevented. An integrated approach means that the following measures are taken at least:

- minimise the amount of soil that needs to be excavated or replaced due to construction and to make sure that excavated soil material is treated carefully (in order to avoid harmful changes of soil properties);

- minimise the input of substances into the soil by leakage, aerial deposition and inappropriate storage of raw materials, products or residues during the operational phase of a facility;

- assessment of historical contamination to take account of conditions prior to regulation to ensure a clean closure when a facility is shut down, e.g. clean up and rehabilitation with regard to the future use of the area. Natural soil functions should be safeguarded, if feasible.

2.17 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous section. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this section are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation.

In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

It is not possible to conclude the Best Available Techniques for all of the common process stages because of the influence of the specific metal group. For example the selection production process can only be done on a metal by metal basis after taking account of the various influences of raw materials that are available etc. The Best Available Techniques included in this section for the common processes are: -

- Materials handling and storage;
- Process control;
- Fume and gas collection;
- Sulphur removal;
- Prevention and destruction of dioxins; and
- Removal of mercury from process gases.

2.17.1 Materials handling and storage

The techniques that are used depend to a large extent on the type of material that is being used. For example large, heavy items are treated by a completely different range of techniques to fine, dusty material. These issues are specific to individual sites and materials. There are however, several techniques that are considered to be BAT in preventing emissions from material storage and handling processes.

These techniques are listed earlier in this chapter under techniques to consider in the determination of BAT. There are however, several techniques that are considered more effective in preventing releases from raw material handling. These techniques are:

- The use of liquid storage systems that are contained in impervious bunds that have a capacity capable of containing at least the volume of the largest storage tank within the bund. Various guidelines exist within each Member State and they should be followed as appropriate. Storage areas should be designed so that leaks from the upper portions of tanks and from delivery systems are intercepted and contained in the bund. Tank contents should be displayed and associated alarms used. The use of planned deliveries and automatic control systems to prevent over filling of storage tanks.

- Sulphuric acid and other reactive materials should also be stored in double walled tanks or tanks placed in chemically resistant bunds of the same capacity. The use of leak detection systems and alarms is sensible. If there is a risk of ground water contamination the storage area should be impermeable and resistant to the material stored.

- Delivery points should be contained within the bund to collect spilled of material. Back venting of displaced gases to the delivery vehicle should be practised to reduce emissions of VOCs. Use of automatic resealing of delivery connections to prevent spillage should be considered.

- Incompatible materials (e.g. oxidising and organic materials) should be segregated and inert gases used for storage tanks or areas if needed.

- The use of oil and solid interceptors if necessary for the drainage from open storage areas. The storage of material that can release oil on concreted areas that have curbs or other containment devices. The use of effluent treatment methods for chemical species that are stored.

- Transfer conveyors and pipelines placed in safe, open areas above ground so that leaks can be detected quickly and damage from vehicles and other equipment can be prevented. If buried pipelines are used their course can be documented and marked and safe excavation systems adopted.

- The use of well designed, robust pressure vessels for gases (including LPG’s) with pressure monitoring of the tanks and delivery pipe-work to prevent rupture and leakage. Gas monitors should be used in confined areas and close to storage tanks.

- Where required, sealed delivery, storage and reclamation systems can be used for dusty materials and silos can be used for day storage. Completely closed buildings can be used for the storage of dusty materials and may not require special filter devices.

- Sealing agents (such as molasses and PVA) can be used where appropriate and compatible to reduce the tendency for material to form dust.

- Where required enclosed conveyors with well designed, robust extraction and filtration equipment can be used on delivery points, silos, pneumatic transfer systems and conveyor transfer points to prevent the emission of dust.

- Non-dusty, non-soluble material can be stored on sealed surfaces with drainage and drain collection.

- Swarf, turnings and other oily material should be stored under cover to prevent washing away by rain water.

- Rationalised transport systems can be used to minimise the generation and transport of dust within a site. Rainwater that washes dust away should be collected and treated before discharge.

- The use of wheel and body washes or other cleaning systems to clean vehicles used to deliver or handle dusty material. Local conditions will influence the method e.g. ice formation. Planned campaigns for road sweeping can be used.

- Inventory control and inspection systems can be adopted to prevent spillages and identify leaks.

- Material sampling and assay systems can be incorporated into the materials handling and storage system to identify raw material quality and plan the processing method. These systems should be designed and operated to same high standards as the handling and storage systems.

- Storage areas for reductants such as coal, coke or woodchips need to be surveyed to detect fires, caused by self-ignition.

- The use of good design and construction practices and adequate maintenance.

The following table summarises the techniques on the basis of type and characteristics of the material.

Raw material	Metal group	Method for handling	Method for storage	Comments
Concentrates: - Dust forming Non dust forming	All	Enclosed conveyors or pneumatic Covered conveyors	Enclosed building Covered store	Prevention of water contamination.
Fine grained material like metal powder	Refractory metals	Enclosed conveyors or pneumatic Covered conveyors	Closed drum, bins and hoppers	Prevention of water contamination and fugitive air emissions
Secondary raw materials: - Large items Small items Fines Swarf	All	Mechanical loader Charge skips Enclosed or agglomerated	Open Covered bays Enclosed if dusty Covered	Prevention of water contamination. Reactions with water. Oily drainage.
Fluxes: - Dust forming Non dust forming	All	Enclosed conveyors or pneumatic Covered conveyors	Enclosed building Covered store	Prevention of water contamination.
Solid fuel & coke: -	All	Covered conveyors	Covered store	If not dust forming.
Liquid fuels and LPG	All	Overhead pipeline	Certified storage Bunded areas.	Back venting of delivery lines
Process gases: - Oxygen Chlorine, CO	All Al, PM, Ni	Overhead pipeline Reduced pressure pipeline	Certified storage	Pressure loss monitoring, Alarms for toxic gases.
Solvents	Cu, Ni, Zn group, Precious metals, Carbon	Overhead pipeline Manual	Drums, tanks	Back venting of delivery lines.
Products – Cathodes, wire-rod, billets, ingots, cakes etc.	All	Depends on conditions.	Open concrete area or covered storage.	Appropriate drainage system.
Process residues for recovery.	All	Depends on conditions.	Open, covered or enclosed depending on dust formation and reaction with water.	Appropriate drainage system.
Wastes for disposal. (e.g. furnace linings)	All	Depends on conditions.	Open covered or enclosed bays or sealed (drums) depending on the material.	Appropriate drainage system.

Table 2.28: Summary of handling and storage techniques

2.17.2 Process control

The principles of Best Available Techniques include the concepts of how a process is designed, operated, controlled, manned and maintained. These factors allow good performance to be achieved in terms of emission prevention and minimisation, process efficiency and cost savings. Good process control is used to achieve these gains and also to maintain safe conditions.

Process operation and control has developed recently in this sector and is applied to a variety of processes. The following techniques are used: -

Sampling and analysis of raw materials to control plant conditions. Good mixing of different feed materials should be achieved to get optimum conversion efficiency and reduce emissions and rejects.

The use of feed weighing and metering systems.

The use of microprocessors to control material feed-rate, critical process and combustion conditions and gas additions. Several parameters can be measured to allow processes to be controlled, alarms are provided for critical parameters: -

- On-line monitoring of temperature, furnace pressure (or depression) and gas volume or flow is used.
- Gas components (O_2, SO_2, CO) are monitored.
- On-line monitoring of vibration is used to detect blockages and possible equipment failure.
- On-line monitoring of the current and voltage of electrolytic processes.
- On-line monitoring of emissions to control critical process parameters.

Monitoring and control of the temperature of melting furnaces to prevent the production of metal and metal oxide fume by overheating.

Operators, engineers and others should be continuously trained and assessed in the use of operating instructions, the use of the modern control techniques described and the significance of and the actions to be taken when alarms are given.

Optimisation of levels of supervision to take advantage of the above and to maintain operator responsibility.

2.17.3 Fume and gas collection

Emissions to air arise from the storage, handling, pre-treatment, pyro-metallurgical and hydrometallurgical stages. Transfer of materials is particularly important. Data provided has confirmed that the significance of fugitive emissions in many processes is very high and that fugitive emissions can be much greater than those that are captured and abated. In these cases it is possible to reduce environmental impact by following the hierarchy of gas collection techniques from material storage and handling, reactors or furnaces and from material transfer points. Potential fugitive emissions must be considered at all stages of process design and development. The hierarchy of gas collection from all of the processes stages are: -

- Process optimisation and minimisation of emissions such as thermal or mechanical pre-treatment of secondary material to minimise organic contamination of the feed.
- The use of sealed furnaces or other process units to prevent fugitive emissions, allow heat recovery and allow the collection of process gases for other use (e.g. CO as a fuel and SO_2 as sulphuric acid) or to be abated.
- The use of semi-sealed furnaces where sealed furnaces are not available.
- The minimisation of material transfers between processes.

- Where such transfers are unavoidable, the use of launders in preference to ladles for molten materials.
- In some cases, restricting techniques to those that avoid molten material transfers would prevent the recovery of some secondary materials that would otherwise enter the waste stream. In these cases the use of secondary or tertiary fume collection is appropriate.
- Hooding and ductwork design to capture fume arising from hot metal, matte or slag transfers and tapping.
- Furnace or reactor enclosures may be required to prevent release of fume losses into the atmosphere.
- Where primary extraction and enclosure are likely to be ineffective, then the furnace can be fully closed and ventilation air drawn off by extraction fans to a suitable treatment and discharge system.
- Roofline collection of fume is very energy consuming and should be a last resort.

2.17.4 Sulphur dioxide removal

The Best Available Techniques for the removal of sulphur dioxide removal depends on the degree of fixation of sulphur in a matte or slag to prevent the formation of sulphur dioxide and on the strength of the gas that is produced. For very low strength gases a wet or semi-dry scrubber, producing gypsum for sale if possible, is considered to be BAT.

For higher strength gases the recovery of sulphur dioxide using cold water absorption followed by a sulphuric acid plant for the remaining gas and the stripping and production of liquid sulphur dioxide from the absorbed liquor is considered to be BAT where local markets exist for the material. The use of a double contact sulphuric acid plant with a minimum of four passes is considered to be BAT. The principle of maximising the inlet gas concentration is also considered as BAT so that the subsequent removal process can operate at maximum efficiency. The following factors are considered to be BAT for a sulphuric acid plant using smelter off-gases.

- A double contact, double absorption plant with a minimum of 4 passes can be used in a new installation. A caesium doped catalyst can be used to improve conversion. It may be possible to improve existing catalysts during maintenance periods by incorporating caesium doped catalysts when catalyst additions are made. This can be particularly effective when used in the final passes where the sulphur dioxide content is lower but to be fully effective must be accompanied by improvements in other areas.

- Gases are diluted before the contact stages to optimise the oxygen content and give a sulphur dioxide content to ~ 14% or slightly above to suit the thermal limits of the catalyst carrier material. Caesium oxide doping is required for such high inlet concentrations as it allows a lower first pass inlet temperature.

- For low, varying sulphur dioxide concentrations (1.5 to 4%) a single absorption plant such as the WSA process, could be used for existing plants. The use of a caesium oxide doped catalyst in the final pass can be used to achieve optimum performance and can be incorporated during routine catalyst changes or during maintenance. To be fully effective this should be accompanied by improvements in other areas such as gas cleaning to protect the catalyst from poisoning. Conversion to double contact is complex and expensive but the use of a single contact plant with tail gas de-sulphurisation if necessary, to produce gypsum for sale can allow energy savings and lower waste generation.

- Fluorides and chlorides should be removed to prevent damage to downstream plant structure.

- Dust should be removed from the gas stream prior to the catalyst stages, giving a final gas quality of < 1mg dust /Nm^3 (optically clear). Mercury should also be removed at this stage if the mercury content of the feed material warrants this. Existing plants without mercury removal could use an ion exchange process or precipitation, for example as mercury thiosulphate, to remove mercury from the acid if this is necessary.

- Sulphur trioxide should be reduced to give an inlet gas concentration below ~15 - 25 mg/Nm^3. The weak acid produced can be decomposed and used for acid production.

- Gas heating systems with automatic control should be used where the gas is very weak and the heat of reaction is insufficient to maintain the catalyst bed temperature.

- Gases are cooled to a temperature satisfying the acid plant water balance. The temperature is dependent on the SO_2 concentration of the gas and the concentration of the acid produced. A gas with 4 - 6% SO_2 requires cooling to temperatures below 30 °C while a gas with an SO_2 content well above 10% can tolerate gas temperatures of approximately 35 - 40 °C, when producing 98.5% grade acid.

- The use of candle filters to remove acid mists prior to the final stack is considered to be BAT in cases where an acid mist is produced.

2.17.5 Prevention and the destruction of dioxins

The presence of dioxins or their formation during a process needs to be considered for many of the pyro-metallurgical processes used to produce non-ferrous metals. Particular instances are reported in the metal specific chapters and in these cases the following factors are considered to be BAT for the prevention of the formation of dioxins and the destruction of any that are present. These techniques may be used in combination. Some non-ferrous metals are reported to catalyse de-novo synthesis and it is sometimes necessary to have a clean gas prior to further abatement.

- Quality control of scrap inputs depending on the process used. The use of the correct feed material for the particular furnace or process. Selection and sorting to prevent the addition of material that is contaminated with organic matter or precursors can reduce the potential for dioxin formation.

- The use of correctly designed and operated afterburners and rapid quenching of the hot gases to < 250 °C.

- The use of optimum combustion conditions. The use of oxygen injection in the upper part of a furnace to ensure complete combustion of furnace gases if necessary to achieve this.

- Absorption onto activated carbon in a fixed bed or moving bed reactor or by injection into the gas stream, and removal as filter dust.

- Very high efficiency dust removal, for example ceramic filters, high efficiency fabric filters or the gas cleaning train prior to a sulphuric acid plant.

- The use of a catalytic oxidation stage or fabric filters that incorporate a catalytic coating.

- Treatment of collected dusts in high temperature furnaces to destroy dioxins and to recover metals.

The emission concentrations that are associated with the above processes are < 0.1 to 0.5 ng/Nm^3 depending on the feed, the smelting or melting process and the techniques or combination of techniques that are used for dioxin removal.

2.17.6 Removal of mercury

Mercury removal is necessary when using some raw materials that contain the metal. Specific instances are referred to in the metal specific chapters and in these cases the following techniques are considered to be BAT.

- The Boliden/Norzink process with the recovery of the scrubbing solution and production of mercury metal.
- Bolchem process with the filtering off the mercury sulphide to allow the acid to be returned to the absorption stage.
- Outokumpu process.
- Sodium thiocyanate process.
- Activated Carbon Filter. An adsorption filter using activated carbon is used to remove mercury vapour from the gas stream as well as dioxins.

For processes where mercury removal from the gases is not practicable the two processes to reduce the mercury content in sulphuric acid produced during the production of non-ferrous metals are considered to be BAT.

- Superlig Ion Exchange process.
- Potassium iodide process.

The emissions associated with the above processes are related to any residual mercury that will be present in the acid that is produced, the product specification is normally < 0.1 ppm (mg/l) and is equivalent to ~ 0.02 mg/Nm^3 in the cleaned gas.

2.17.7 Effluent treatment and water reuse

The best available techniques are a combination of the different treatment methods and can only be chosen on a site by site basis by taking into account the site-specific factors. The most important factors to decide, which in a specific case would be the best solution in order to minimise the amount of wastewater and the concentration of the pollutants are:

- The process where the wastewater is generated,
- The amount of water,
- The pollutants and their concentrations,

The most common pollutants are metals and their compounds and initial treatment focuses on precipitation of the metals as hydroxides or sulphides using one or more stages followed by the removal of the precipitate by sedimentation or filtration. The technique will vary depending on the combination of pollutants but the following table summarises the methods described earlier.

Source of wastewater	Associated metals produced	Minimisation methods	Treatment Methods
Process water	• Alumina production, • Lead-acid battery breaking. • Pickling.	• Return to process as far as possible.	• Neutralisation precipitation and settlement. • Electrolysis.
Indirect cooling water	• Furnace cooling for most metals. • Electrolyte cooling for Zn	• Use of sealed cooling system. • System monitoring to detect leaks.	• Settlement.
Direct cooling water	• Cu castings. • Carbon electrodes.	• Settlement or other treatment. • Closed cooling system.	• Settlement. • Precipitation if needed.
Slag granulation	• Cu, Ni, Pb, Precious metals, ferro alloys	•	• Settlement. • Precipitation if needed.
Electrolysis	• Cu, Ni, Zn	• Sealed system. • Electro-winning of electrolyte bleed.	• Neutralisation and precipitation.
Hydro-metallurgy (blow-down)	• Zn, Cd	• Sealed system. • Blow-down treatment.	• Settlement. • Precipitation if needed.
Abatement system (blow-down)	• Wet scrubbers. • Wet EPs and scrubbers for acid plants.	• Blow-down treatment reuse of weak acid streams if possible.	• Settlement. • Precipitation if needed.
Surface water	• All	• Good raw materials storage	• Settlement. • Precipitation if needed. • Filtration.

Table 2.29: Overview of wastewater streams

2.17.8 Other common processes

The Best Available Techniques for all of the other processes that have been discussed in this chapter are those that comprise the techniques to consider in the determination of BAT in the various sub sections. These techniques to consider should therefore be referred to. Further details are given in the metal specific chapters when individual factors that may affect the choice of technique are discussed where they are appropriate.

2.18 Emerging Techniques

Emerging techniques are reported here only for the common processes described above under the section Best Available Techniques. Emerging Techniques for other processes are reported on in the subsequent chapters.

No additional techniques were reported for Materials Handling and Storage, Removal of Mercury and Prevention and Destruction of Dioxins.

2.18.1 Sulphur removal

The following emerging techniques have been identified [tm 209, JOM 1999].

- A combination of a single contact sulphuric acid plant and a modified tower acid plant is reported to achieve a sulphur removal efficiency two orders of magnitude greater than conventional processes. Tail gas SO_2 concentration is reported to be < 3ppm.
- A biological flue gas de-sulphurisation process that converts SO_2 from emissions to air or water into elemental sulphur with better than 95% removal efficiency.

3 PROCESSES TO PRODUCE COPPER AND ITS ALLOYS (INCLUDING Sn AND Be) FROM PRIMARY AND SECONDARY RAW MATERIALS

3.1 Applied Processes and Techniques

3.1.1 Primary copper

Primary copper may be produced from primary concentrates and other materials by pyrometallurgical or hydrometallurgical routes [tm 22, EC 1991; tm 27, HMIP Cu 1993; tm 26, PARCOM 1996]. Concentrates contain various amounts of other metals besides copper and the processing stages are used to separate these and recover them as far as possible [tm 92, Copper Expert Group 1998]. The generic processes are discussed below.

3.1.1.1 The pyrometallurgical route

This entails a number of steps depending on the concentrate used. The majority of concentrates are sulphidic and the stages involved are roasting, smelting, converting, refining and electro-refining. Overviews of all of the furnaces mentioned in this section are given in Chapter 2 and more detail is provided in this chapter under techniques [tm 92, Copper Expert Group 1998].

3.1.1.1.1 Concentrate to matte smelting

Partial roasting converts the complex sulphides of iron and copper in the concentrate into the simple sulphides by heating the ore or concentrate under oxidising conditions. The sulphur-based gases generated by this process are directed to on-site acid plants to be used as a raw material in the production of sulphuric acid or the production of liquid SO_2. The smelting stage is then used to separate the copper sulphide from the other solids present in ores by the formation of silicates particularly iron silicates. This reaction depends on the high affinity of copper to sulphur compared to other metallic impurities. Partial roasting is not normally used.

Roasting and smelting are usually carried out simultaneously in a single furnace at high temperatures to produce a melt that can be separated into a matte (copper sulphide with some iron sulphide) and a slag rich in iron and silica. A fluxing agent containing silica and if required, lime (CaO) is usually added to the melt to aid the formation of the slag.

There are two basic smelting processes in use, bath smelting and flash smelting. The flash smelting process uses oxygen enrichment to produce auto-thermal (autogenic) or nearly auto-thermal operation. Bath smelting processes generally use a lower degree of oxygen enrichment. The use of oxygen also gives higher sulphur dioxide concentrations that make the collection of the gas more effective using one of the sulphur recovery systems (usually the production of sulphuric acid or production of liquid sulphur dioxide).

Bath smelting is carried in a number of proprietary furnaces such as the Reverberatory, Electric, ISA Smelt, Noranda, Mitsubishi, Teniente, Baiyin, Vanyucov Furnaces [tm 22, EC 1991; tm 26, PARCOM 1996; tm 137, Cu Expert Group 1998]. All of the processes rely on the roasting and smelting processes taking place in a molten bath with slag and matte separation and tapping taking place in various ways. Some furnaces can operate without the pre-drying of the concentrate but the super heated water vapour increases the gas volume.

Smelting Process	Status of Development		Economic Aspects		Remarks
	Industrial scale operation status	**Environmental performance: Potential or constraints**	**Economic feasibility**	**Production level: Potential and / or limitations**	
Reverberatory furnace smelting	Established	Limited to a certain extent	Acceptable	Limitation for smelting rate of one unit	
Partial roasting & electric furnace smelting	Established	Good	Good	Limitation for production rate.	Possible roaster size limiting factor?
Outokumpu flash smelting & Peirce-Smith converting	Established	Good	Good	Very high smelting rate possible in 1 unit, depending of the furnace design and the type of concentrates.	World-wide the ”standard” primary copper smelting concept still with potential for improvement
Inco Flash smelting	Established	Good	Good	Limitation of proven smelting rate per unit	Size of furnaces installed. Still further potential.
Contop Application	Operating in 1 plant	Probably good	Probably acceptable	Limitation set by size of settling. Furnace and number of burners possible to be installed.	Cyclone burner only. Process feature introduced in industrial scale.
Teniente Converter, Noranda process	Established	Good	Good	Limitation of smelting rate by reactor size and O_2 enrichment limits	Related to other processes relatively higher ingress air ratio requiring increased effort for process gas capture
ISA Smelt	Operating in 3 plants	Good	Good	Upper production rate per unit not tested.	Potential for further improvement
Vanyucov process	6 industrial scale furnaces in Russia and Kazakstan	Potentially good	Probably good	No definite analysis available	Information for a substantiated judgement not available; in general technology may have considerable potential
Baiyin process	Exact number not known. At least 2 industrial units in operation.	Potentially good	Not known.	No definite analysis available; information available suggests production rates up to 75000 t/a Cu achieved.	Information not available to substantiate. May have considerable potential.
Outokumpu direct blister flash smelting	Established	Good	Good		Applicable to concentrates with low iron / low slag fall
Mitsubishi process for continuous copper smelting	Established	Good	Good	So far > 200000 t/a production level reached	Potential for further development
Kennecott/Outokumpu continuous flash converter	Operating in one plant. Second plant ordered.	Good	Good	Higher production rate used to justify investment	Potential for substantial further development
Noranda continuous converter	Recently commissioned in Horne on industrial scale	Good	No data for final analysis available	No data for final analysis available	Effectively available potential still to be evaluated when data from operation available.

Table: 3.1: Primary copper smelting technologies
[tm 137 Copper Expert Group 1998]

The differences between these processes can be great, for example in the position of air/oxygen or fuel addition points, some processes operate on a batch basis. Bath smelters are generally operated with a holding furnace or a separate settler. The general descriptions are covered in Chapter 2 and elsewhere [tm 137, Cu Expert Group 1998].

Flash Smelting is carried out in either the Outokumpu or INCO Flash Smelters [tm 22, EC 1991; tm 26, PARCOM 1996] or in a cyclone furnace (Contop). The Outokumpu and cyclone processes use oxygen enrichment and the INCO process uses technical oxygen. Flash smelting relies on the roasting and smelting of dry concentrate in airborne particles. The reacted particles fall into a settling chamber where the separation of the matte and slag takes place, sometimes additional fuel is used in the settler to maintain the temperature.

Matte and slag are subsequently tapped and processed further and gases pass from the furnace through a vertical chamber to a heat exchanger.

In addition to the techniques reported above other techniques may be encountered Worldwide as bath or flash smelting processes [tm 137, Copper Expert Group 1998].

Top Blown Rotary Converters (TBRCs) have also been used in the past in primary copper smelting. It is no longer used mainly due to the high operating costs.

The reverberatory furnace is also used for matte smelting but not within EU. It does not use the energy content of the sulphur and the iron in the concentrate and relies on the use of fossil fuel to melt the concentrates by the hot combustion gases sweeping over the hearth. The process is therefore not as efficient as the other processes described. The combustion gases add to the overall gas volume and result in a very low sulphur dioxide content, which is very difficult to remove effectively. The use of reverberatory furnaces has declined significantly since the 1970’s. The SO_2 content of the off-gases is normally very low so that they cannot be treated in an acid plant.

Process	**Number of smelters using that technology**	**Number of furnaces**	**Blister production 1998 '000 t/a**
Outokumpu Flash Smelting	26	26	3801
Outokumpu Flash Smelting, Direct Blister	2	2	238
Reverberatory furnace	27	37	1604
El Teniente reactor	7	12	1344
Electric Furnace	6	8	560
Blast Furnace	14	29	548
Mitsubishi process	4	4	497
Inco Flash Smelting	3	3	448
Vanuykov process	3	5	448
ISA Smelt	3	3	269
Noranda reactor	2	2	197
Contop	1	1	116
Bayin process	1	1	57
Kivcet	1	1	15

Table 3.2: Worldwide use of the smelting technologies

3.1.1.1.2 Converting

Two types of converter process are used: - the conventional batch process, which is most commonly used and the continuous converting process [tm 137 Copper Expert Group 1998].

a) Batch converting

The batch converting process comprises two stages. It is carried out by blowing an air/oxygen mixture through the matte recovered from the smelting operation. A cylindrical bath furnace is most commonly used [tm 22, EC 1991; tm 26, PARCOM 1996] and flux additions are made. In the first stage iron and part of the sulphur are oxidised and slag and sulphur dioxide gas are formed; the slag is skimmed off periodically and is further processed to recover copper. Normally the first stage blow is carried out in several steps with incremental matte additions. In the second stage, the copper blow, the copper sulphide is oxidised to blister copper (98.5% Cu) and more sulphur dioxide gas is formed. The blister copper is tapped at the end of the copper blow. The process is operated to control the residual sulphur and oxygen in the blister copper. The sulphur dioxide that is formed is further treated for sulphur recovery, normally in a sulphuric acid plant.

The reaction is strongly exothermic and also volatilises metallic impurities such as lead and zinc that are then captured in abatement plant and recovered. The process heat can also be used to melt anode scrap and other copper scrap without the addition of primary heat. There can be variations in sulphur dioxide concentration during the various stages of conversion depending on the type of furnace used.

The Peirce–Smith (P.S.) and the Hoboken type converters are operated batch-wise, (they are referred to as Peirce-Smith or similar converters during this chapter). They are cylindrical bath furnaces with laterally arranged tuyeres for air/oxygen blowing. [tm 22, EC 1991; tm 26, PARCOM 1996]. The ISA Smelt furnace has also been used for the batch-wise conversion of matte into blister copper.

Top Blown Rotary Converters (TBRC) have been used in the past for batch-wise conversion of primary copper material to blister copper but are not in use anymore.

b) Continuous converting

The continuous converting processes that are in industrial use are the Kennecott / Outokumpu flash converting furnace [tm 53 & tm 67 Kennecott 1997; tm 63 Outokumpu 1995], the Mitsubishi furnace (which forms part of the integrated Mitsubishi process) and – very recently - the Noranda converter [tm 137 Copper Expert Group 1998].

The Mitsubishi and the Noranda converters receive molten feed for conversion. In contrast the Kennecott / Outokumpu process has the following features: - Matte from a smelting furnace is first granulated in water, crushed and dried. The material is then blended with slagging agents and fed into the concentrate burner of a specific flash furnace using an oxygen rich atmosphere; conversion takes place in the air borne particles. The process produces a high and constant concentration of sulphur dioxide that is recovered. Slag and blister copper are tapped for further processing. The use of ground matte allows the matte quality to be balanced with feed rate and degree of oxygen enrichment to produce the optimum conversion efficiency and also allows the matte production and conversion stages to be de-coupled.

There are significant differences between batch-wise and continuous converter concepts in operation and sulphur dioxide output variations throughout the converting cycles. There are also variations in the ease of collecting fume during charging and in the ability to melt scrap anodes. Some furnaces rely on ladles for the transfer of matte, slag and blister copper and fugitive emissions may result. In one case the ventilation gases from the converter aisle are collected and treated, in another case an intelligent secondary fume collection system is used [tm 201, Velten 1999].

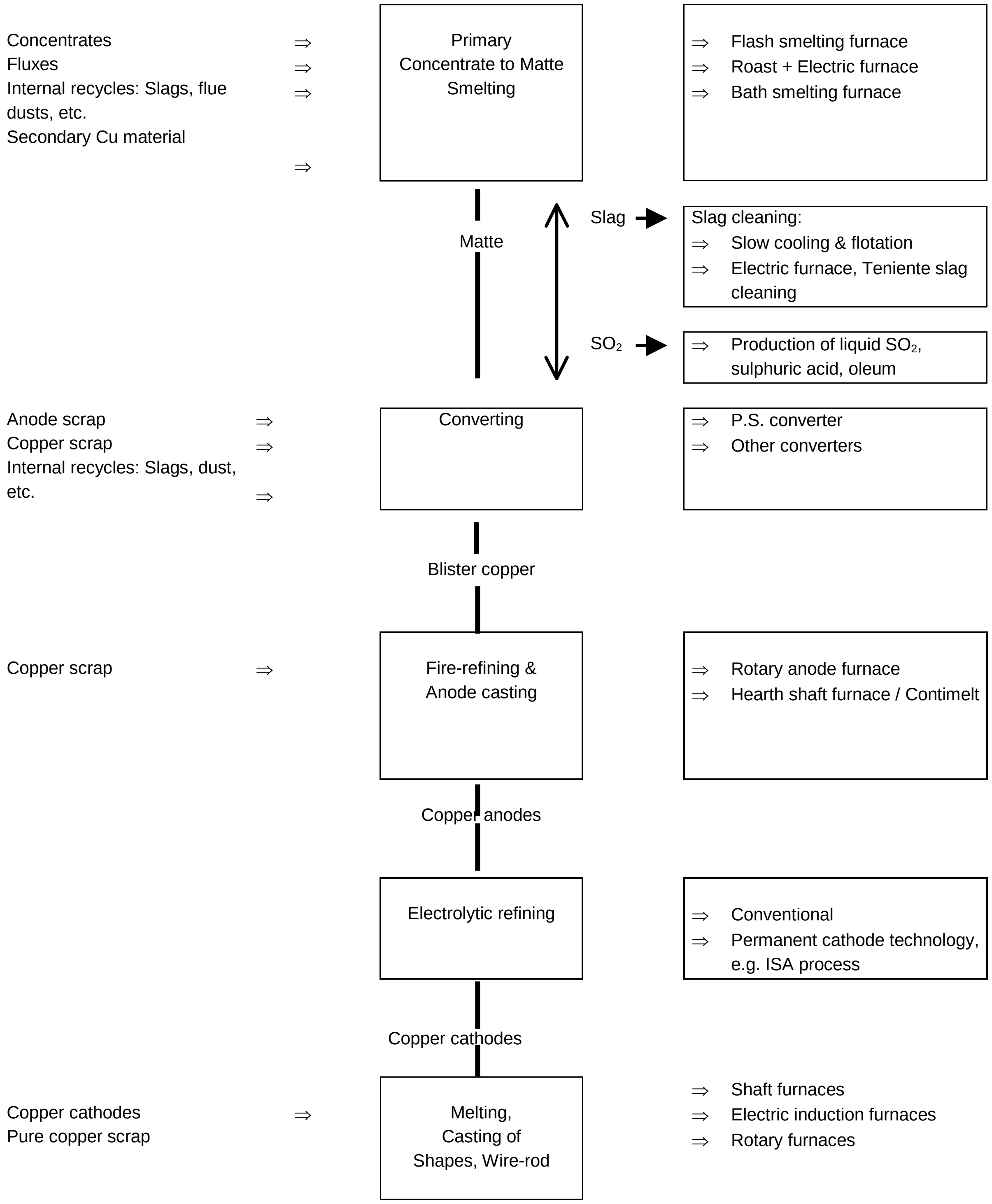


Figure 3.1: Primary Copper Production Route

3.1.1.1.3 Fire refining

This is a further purification step applied to the crude metal (blister copper) produced by the conversion stage. The refining step involves the addition of air and then a reductant (e.g. hydrocarbons etc) to reduce any oxide present [tm 22, EC 1991; tm 26, PARCOM 1996; tm 92 Copper Expert Group 1998].

Fire refining is achieved by first blowing air through the molten metal to oxidise impurities and remove final traces of sulphur producing a small amount of slag. A source of reducing agent, such as natural gas or propane, is then added to reduce any copper oxide formed. Ammonia may also be used as a reductant but has been reported to increase NO_x levels [tm215, Mining Engineering July 1999]. Historically wooden poles or logs were used as the source of reductant (and are still used in a small number of cases) and the process is therefore termed "Poling". Several installations use an afterburner to treat the gases during the poling stage. In primary and some secondary smelters cylindrical rotary furnaces (Anode Furnaces) are used for fire refining. These furnaces are similar to the Peirce-Smith converter and use tuyeres for gas additions. They are charged with molten copper. Some secondary processes use a reverberatory furnace with lances for air additions, they are fed with converter copper and copper scrap. Some reverberatory furnaces are tiltable and are fitted with tuyeres.

The Contimelt system is also used for fire refining when the feed is solid and needs to be melted first. During semis production, fire refining is also sometimes performed. Combinations of hearth shaft furnaces (for batch-wise melting) and rotary furnaces (for batch-wise reduction) are also used. These systems can be applied for primary (blister) and secondary (scrap) materials.

The metal from the anode furnace is then cast into anodes. The most commonly used technique is a casting wheel that comprises a series of anode shaped moulds on the circumference of a rotating table. Molten metal is metered into the moulds to obtain a consistent anode thickness and the wheel rotates taking the anodes through a series of water jets to cool them.

As an alternative to the stop-to-cast mould on a wheel system, copper anodes are also produced continuously using a Hazelett twin belt caster. A copper strip with the desired anode thickness is produced. From the strip, anodes can be obtained by shearing into the traditional anode shape or, according to the "Contilanod" system, by casting anode lugs in special side dam blocs spaced in defined intervals in the caster. The pre-formed anode plates are cut off using a plasma torch or special shears. The advantage of the method is the uniformity of the anodes produced; however, the system requires careful maintenance and the operating costs are comparatively higher.

3.1.1.1.4 Electrolytic refining

An electrolytic cell is used consisting of a cast copper anode and a cathode, placed in an electrolyte containing copper sulphate and sulphuric acid. The cathode is either a thin blank of pure copper (starter sheet) or a stainless steel former sheet – permanent cathode plate (Mount ISA process and Noranda/Kidd Creek system) [tm 22, EC 1991; tm 26, PARCOM 1996; tm92, Copper Expert Group 1998]]. At high current density and low voltage, copper ions are dissolved from the impure anode and pass into solution from where they are deposited onto the cathode. Copper is removed from the anode to the extent that the remaining anode is still mechanically strong enough to prevent a collapse. The remaining anode is then recycled to the production process, usually the converter, to cool the reaction and recover the copper. When using permanent cathode plates the pure copper deposits can be stripped and then like solid copper cathode plates, melted and cast into the required shape.

During electro-refining other metals contained in the anodes are separated, soluble metals like Ni are dissolved in the electrolyte and insoluble metals like the precious metals, Se and Te form an anode slime that settles in the electrolytic cells. Anode slimes are periodically removed from the cells and the valuable metals recovered (see Chapter 6; precious metals).

A portion of the electrolyte is bled from the system. Copper is eliminated by electro-winning or in some plants, a portion is recovered as copper sulphate. Evaporation, crystallisation and further refining recover nickel as nickel sulphate. The following techniques are used for the treatment and elimination of arsenic: - Solvent extraction; Precipitation during the final copper electro-winning; Precipitation from the 'black acid". In some cases copper arsenate is produced and is converted to copper chrome arsenate for use as a wood preservative.

The removal of impurities during electro-refining is targeted to produce a cathode copper with a quality at least equal or better than the "grade A" quality standard of the London Metal Exchange. In the following table an example is shown of the anode composition and the cathode quality achieved. It should be noted that the level of impurities in the anode affects the cathode quality; the impurity level in anodes also depends on the source of the concentrate or secondary material.

Element	**Content in Anode* g/t**	**Content in Cathode g/t**
Silver	600 - 720	9 - 10
Selenium	50 - 510	< 0.5
Tellurium	20 - 130	< 0.5
Arsenic	700 - 760	< 1
Antimony	330 - 700	< 1
Bismuth	60	< 0.5
Lead	990 - 500	< 1
Nickel	1000 - 5000	< 3
Note. *Anode quality depends on raw material contents.		

Table 3.3: Example of impurity removal during electro refining
[tm 124, DFIU Cu 1999]

The current trend is for larger cells with a greater number of electrodes to be used in the tank house and for stainless steel cathode formers to be used [tm 92, Copper Expert Group 1998]. A gain in efficiency is seen when these factors are coupled with good quality control of anodes. Quality control is needed to ensure that anodes are straight, flat, have good electrical contact and have been adequately fire refined. Similarly there is also an improvement in cathode quality using stainless steel blanks as less impurities are mechanically carried over and subsequently incorporated into the cathode. These cathode blanks give an increase in current efficiency to 97% or even more. Modern tank houses use a high degree of automation for cathode and anode changes and the stripping cathode deposits from permanent cathode plates [tm 22, EC 1991; tm 26, PARCOM 1996]. Mechanically prepared copper starter sheets can also be used instead of stainless steel blanks.

3.1.1.1.5 Slag treatment

The slags produced from the primary smelting with high matte grades and converting stages are rich in copper and are subjected to a number of slag treatment processes [tm 92, Copper Expert Group 1998]. One process is the use of an electric furnace for the reaction of slag with carbon in the form of coke breeze or the electrodes themselves and for the settling of copper matte that is formed to produce an inert slag. The electric furnaces can be operated continuously or on a batch basis. Converter slag can also be returned directly to the electric slag-cleaning furnace or to the smelting furnace. Alternatively, flotation processes are also used after the slag has been slow cooled, crushed and milled, the flotation concentrate obtained is a copper rich portion and is returned to the smelter. This method is only used where sufficient space is available and the where the tailings can be adequately treated and disposed of.

Electric furnace treatment of smelting furnace slag and separate handling of converter slag by slow cooling and flotation is also practised. Slags from the slag treatment processes are used for civil engineering projects, road construction, river embankment and similar applications as well as shot blasting, they often have properties that are superior to alternative materials.

Other slags rich in copper like the refining slag are normally re-circulated to a prior process stage, mostly converting, or, in secondary smelters, to the smelting stage.

3.1.1.2 The hydrometallurgical route

This process is usually applied to oxide or mixed oxide/sulphide ores at the mine site where there is sufficient space to form the leaching and treatment areas. The process is particularly useful for ores that are difficult to concentrate by conventional means and which do not contain precious metals [tm 55 & tm 56 Outokumpu 1997; tm 137, Copper Expert Group 1998]. Some proprietary processes are in the development stage and these are reported later under emerging techniques.

The hydrometallurgical route involves the crushing of the ore followed by leaching using sulphuric acid, sometimes in the presence of biological species, using heap, vat or agitation processes [tm 137, Cu Expert Group 1998]. The liquor produced from leaching is then clarified and purified and concentrated by solvent extraction. The generic hydro-metallurgical flow-sheet is shown below.

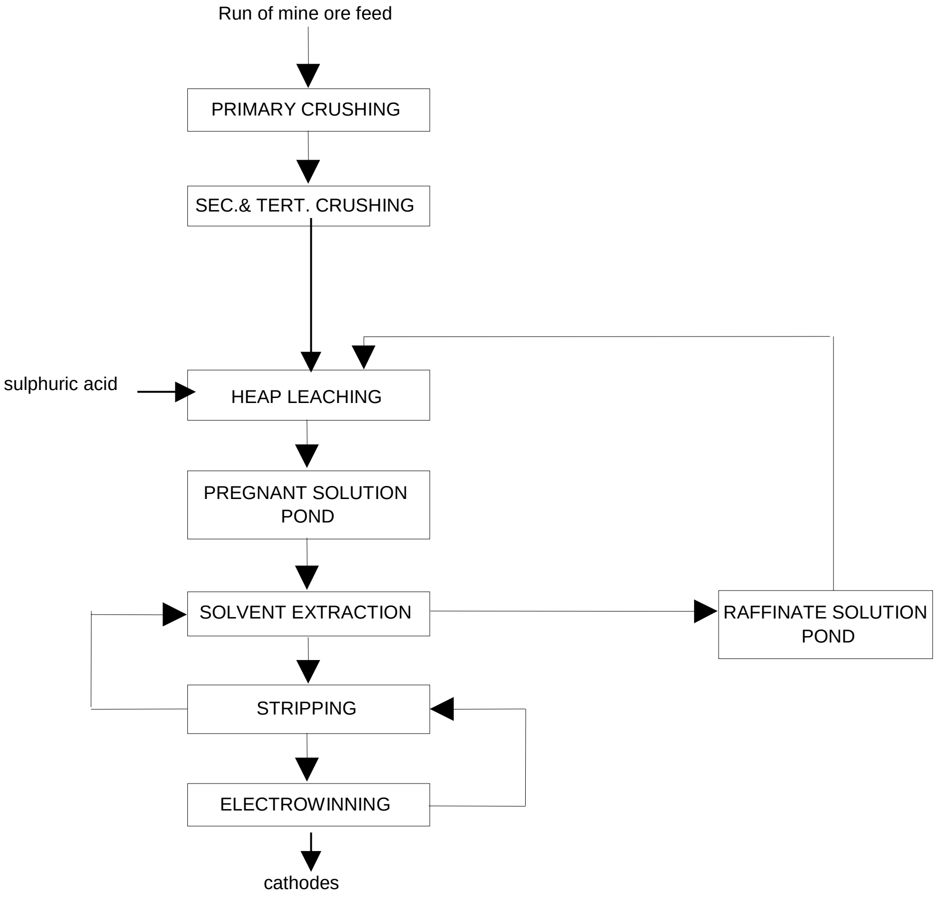


Figure 3.2: Flowsheet of a heap leaching process
[tm 140, Finland Cu 1999].

The copper is then removed by electro-winning. The electro-winning process differs from the electro-refining process in the form of the anode. Electro-winning uses an inert anode such as lead or titanium and the metal ions are removed from the solution and deposited on the cathode in the same manner as electro-refining. Cathodes are then stripped in the same way if permanent cathode blanks are used. The electrolyte is circulated through a series of cells and finally is depleted of copper. Electrolyte is then returned to the solvent extraction circuit. Some electrolyte is normally bled for the control of impurities, which might have been carried over during solvent extraction.

3.1.2 Secondary production

Secondary copper is produced by pyro-metallurgical processes. The process stages used depends on the copper content of the secondary raw material, it's size distribution and the other constituents [tm 92, Cu Expert Group 1998; tm 124, DFIU Cu 1999]. As in primary copper, the various stages are used to remove these constituents and to recover metals as far as possible from the residues that are produced.

Secondary feed material can contain organic materials like coatings, or be oily in nature and installations take this into account by using de-oiling and de-coating methods or by correct design of the furnace and abatement system. The aim is to accommodate the increase in combustion gas volumes, destroy VOCs and to minimise the formation of dioxins or destroy them. The type of pre-treatment applied or the furnace used depends on the presence of organic materials, type of feed i.e. copper content and other metals contained and whether oxidic or metallic.

If a furnace such as a converter is used to smelt impure brass scrap to separate the metals contained in it the alloying elements are fumed from the copper to produce black copper and a zinc rich filter dust.

A wide range of secondary raw materials are used and some of them are described in the following table.

Type of material	Cu-content [wt-%]	Sources
Mixed copper sludges	2 – 25	Electroplating
Computer scrap	15 – 20	Electronics industry
Copper mono-sludges	2 – 40	Electroplating
Copper-iron material (lumpy or comminuted) from armatures, stators, rotors etc.	10 – 20	Electrical industry
Brass drosses, copper-containing ashes and slags	10 – 40	Foundries, semi-finished product plants
Red brass drosses, copper-containing ashes and slags	10 – 40	Foundries, semi-finished product plants
Shredder material	30 – 80	Shredder plants
Copper-brass radiators	60 – 65	Cars
Mixed red brass scrap	70 – 85	Water meters, gear wheels, valves, taps, machine components, bearing boxes, propellers, fittings
Light copper scrap	88 – 92	Copper sheets, eaves, gutters, water boilers, heaters
Heavy copper scrap	90 – 98	Sheets, copper punchings, slide rails, wires, pipes
Mixed copper scrap	90 – 95	Light and heavy copper scrap
Copper granules	90 – 98	From cable cominution
Pure No. 1 scrap	99	Semi-finished products, wire, cuttings, strip

Table 3.4: Secondary raw materials for copper production
[tm 124, DFIU Cu 1999]

The stages used for secondary copper production are generally similar to those for primary production but the raw material is usually oxidic or metallic and process conditions are therefore varied. Smelting of secondary raw materials therefore uses reducing conditions.

3.1.2.1 Secondary smelting stage

A number of furnaces such as the Blast, Mini Smelter, Top Blown Rotary Furnaces (TBRC), Sealed Submerged Arc Electric Furnace, ISA Smelt, Reverberatory, and Rotary are used for low and medium grade material [tm 27, HMIP Cu 1993; tm 92, Cu Expert Group 1998; tm 124, DFIU Cu 1999]. The type of furnace and the process steps used depends on the copper content of the secondary raw material, it's size and other constituents. The smelting and refining of secondary copper is therefore complex and the type of secondary material, which can be processed is dependent on the particular facilities and furnaces available [tm 92, Copper Expert Group 1998]. Details of furnaces are given in section 2.

Iron (in the form of irony copper, normal iron scrap, etc.), carbon (in the form of coke or natural gas) and fluxing agents are added to reduce metal oxides if required and the processes are operated to suit the feed material. The fume from the furnaces contains volatile metals and metal oxides such as those from zinc, lead and tin, which can be recovered as refined metal, alloy or oxide and also contains dust, sulphur dioxide, dioxins and VOCs, depending on the raw materials.

The Mini-Smelter is also used for secondary copper production using scrap that contains iron and tin. In this application the iron is the reductant in the fist stage to produce metallic copper and then oxygen is blown into the melt to oxidise iron and the other metals (Pb, Sn) present which are recovered in the slag. The oxidation of the iron content provides the heat to drive the process.

3.1.2.2 Converting, fire refining, slag treatment and electro-refining, processing of pure alloy scrap

Converting and refining furnaces are very similar to those used for primary production and the slag treatment systems and electro-refining processes are the same. The main difference is that converters used for secondary production treat metal and not matte. They use coke as fuel for melting and to make up for process heat deficits while in primary converters the matte provides the necessary process heat [tm 92, Copper Expert Group 1998]. Secondary converters also oxidise and slag minor elements like iron and separate other metals like zinc or tin by volatilisation. They produce a converter copper in a quality that suits fire-refining. The heat of reaction when air is blown into the converter is used to volatilise metallic components, slagging agents are used to remove iron and some lead. Fire refining furnaces are used also to melt higher grade scrap. The comments made about potential fugitive emissions also applies to the secondary processes.

The electro-refining slimes and spent solutions are also sources of precious metals and other metals such as nickel. These are recovered in the same manner as those from primary production.

Copper alloys such as bronzes and brasses are also used as secondary raw materials in a number of processes. If impure or mixed with different other alloys they are processed in the secondary smelting and refining circuits as described above.

The pure alloy is used directly for semis fabrication. Induction furnaces are used to melt the clean material followed by casting into shapes suited for the further fabrication step. Charge analysis and control is practised to produce the desired alloy without major additions of virgin metal. Zinc oxide can be collected from the filter dust.

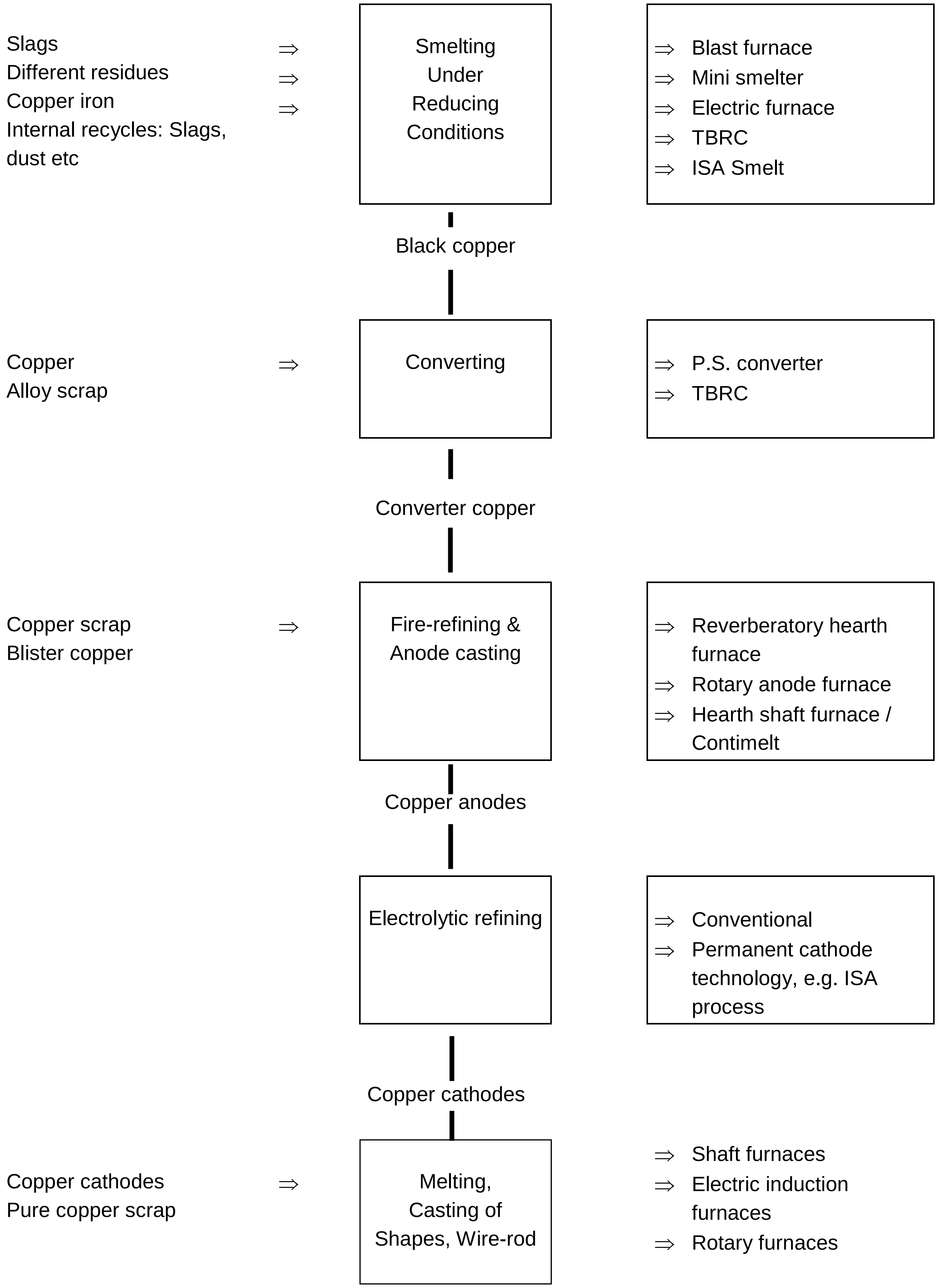


Figure 3.3: Generic flow sheet for secondary copper production

The pure alloy is used directly for semis fabrication. Induction furnaces are used to melt the clean material followed by casting into shapes suited for the further fabrication step. Charge analysis and control is practised to produce the desired alloy without major additions of virgin metal. Zinc oxide can be collected from the filter dust.

Depending of the type of feed materials in some plants a flue dust is produced in the first stage that is rich in zinc and lead, for example during blast furnace smelting of lower grade material. These dusts contain up to 65% combined zinc and lead and are a feed material very suited to be processed in the Imperial Smelting Furnace for the production of lead and zinc.

3.1.3 Tin

Tin is recovered from the residues produced during some of the secondary copper refining processes, from the de-tinning of coated steel cans and from ores. At the time of writing there is no production of tin in EU directly from ores.

At one secondary copper smelter, a second reduction stage is used [tm 92, Cu Expert Group 1998]. Lead and tin are reduced with scrap steel or tin cans in a TBRC. Lead/tin scrap, slag and residues are added and a tin/lead alloy is produced. The alloy passes to a shaking ladle to remove residual copper, nickel and silicon and the decopperised alloy is then treated in a three stage vacuum distillation system to separate tin and lead. The tin is refined by crystallisation before the second vacuum distillation stage.

Another method practised in other copper smelters uses the flue dust from the secondary copper converter (sometimes also from the blast furnace) as feed material. Under reducing conditions zinc is volatilised and recovered as oxide while lead and tin are produced in the form of an alloy.

Steel scrap is de-tinned by either electrolytic or chemical leaching processes using caustic soda and sodium nitrite [tm 9, HMIP-Sn 1993]. In the latter case, ammonia is released (0.048 kg per kg of tin). Tin is dissolved and then recovered by electrolysis, the tin is removed from the cathodes by dipping in a molten bath of tin. Ingots or tin powder are produced and these are used to produce a range of alloys and coating materials.

Tin is melted in kettles similar to those used for lead and alloys are produced. Scrap tin is also recovered in the melting processes. The most common range of alloys is known as solders and they use lead as the alloying material. Other melting furnaces are used but temperature control is not as easy.

Tin is refined using a number of processes. Electrolytic refining using steel cathodes is carried out and a pyro-metallurgical refining process can also carried out in a similar manner to lead refining. In the case of tin refining, iron is removed by liquation, copper is removed by the addition of sulphur and arsenic or antimony are removed by the addition of aluminium or sodium.

3.1.4 Wire-rod production

Wire-rod is manufactured from high purity electrolytically refined copper cathodes thus ensuring that trace impurities, which may affect conductivity, annealability and hot shortness, are minimised. Attention is paid to controlling the furnace conditions to minimise oxygen absorption with the metal. The following processes are used [tm 117, Copper Expert Group 1998]:

3.1.4.1 Southwire process

Shaft furnaces are used for melting copper cathodes and other pure copper scrap material. Melting rates of up to about 60 t/h are in use.

The feed materials are melted by natural gas, propane or similar fired burners arranged in rows around the furnace shell. The fuel is burnt under closely controlled combustion conditions to maintain a slightly reducing atmosphere (less than 0.5 to 1.5% of CO or H_2) in the areas where the gases are in contact with the copper to minimise the oxygen content of the copper. This is achieved by independent control of the fuel/air ratio for each burner with monitoring of the CO or H_2 content of the combustion gases from each burner in turn.

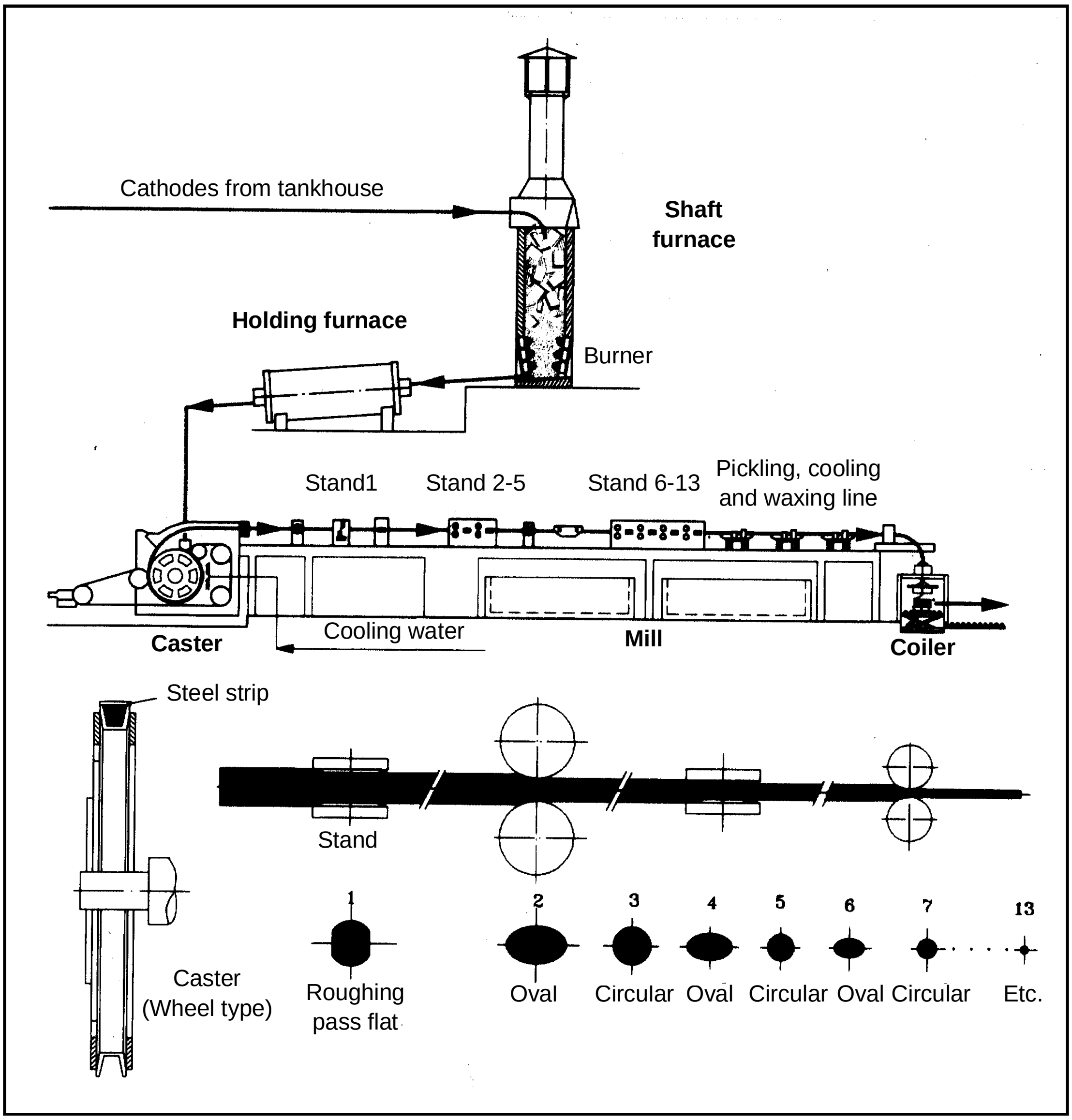


Figure 3.4: Example of the Southwire process
[tm 124, DFIU Cu 1999]

Gases from the furnace are cooled and dust is removed using fabric filters. After-burning can also be used to destroy CO if the concentration is high.

Molten copper is discharged from the base of the shaft furnace and flows to a cylindrical holding furnace for temperature adjustment and balancing of the metal and for metallurgical treatment. Natural gas fired burners are provided to maintain the temperature of the molten cooper and a reducing atmosphere in the launders. The holding furnace, which is also natural gas or similar fuel fired, serves as a reservoir to provide a constant flow of metal to the casting process and, if required, can be used to superheat the metal.

Molten copper flows from the holding furnace via a tundish equipped with flow control to the casting wheel. A water-cooled, steel band encloses over half of the circumference of the wheel, forming the casting cavity in which the molten copper solidifies to form a trapezoidal cast bar ranging between 5000 and 8300 mm². Acetylene, burnt with air is used to produce a soot dressing for the casting wheel and steel band. After being levelled and shaved, the cast bar is fed by pinch rolls to a rolling mill consisting of a roughing section and one finishing section which reduces the bar to its final diameter. A mineral oil emulsion or synthetic solution in water is used as a rolling fluid.

3.1.4.2 Contirod process

A shaft furnace as described above is used to melt copper. Molten copper from the furnace flows via a launder equipped with siphons into a rotating, gas heated holding furnace. The copper then flows to the pouring funnel, which automatically controls the feeding rates to the caster [tm 117, Copper Expert Group 1998].

The twin belt Hazelett casting machine is used [tm 124, DFIU Cu 1999]. The two belts are cooled by a continuous film of water that moves at high speed along the length of their surface. The side blocks are automatically cooled in a specially designed cooling area located on the return strand of the loop. Depending on plant size, cast bar area can range between 5000 mm^2 and 9100 mm^2 and production capacities between 25 and 50 tonnes per hour. The rectangular bar is cooled, the four corners are milled to remove any flash and then enters a rolling mill comprising alternative horizontal and vertical passes to produce a final product. A mineral oil emulsion or synthetic solution in water is used as a rolling fluid.

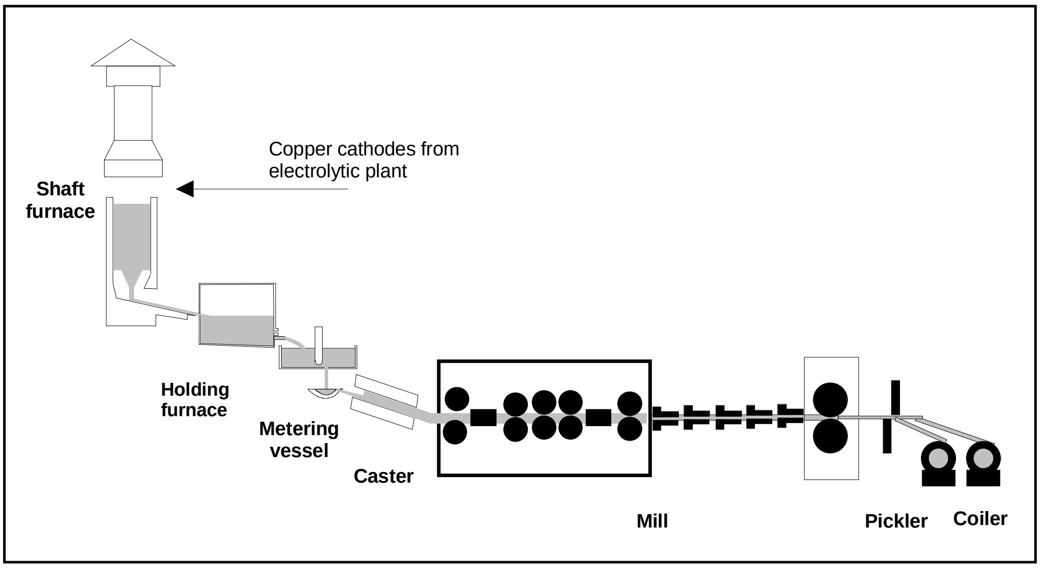


Figure 3.5: Example of the Contirod process
[tm 124, DFIU Cu 1999]

3.1.4.3 Properzi and Secor processes

The continuous Properzi and Secor processes are similar to the Southwire concept with variations in casting geometry [tm 117, Copper Expert Group 1998]. The features described for the Southwire process are also valid for these two copper wire-rod fabrication systems.

3.1.4.4 Upcast process

Copper is melted in a channel induction furnace. The melt is transferred in batches into an induction holding furnace. For small production capacities a single combined melting-holding furnace may be sufficient [tm 117, Copper Expert Group 1998].

The Upcast withdrawal machine is located above the holding furnace. Water cooled graphite dies are submerged a certain depth into the melt and the molten copper runs continuously into the dies where it solidifies and is drawn up to the pinch rollers. The solidified wire rod is pulled upward by the pinch rollers.

3.1.4.5 Dip Forming process

The preheated feed material is discharged into a channel induction-melting furnace. Copper passes to the holding furnace and crucible that is attached to the holding furnace. A mother rod, 12.5mm diameter, is drawn through an inlet die at the base of the crucible. Drawing the core wire through the metal pool and controlling the final diameter through the upper die increases the diameter. The cast rod is directed via dancers to a three-stand rolling mill producing 8.0mm and 12.5mm rod [tm 117, Copper Expert Group 1998].

3.1.5 Production of semi finished products of copper and copper alloys

Copper and copper alloys are melted continuously or in batches and cast for the production of shapes suited to the further fabrication step. The cast products are precursors for a variety of materials such as sheets, strips, sections, bars, rods, wires and tubes. Generally the following routes are taken [tm 117, Copper Expert Group 1998].

1. Billets are mostly made from copper and copper alloys for the production of tubes or sections and rods.
2. Slabs and cakes are cast from copper and copper alloys for the production of sheets or strips.
3. Special processes are applied for specific products from copper and copper alloys: Upcast process for wires and tubes, horizontal continuous casting for strip and sections, vertical strip casting and roll process for fabrication of copper tubes.

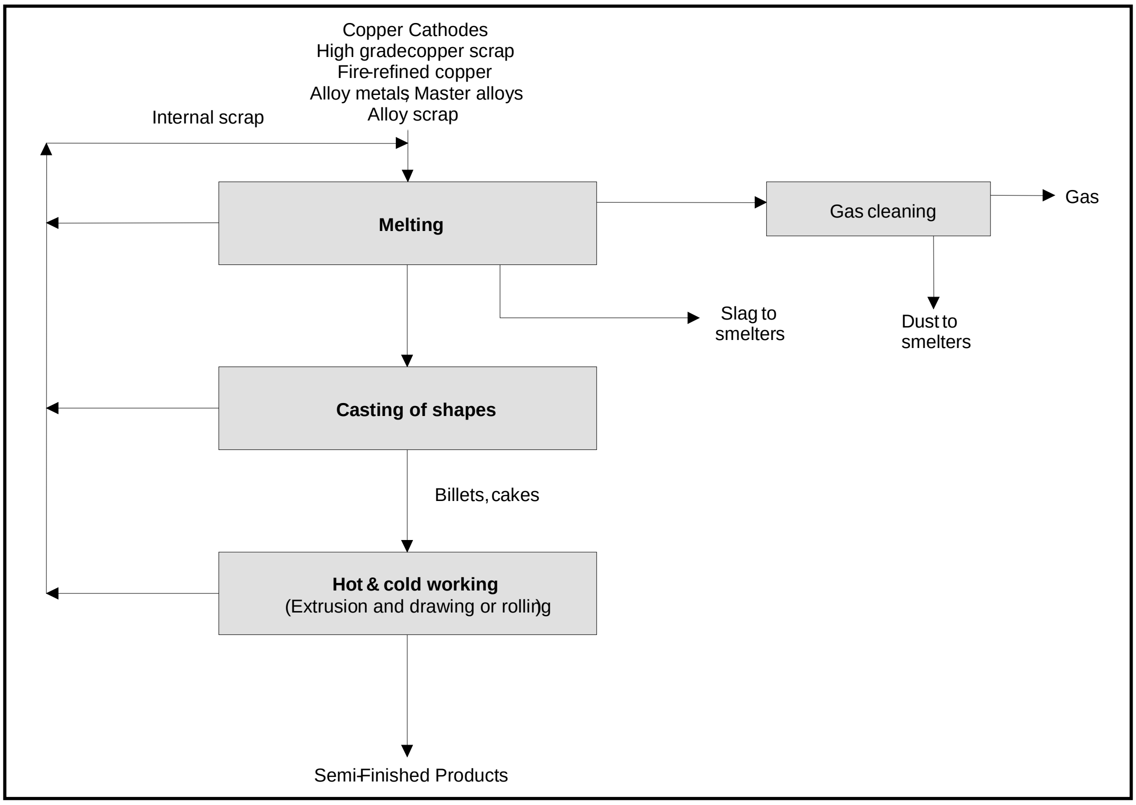


Figure 3.6: General flow-sheet of semi-finished product fabrication
[tm 124, DFIU Cu 1999]

3.1.5.1 Melting processes

Copper or copper alloys can be melted in batches in an electric or induction furnace. When high melting rates are required copper is also melted continuously in a shaft furnace. Crucible or reverberatory furnaces are also used for melting and fire refining copper. The fume collection and abatement systems are chosen according to the raw material and the degree of contamination present. The gas collected from electric furnaces is normally cleaned in cyclones followed by fabric filters. For gas fired shaft furnaces the control of the burners is a critical factor to minimise the CO content of the gases emitted. An afterburner followed by heat recovery systems are in use if the CO content is high enough (e.g.> 5% CO); fabric filters are also used for de-dusting in shaft furnaces.

Copper cathode and copper and alloy scrap is used as the raw material and is normally stored in open bays so that the different alloys can be blended to produce the final alloy. This pre-blending is an important factor to reduce the time taken in preparing the melt, which minimises the energy used and reduces the reliance on expensive Master Alloys. With induction furnaces scrap is cut into small sizes to improve melting efficiency and allow easy deployment of hoods etc.

Raw materials are also brasses or copper turnings and borings and in this case are coated with lubricants. Care is taken to prevent oil leaking from the storage area and contaminating ground and surface water. Similarly swarf dryers or other furnaces and solvent or aqueous de-oiling methods are used to remove lubricants and other organic contamination.

When brasses or bronzes are melted, zinc is fumed from the furnace, good control of the temperature can minimise this. Fume is collected in the gas extraction system and removed in a fabric filter. The zinc oxide is normally recovered. A degree of fire refining is also carried out and the resulting fumes are taken into account in the design of the fume collection and abatement systems.

3.1.5.2 Casting

Normally molten metal from the furnace or holding section can be cast continuously or in batches [tm 117, Cu Expert Group 1998]. Continuous casting uses either vertical or horizontal modes but discontinuous casting normally uses the vertical mode. Upcast techniques are also used. Billets and cakes/slabs are produced and are processed further.

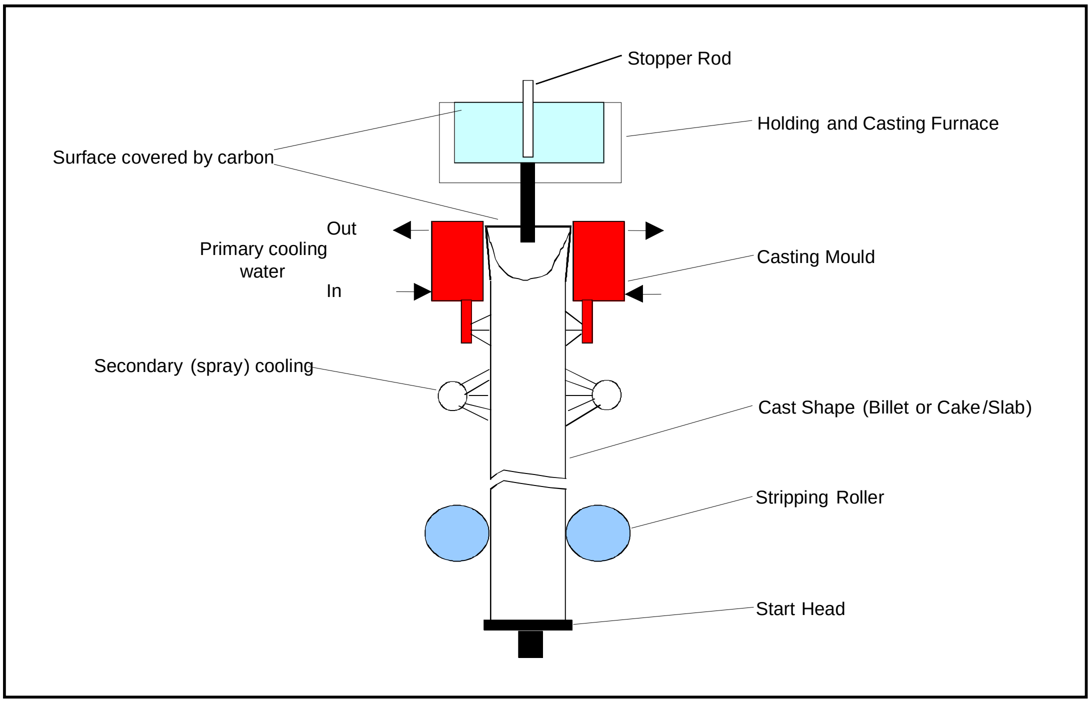


Figure 3.7: Principle of continuous or semi-continuous casting [tm 124, DFIU Cu 1999]

In the case of the production of billets, slabs or cakes, metal is melted and passes via a holding furnace into a vertical or horizontal billet caster. Sections of billets are sawn off for further fabrication.

Special processes are applied for specific products from copper and copper alloys: Upcast process for wires and tubes, horizontal continuous casting for strip and sections, vertical strip casting and roll process for fabrication of copper tubes.

3.1.5.3 Fabrication of tubes, sections and rod

Billets of copper or copper alloy are preheated and extruded and drawn into tubes with a variety of diameters and thickness in a number of “passes”. The drawing machines use a variety of oils and soaps as lubricant that contaminates the tubes and off cuts. The products are normally annealed and degreased before transport and the off cuts are de-oiled in a furnace or other de-greasing process before being returned to the furnace for melting.

Copper tubes may be also produced utilising an extrusion press with piercer in which billet sections are extruded to tube shell pieces; the tube shell pieces are then rolled in a breakdown roller (Pilger mill) and finally drawn to size in drawing blocks. The oil utilised (in small quantities) for the drawing operations is neutralised in in-line degreasing/pickling systems often connected with the annealing section.

Products are annealed in a variety of furnaces under reducing conditions using as protection gas “exogas” or hydrogen/nitrogen mixtures.

3.1.5.4 Fabrication of sheets and strips

Slabs/cakes of copper or copper alloy are the start material for the fabrication of sheets and strips. The material is preheated in gas or oil fired furnaces, hot and cold rolled and then sent to the finishing operation, which includes re-rolling, cutting to length and width. Surface milling, annealing, pickling, washing and drying are required as intermediate steps to produce high quality strips and sheets [tm 117, Copper Expert Group 1998].

Hot rolling is usually done with a dual rolling mill equipped with benches up to 200 m and a final coiling device. The cooling water for the rolls has small amounts of lubricant added for improving the attachment to the steel rolls. The vapour generated is vented and the vent gas is de-misted prior to release to atmosphere.

Further cold rolling operations are then performed. Cold rolling results in a hardened metal. In most cases the coil is annealed prior to cold rolling. Annealing is done under reducing conditions to avoid oxidation. A protection gas “exogas” or nitrogen/hydrogen mixtures are used. Exogas is produced at site from natural gas in a special reactor, which is indirectly fired. N_2 and H_2 are purchased and stored at site in special tanks. The N_2/H_2 protection gas mixtures are produced from the storage tanks by mixing the components in the ratio required. For annealing before cold rolling bell type furnaces are used with electric heating or indirectly fired by natural gas or fuel oil. Tower type furnaces are applied for intermediate annealing of pre-rolled coils.

The sheet thickness is further reduced by stepwise cold rolling operations on different reversing mills. For cold rolling different types of mills called Duo, Quarto, Sexto, Sendzimir (12 rolls) are used. Rolling mill designs as single-stand which are combined to an in-line multi-stand rolling mill are also applied. It depends on the thickness of the sheet on the coils and on the finishing status the coil has already been reached which combination of the different types is applied.

During cold rolling an emulsion or oil is used for roll protection. Therefore, the roll stands are vented and the ventilation gases are cleaned by mechanical filters, wet electrostatic precipitators or scrubbing. The emulsion and the oil is cleaned from metal and cracked oil particles are removed by paper or textile band filters.

Hot rolling	
Type of mill	Mainly Duo
Dimensions start	250 – 130 mm thickness, 450 – 1000 mm width
Final dimensions	15 – 12 mm thickness, 450 – 1000 mm width
Temperature	750 – 800 °C
Rolling force	~ 10 - 12 kN/mm sheet width
Surface milling	0.3 – 0.7 mm cutting of both surfaces
1st Cold rolling	
Type of mill	Mainly Quarto
Rolling force	~ 15 – 20 kN/mm sheet width
Dimension reduction and rolling speed	Reduction 15 mm to 4 mm thickness in multiple passes, speed 100 - 200 m/min
Conversion ratio	70 - 80%
Annealing*) (re-crystallisation)	
Temperature	550 – 600 °C
2nd and final rolling	
Type of mill	Mainly Quarto, alternatively, depending on sheet thickness, Sexto or stands with 20 rolls are used
Rolling force	~ 2 – 10 kN/mm sheet width, depending of type of mill used
Rolling speed	Reduction 4 to 1 mm: 300 – 500 m/min, multiple passes Reduction 1 to 0.1 mm: 500 - 1000 m/min, multiple passes
Cutting of sheets to strips	
Type of equipment	Longitudinal strip cutting machine
Note. *Annealing is required after every conversion ratio of more than 70 - 80%. Annealing temperatures selected depending of material properties to be achieved.	

Table 3.5: Typical data for a process to produce brass strip
[tm 124, DFIU Cu 1999]

3.1.6 Copper and copper alloy ingots

Ingots of copper or its alloys are produced for the foundry industry using a fixed mould casting process. A wide variety of alloys are produced with other metals such as Ni, Sn, Zn Al etc.

The production of ingots requires the production of an accurate alloy composition. This is achieved at the raw material reception and storage stage by segregation and sorting. Old scrap is normally stored in open bays so that the different alloys can be blended to produce the final alloy. Pre-blending is an important factor to reduce the time taken in preparing the melt, which minimises the energy used and reduces the reliance on expensive Master Alloys. Copper or copper alloys can be melted in batches in rotary or induction furnaces. Rotary furnaces are normally used for dirtier scrap, oxy-fuel burners are used frequently. Fluxes can be added to separate unwanted components in particular iron and the slag is tapped separately from the metal. The yield of metal ranges from 70 to 97% but depends on the raw materials used [tm 106, Farrell 1998].

The fume collection and abatement systems are chosen according to the raw material and the degree of contamination present. Access to an induction furnace for charging and tapping means that a movable hooding system is used. The hoods are robust so that they can withstand some mechanical impact. The gas collected from induction furnaces is normally cleaned in cyclones followed by fabric filters. An afterburner followed by a heat recovery system can be used for cases where there is organic contamination, alternatively the furnace combustion control system should be able to accommodate the combustion of contaminants.

When brasses or bronzes are melted, zinc is fumed from the furnace, good control of the furnace temperature can minimise this. Fume is collected in the gas extraction system and is usually removed in a fabric filter. The zinc oxide is normally recovered. A degree of fire refining is also carried out to adjust alloy composition and the resulting fumes are taken into account in the design of the fume collection and abatement systems.

The furnace melt is sampled and analysed and final alloy adjustments made. Metal is then tapped in to covered launders that feed a chain of ingot moulds. The moulds are normally treated with a mineral to prevent sticking and oil fume is produced. This can be collected and burnt.

Cooled ingots are stacked, bound and stored in the open in the form of pallets.

3.1.6.1 Master alloys

The furnace charge is normally pre-adjusted to suit the alloy to be used but molten metal can be transferred to a ladle or holding furnace so that alloy composition can be finely adjusted before casting. Master alloys such as CuP, CuNi, CuZnPb, CuBe etc are used for this purpose. These master alloys are produced in similar furnaces to those described above, the nature of fume and dust from the production of master alloys influences the process control, collection and abatement systems that used. More stringent operating and abatement systems are particularly appropriate when extremely hazardous materials such as beryllium are used or when reactive materials such as phosphorus are added to produce an alloy. For example phosphor copper master alloy is made in the following way: -

Two furnaces (induction furnaces are commonly used) are operated in series. Copper is melted in the first furnace and transferred to the second where molten phosphorus is injected by a lance to form the alloy. The rate of injection is controlled to minimise phosphorous pentoxide fume particularly during the final stages when the metal is approaching saturation (< 14%P). The phosphor copper is then tapped into moulds. Phosphorous pentoxide fumes continue to be emitted as the alloy cools if the phosphorous content is too high.

Phosphorous pentoxide is very hygroscopic and as a consequence the fume cannot be filtered using a conventional fabric filter as the fume will absorb moisture and coat the bags with phosphoric acid. Conventional wet scrubbing has a limited effect as the fine fume forms a fine mist and fails to contact the scrubbing medium. Effective reduction of the concentration of phosphorus compounds in the gas stream can be achieved by using high-energy venturi scrubbers or fibrous mat filters. In theory a weak acid could be produced for further processing but this is difficult in practice.

3.1.7 Pickling operations

Wire, tube, strip and some other materials are pickled to produce a bright finish before packing or, in the case of copper wire, to remove oxide from the surface prior to wire drawing. Sulphuric acid solutions are used and sometimes a mixture of dilute sulphuric and nitric acids are used. In the latter case nitric fumes can be emitted if higher strength acids are used.

3.1.7.1 Non acid pickling of copper rod

This process operates in a sealed circuit. Rod can be pickled in an in-line system that consists of a compartmentalised horizontal steel pipe. A 2.5% to 3.5% solution of isopropanol alcohol (IPA) in water is used. The process of converting the cuprous oxide scale with alcohol to form copper (partly left on the rod), is known as the Burns process [tm 117, Cu Expert Group 1998]. In copper wire rod fabrication normal practice is to recycle the solution to pickling, after copper sludge removal by settling or filtration; the IPA concentration is adjusted as required.

After pickling, the rod is dried using compressed air. Then it is given a coating of wax, applied as a fine spray of a 4% wax emulsion, which prevents oxidation of the surface of the rod. The rod is down coiled on to wooden pallets and compacted strapped and wrapped in plastic sheet.

3.1.7.2 Acid pickling of copper rod and semis of copper and copper alloys

a) Copper wire rod

Acid pickling of copper wire-rod uses a compartmentalised horizontal stainless steel pipe [tm 117, Cu Expert Group 1998]. In a first stage the rod is pickled with diluted sulphuric acid; then the residual acid is washed in several stages of from the rod surface by water sprays followed by drying using compressed air and coating by wax.

Alternatively, after partial cooling in a long water-filled tube, the rod is formed into spirals corresponding to the diameter of the coil. These spirals are spread onto a roller table where the temperature is reduced to 20 ºC by water sprinklers. An acid-resistance alloy conveyor carries these spirals into the pickling tanks where the rod is pickled with a 20% sulphuric acid solution. The acid lay pickling system ensures a perfect removal of all oxides form the rod surface. The loops are then washed with rinsing water and finally protected by a wax solution.

Electro-winning, to recover the copper dissolved by the pickling acid is used or the wash solution also may be transferred as make-up to a tank-house at the same site or treated by ion exchange.

b) Semis of copper and copper alloys

Surface pickling of sheets and strips is usually performed with sulphuric acid (8 - 10%) but for some special alloys, mixtures of sulphuric and nitric acids are used in continuous lines or automatic systems. Gas cleaning is used to remove nitric acid fumes. The acid is changed from time to time in order to ensure that surface quality is not affected.

Spent acid is sent for treatment and recovery of metal in internal or external treatment plants. The pickling systems are vented for worker protection. The products are rinsed and the rinse water is sent for treatment, sludges are recycled if possible. For surface degreasing of rolled products, detergents containing water are used. The spent water is cleaned by ultra filtration.

3.2 Present Emission and Consumption Levels

The main environmental issues of the refined copper industry are air and water pollution [tm 28, WRC 1993; tm 210, Copper Expert Group 1999]. The facilities generally have their own wastewater treatment facilities and wastewater recycling is usually practised. Most potential wastes are reused.

Some local aspects, like noise, are relevant to the industry.

Due to the hazardous nature of some solid and liquid waste streams, there is also a significant risk for soil contamination unless they are stored and handled correctly.

Fugitive emissions can be highly significant. Measurements have been carried out at one major copper smelter producing primary and secondary copper. The results clearly show that fugitive emissions predominate even after improvements were made to secondary fume capture systems [tm 161, Petersen 1999]. In this example the dust loads that were measured are as follows.

	Dust emission kg/a	
	Before additional secondary gas collection (1992)	**After additional secondary gas collection (1996)***
Anode production t/a	220000	325000
Fugitive emissions		
Total Smelter	66490	32200
Smelter roofline	56160	17020
Primary smelter stack emissions		
Smelter/acid plant	7990	7600
Stack-secondary hoods	2547	2116
Note. * Emissions after an investment of 10 million Euros to give an improved fugitive gas capture and treatment system. Additional energy = 13.6 GWh/a		

Table 3.6: Comparison of abated and fugitive dust loads at a primary copper smelter [tm 161, Petersen 1999]

3.2.1 Energy usage in copper production

Copper production requires energy in most stages, the energy use of the electrolytic process is most significant [tm 26, PARCOM 1996]. The production energy (nett) requirement for a number of processes using copper concentrate is in the range 14 – 20 GJ/t of copper cathode [tm 210, Cu Expert Group 1999]. The exact figure depends mainly on the concentrate (% S and Fe), but also on the smelting unit used, the degree of oxygen enrichment and the collection and use of process heat. Comparative data based solely on the type of smelter are therefore liable to inaccuracies. The utilisation of the energy content of the concentrate is more important and smelters that achieve autogenic operation have lower energy use.

The energy consumed by the electro-refining stage of copper production is reported to be 300 - 400 kWh per tonne of copper [tm 137, Cu Expert Group 1998]. The type of blank cathode used (stainless steel or copper) mainly influences the efficiency of tank house [tm 92, Cu Expert Group 1998] and this can range from 92 to 97% in terms of current efficiency.

3.2.2 Emissions and consumption data

The main sources of emissions and consumption for the production of copper are as follows: -

3.2.2.1 Primary copper input and output

The input and output data for a primary smelter depends on the copper content of the concentrate, the concentration of other metals (As, Se, Hg, Ag, Au etc) and the use of copper scrap or other copper containing material in the various parts of the process.

The following diagram illustrates the inputs and potential outputs from a typical process to produce primary copper.

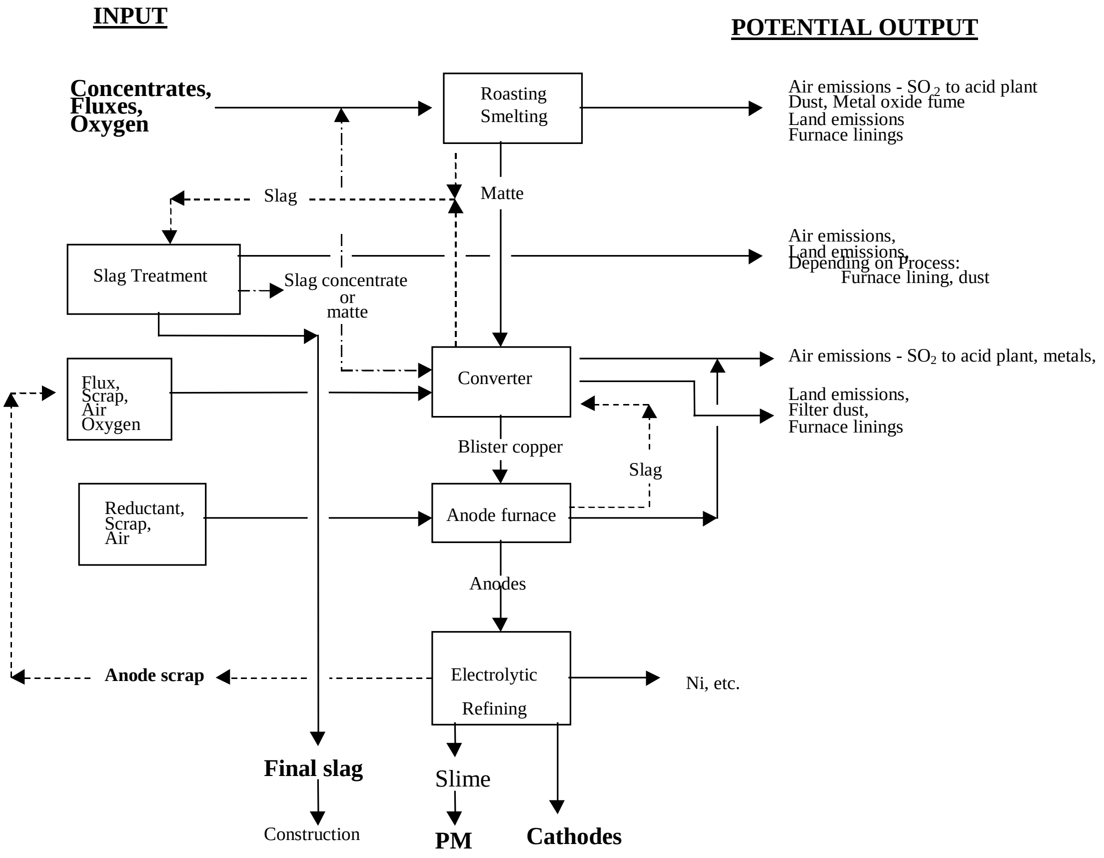


Figure 3.8: Generic input and output diagram for primary copper

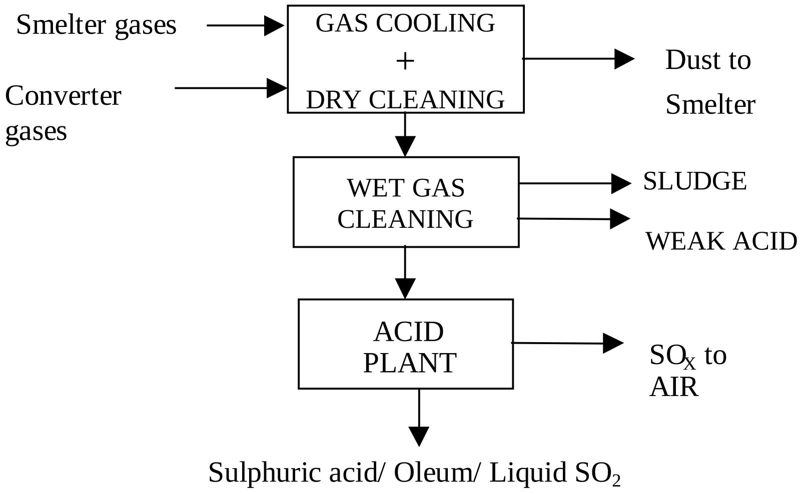


Figure 3.9: Treatment of smelter and converter gases

Some primary copper smelters are integrated with secondary smelting facilities or with the production of lead or zinc oxide dust from mixed concentrates etc. The input and output data is therefore very difficult to compare. Values for a complex process are given below. It should be noted that the main influence on the input and output data is the copper content of the concentrate or other raw material and so there can be variations of the data and comparisons are not significant. The recovery of copper during smelting and refining is more meaningful and is greater than 96%.

Input materials	Quantity [t/a]	Products	Quantity [t/a]
Copper concentrates	690000	Copper cathode	370000
Copper scrap	95000	Copper salts	6500
Shredded material from electronic scraps	1200	Nickel sulphate	1800
External intermediate products	86000	Precious metals	150
		Refined lead	9000
		Sulphuric acid	660000
		Slags	410000

Table 3.7: Example input and output data for a primary copper smelter/refinery [tm 124, DFIU Cu 1999]

3.2.2.2 Secondary copper input and output

As reported above, secondary raw material can be fed into various parts of the secondary processes depending on the purity, content of other metals and degree of surface contamination. The degree of organic contamination affects the potential emissions and in several process stages afterburners are used to destroy organic components such as dioxins depending on the degree of organic contamination present. The following diagram shows a generic input and output diagram for secondary copper.

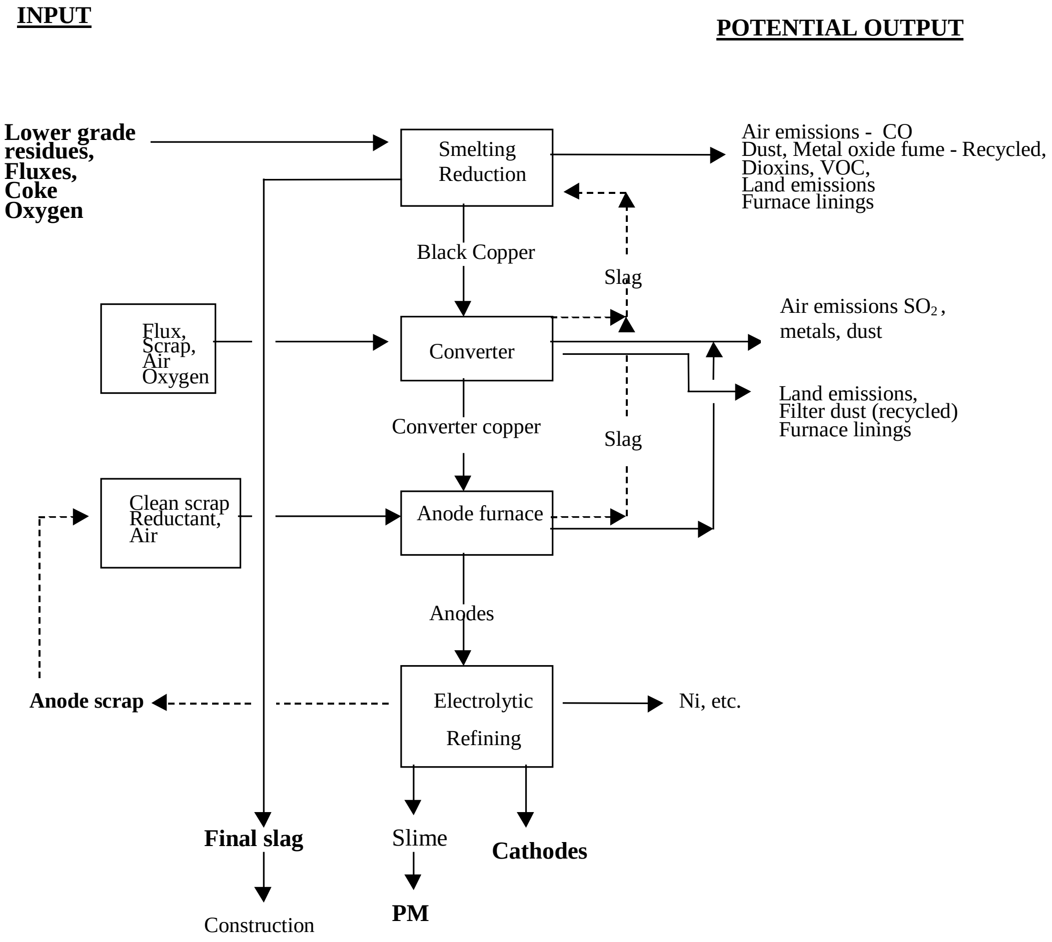


Figure 3.10: Generic input-output diagram for secondary copper smelting

Many residues are recycled within the process and to other associated processes. Producers of non-ferrous metals, for example lead, zinc and tin, use many of the residues as raw materials for their processes. Several sites have incorporated on-site processes to recover other metals from these residues.

The following diagram gives an example of how the production of copper and other metals from secondary raw materials can be a complex, integrated process. The accompanying table also shows the input and output quantities associated with this particular example.

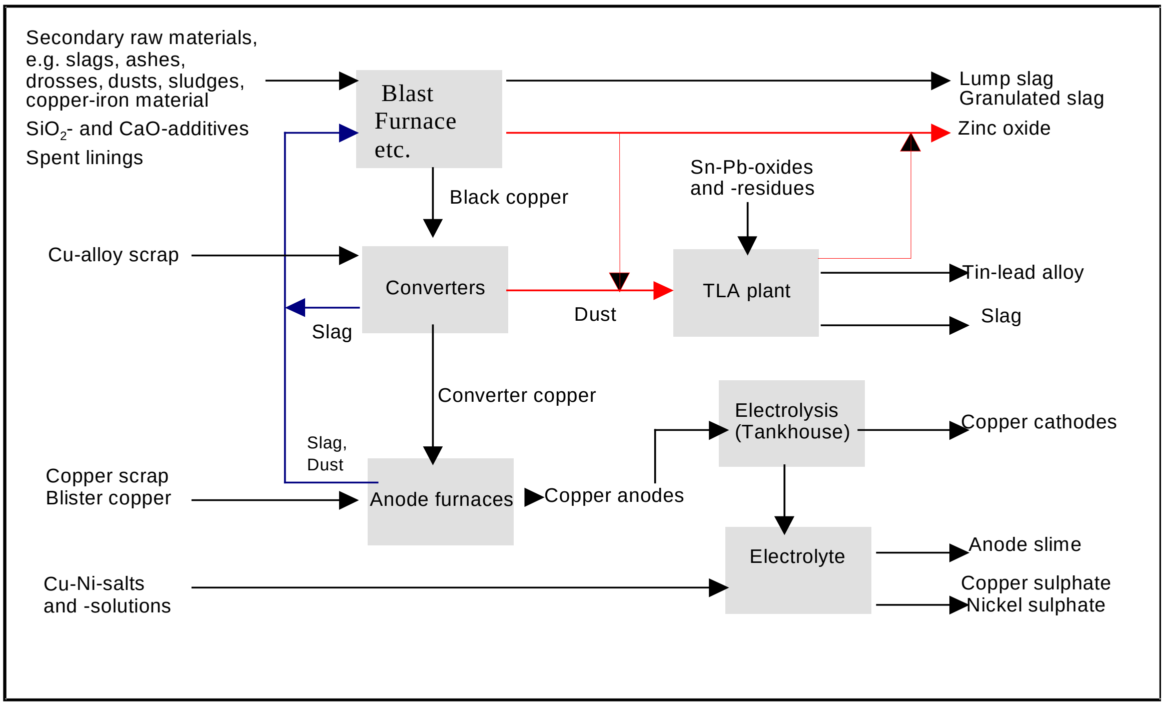


Figure 3.11: Example of an Input–Output diagram from a secondary copper production site with a tin/lead recovery process
[tm 124, DFIU Cu 1999]

Inputs	Quantity [t/a]	Outputs	Quantity [t/a]
Copper scrap$^{*)}$	130000	Copper cathodes	176000
Blister copper	20000	Copper sulphate	2200
Copper alloy scrap	35000	Nickel sulphate	2400
External intermediate materials (e.g. slags, dusts, ashes, sludges, sweepings, etc.)	40000	Zinc oxides	9000
Copper-iron material$^{*)}$	25000	Lead-tin alloys	3700
Limestone	13000	Anode slime	1000
Silica	11000	Slag	80000
Coke	25000		
Coal	15000		
Fuel (oil)	11000		

Note. $^{*)}$ including electronic scrap

Table 3.8: Input-Output data for the above secondary copper process diagram
[tm 124, DFIU Cu 1999]

3.2.2.3 Emissions to air

Dust, metal compounds, organic carbon (which can result in the formation of dioxins) and sulphur dioxide can be emitted to air [tm 124, DFIU Cu 1999]. The potential sources and relevance of potential emissions to air are shown in the following table and they are discussed later in this section: -

Emission Source	Dust And Metal Compounds	Dioxins	Organic Carbon	Sulphur Compounds
Material Handling	••			
Storage	•			
Drying	•••		•	•
Scrap Treatment	••	••• (secondary)	••• (secondary)	
Smelting	•••	••• (secondary)	•(secondary)	••• (Treated in a recovery plant)
Converting	••	• (secondary)	• (secondary)	••• (Treated in a recovery plant)
Refining	••	• (secondary)	• (secondary)	•
Melting/Casting	• (•• for alloys)		• (secondary) + CO	
Ladle Transfers	•••			•
Electrolysis				
Slag Treatment	••		•CO	
Note. ••• more significant …………………..• less significant				

Table 3.9: Significance of potential emissions to air from copper production processes

Oxides of nitrogen are relatively insignificant [tm 24, DFIU 1996] but may be absorbed in the sulphuric acid produced from a primary process; the use of oxygen enrichment can sometimes reduce the formation of nitrogen oxides by the thermal route. This depends on the point where oxygen is added, sometimes a higher concentration of nitrogen oxides is produced due to the increase in temperature, however the gas volume and total quantity is lower. Low NO_x burners can be used. The formation of dioxins in the combustion zone and in the cooling part of the off-gas treatment system (de-novo synthesis) may be possible. The emissions can escape the process either as stack emissions or as fugitive emissions depending on the abatement systems used and the quality of plant maintenance. Stack emissions are normally monitored continuously or periodically and reported by on-site staff or off-site consultants to the competent authorities.

3.2.2.3.1 Carbon monoxide

In addition to the emissions outlined above, the melting processes using furnaces that need to maintain a reducing atmosphere can produce a significant concentration of carbon monoxide. This is particularly the case for the melting of high-grade copper in shaft furnaces in combination with shape casting or production of wire-rod as the products require controlled oxygen level to obtain high conductivity. The process therefore operates under reducing conditions and the carbon monoxide content of the gases can be elevated, typical levels are ~ 5000 mg/Nm^3. The burner control systems that are used can also minimise CO and maintain product quality. CO alarms can also be incorporated into the process. Typical CO production in a shaft furnace used for wire-rod or semis production is 2000 to11000 grams per tonne of copper [tm 117, Cu Expert Group 1998]. In some installations after-burning is used to remove hydrocarbons from the gases when scrap coated with organic matter is processed. CO is also destroyed at the same time and the emissions are reported to be ~ 45 grams per tonne of copper [tm 124, DFIU Cu 1999].

It is possible to predict ground level concentrations of CO and this may be used determine the effect of CO on local air quality (there is a proposed EU AQS for CO) so that further abatement needs can be assessed locally. CO elimination by combustion of the shaft furnace gases with these levels of CO would require additional fuel and so the emission of CO_2 would increase exponentially.

Carbon monoxide is also produced during the operation of the slag cleaning furnace and the blast furnace and in some circumstances can be emitted in the off gases. After burning can be used to remove the CO, giving typical concentrations in the range 10 to 200 mg/Nm^3. There is at least one example where oxygen is lanced into the top of a blast furnace above the reaction zone to provide an after-burning zone in the furnace body. This measure also destroys organic compounds such as dioxins. The electric furnaces used for slag cleaning and reduction processes are normally operated with after-burning either within the furnace or in a special reaction chamber.

3.2.2.3.2 Dust and metal compounds

These can be emitted from most stages of the process. The techniques for dealing with emissions from the handling, storage, drying and treatment stages are covered in Chapter 2 and the application of these techniques should be used to prevent and minimise these emissions.

Direct and fugitive dust emissions from the smelting, converting and refining stages are potentially high. The significance of the emissions is also high as these process stages are used to remove volatile metals such as Zn, Pb some As and Cd from the copper and these metals are present in the gas and partly in the dust.

The primary smelters usually contain dust very well and are effectively sealed to minimise fugitive emissions, concentrate burners or lances are used and are therefore easier to seal. Good maintenance of the furnaces and ducts is practised to minimise fugitive releases and the collected gases are treated in dust removal systems prior to the sulphur recovery processes.

Secondary smelters are more prone to fugitive releases during charging and tapping cycles. These furnaces have large charging doors and the warping and miss-sealing of these doors is a significant factor. The gases that are collected are usually cooled and dust is removed from gas streams by electrostatic precipitators or bag filters. High filtration efficiency is usually achieved and dust concentrations after abatement are in the range < 1 - 10 mg/Nm^3 [tm 210, Copper Expert Group 1999; tm 160, Winter Cu 1999].

Because of the batch type of operation the conversion and refining stages can usually not be as well sealed as the smelting stage. The feeding and transfer of matte, slag and metal is a significant potential source of fugitive fume. More importantly the use of a ladle or boat transfer system can inhibit the effectiveness of fume collection hoods, particularly with the Peirce-Smith or similar style of converters. Various secondary fume collection systems are used to minimise these fugitive emissions and operate very successfully. “Through hood” additions of flux and other material can minimise the rollout time. The production of higher-grade matte reduces the number of ladle transfers and therefore reduces the potential for fume. Fugitive or non-collected emissions are therefore very important. These issues are dependent on efficient and effective primary and in some cases secondary fume collection.

The melting and casting stages used during the production of wire-rod, semis etc. are also potential sources of dust and metals. The production of copper alloys such as brasses results in significant fume (ZnO) at the casting stage and this requires efficient collection. The dust burden is generally low but heat/energy recovery if practicable can be used. Efficient fume collection and fabric filters are usually used [tm 117, Cu Expert Group 1998].

Emissions of metals are strongly dependent on the composition of the dust produced by the processes. The composition varies widely and is influenced a) by the process that is the source of dust and b) by the raw materials that are being processed. For example the dust produced from a scrap converter is totally different to that of a matte converter. The following table shows the measured ranges of metals in dust from a number of copper processes.

Component	Concentrate to matte smelting furnace EP dust	Blast furnace dust	Scrap converter dust	Matte converter EP dust	Electric slag cleaning furnace dust	Anode furnace dust
Pb%	0.1 – 5	5 – 40	5 – 30	2 – 25	2 - 15	2 – 20
Zn%	0.1 – 10	20 – 60	25 – 70	5 – 70	25 - 60	5 – 40
Sn%	0.1 – 1	0.2 – 5	1 – 20	0.1 – 4		
Cu%	5 – 30	2 – 12	2 - 15	10 – 25	0.5 – 2.5	15 – 25
As%	0.1 – 4					0.5 – 10
Ni%	0.1 – 1	0.1 - 1		0.1 - 1		

Table 3.10: Main constituents of dust from copper processes

3.2.2.3.3 Organic carbon compounds

These can be emitted during primary production from the drying stage depending on materials used for ore treatment and the fuel used for drying. For secondary production the most significant sources are from the scrap treatment, smelting and refining stages. The conversion stage for secondary copper is also a potential source if scrap contaminated with organic material is added to the converter and complete combustion is not achieved, this is particularly the case for fugitive emissions. For copper wire-rod and semis production VOC can be emitted if oily material is used as feed and can account for 5 – 100 g per tonne of copper. VOCs may also be emitted from solvent degreasing or solvent extraction processes.

3.2.2.3.4 Dioxins

The organic carbon compounds that can be emitted include dioxins resulting from the poor combustion of oil and plastic in the feed material and from de-novo synthesis if the gases are not cooled rapidly enough. Scrap treatment to remove organic contamination can be practised but more usually afterburners are used to treat the gases produced followed by rapid cooling. In cases where it is not possible to treat the gases from the furnaces in an afterburner they can be oxidised by adding oxygen above the melting zone. It is also possible to identify organic contamination of secondary raw materials so that the most appropriate furnace and abatement combination can be used to prevent the emissions of smoke and fume and the associated dioxins.
It has been reported by the Technical Working Group that in the case of primary smelting and converting, the high operating temperatures destroy organic components and the presence of sulphur dioxide inhibits de-novo synthesis of dioxins. Melting scrap that is contaminated with organic material is also a potential source of dioxins in the semis industry.

Chapter 2 describes some of the factors that influence the emissions of dioxin. The techniques used for abatement of dioxins in this sector include after-burning, controlled gas handling and cooling and effective dust removal; activated carbon absorption is also used.

3.2.2.3.5 Sulphur dioxide

The most significant sources of sulphur dioxide are the roasting and smelting and converting stages of primary copper production using sulphide concentrates [tm 24, DFIU 1991]. Fugitive emissions are expected but can be collected in several ways [tm 124, DFIU Cu 1999]. Sulphur dioxide can also be emitted from the concentrate drying stage (mainly from the fuel used in the burner) and from the primary refining stages where the blister copper contains 0.03% to 0.1% dissolved sulphur. The concentration in the gas is usually very low and simple scrubbing of the gases is generally used if required.

If not applying partial roasting and calcine smelting to matte in separate units because of special feed material, roasting of copper concentrates is carried out simultaneously with smelting. The use of sealed furnaces for smelting allows the sulphur dioxide to be collected efficiently. All of the smelters in the EU use oxygen enrichment that produces a high sulphur dioxide concentration. This therefore allows the off gas volumes to be minimised and the gas handling system including the sulphuric acid plant to be reduced in size. Very high levels of oxygen enrichment can increase the concentration of sulphur trioxide in the gases passing to an acid plant. This increased amount of sulphur trioxide in the gas from the furnace is absorbed in the scrubbers and increases the amount of weak acid for treatment, other uses or disposal. Contact sulphuric acid plants with 4 or 5 passes are used to convert the gases. In some cases single contact plants are used if there is a low (< 6%) sulphur dioxide content, otherwise double contact plants are used [tm 92, Copper Expert Group 1998]. If required liquid sulphur dioxide can be produced from part of the sulphur dioxide contained in the gas.

The matte conversion stage also produces a significant concentration of sulphur dioxide. There are two potential problems when using batch fed converters such as the Peirce-Smith or similar style of converter. Firstly, the gas collection is not totally efficient and the same remarks apply as those made under dust. Secondly, the sulphur dioxide concentration in the gases varies significantly depending on the stage of conversion and can cause problems with sulphur dioxide removal systems unless they are designed specifically to take account of this variation. These gases are mixed with the steady, more concentrated gases produced by the primary smelter to maintain auto thermal operation of the sulphuric acid plant. Using several converters in a phased sequential operation combining the off gases can also reduce this effect.

Continuous processes such as the Mitsubishi process and the Kennecott - Outokumpu Flash Smelt/Flash Conversion process maintain a high and constant concentration of sulphur dioxide and do not need ladle transfers [tm 67, Kennecott 1997; tm 73, Mitsubishi 1993]. The gas volumes that are produced are consequently lower. This means that the concentration of sulphur dioxide is higher in the effluent gas but the mass is much smaller, at least during gas handling, cleaning and cooling. In the contact plant the SO_2/ O_2 ratio has to be adjusted and the SO_2 concentration diluted down to the maximum tolerable concentration.

After heat recovery and cleaning in EPs the sulphur dioxide in the gas from the smelting stages is converted to sulphur trioxide (SO_3). Sulphuric acids plants in the European Copper Industry have a conversion efficiency reported as 99.5 to 99.8% (excluding start up etc) [tm 92, Copper Expert group 1998]. A very small amount of SO_3 is not absorbed and is emitted together with the residual SO_2 [tm 124, DFIU Cu 1999]. During start up and shut down there may be occasions when weak gases are emitted. These events need to be identified for individual installations, many companies have made significant improvements to process control to reduce these emissions. The height of the chimney used for the acid plant gases usually takes these factors into account to reduce local impact.

Sulphur dioxide may also be present in the gases produced during secondary smelting stages due to the sulphur content of the fuel or raw materials. In some cases scrubbers are used to remove the SO_2 and in one case the gases from an electric furnace (and a Cu/Pb converter) are diverted to a primary copper smelter sulphuric acid plant when certain raw materials are present.

3.2.2.3.6 Nitrogen oxides

The production stages for copper usually rely on high temperatures but are also associated with the use of oxygen. This reduces the partial pressure of nitrogen in the flame and reduces nitrogen oxide formation provided that nitrogen is not present in great amounts in the very hot areas. Typical levels for the emission of nitrogen oxides for secondary copper are reported to be in the range 50 to 500 mg/Nm^3 depending on the furnace and type of operation. For NO_x, the use of highly efficient processes (e.g. Contimelt) requires a balance to be established locally between energy use and achieved value.

Nitrogen oxides from primary processes are mainly absorbed in the sulphuric acid produced. Nitrogen oxides are therefore not a major environmental issue at the installation.

3.2.2.3.7 Summary of air emissions

Process type	**Dust g/t of product metal**	**Sulphur dioxide g/t of product metal**	**Cu g/t of product metal**	**Pb g/t of product metal**	**As g/t of product metal**
Primary Cu	160 – 1000	6600 – 16000	30 – 250	7 - 35	3 - 20
Secondary Cu	100 – 1000	500 – 3000	8 – 100	10 - 60	0.5 - 5
Melt shop Semis fabrication			1 – 3.5	0.1 - 1	0.01 – 0.2
Wire Rod Production	20 – 500	10 – 50	12 – 260		

Table 3.11: Specific emissions to air from some primary and secondary processes
[tm 124, DFIU Cu 1999; UK Chemical Release Inventory 1998; tm 160 Winter Cu 1999]

Process unit		**Dust** **mg/Nm^3**	**CO** **mg/Nm^3**	**TOC** **mg/Nm^3**
Melt shop	Electric furnace	< 10		< 20
	Rotary furnace	< 10		< 50
	Shaft furnace (ASARCO)	< 10	< 100*	< 20
Rolling mill				< 50
Milling		< 10		
Note. *With afterburner (after-burning depending on type of feed (oil/organic content). Collected emissions only				

Table 3.12: Achievable emissions from a semis fabrication process
[tm 124, DFIU Cu 1999]

Process unit		**Dust** **g/t**	**CO** **g/t**	**TOC** **g/t**	**PCDD/F** **µg/t (I-TEQ)**
Melt shop	Electric furnace	< 70	-	< 80	< 5
	Rotary furnace	< 50	-	< 11	< 10
	Shaft furnace (ASARCO)	< 12			< 10
	without afterburner		< 10000		
	with afterburner		< 45	< 9	
Rolling mill		-		< 100	
Milling		< 20			
Note. *) After-burning depending on type of feed (oil/organic content) Collected emissions only					

Table 3.13: Specific emissions from a semis fabrication process
[tm 124, DFIU Cu 1999]

3.2.2.4 Emissions to water

Pyrometallurgical processes use significant quantities of cooling water (cooling systems are covered in Chapter 2 and in a separate horizontal BREF on cooling systems). Other sources of process water are shown in the table below. Suspended solids, metal compounds and oils can be emitted to water from these sources. All wastewater is treated to remove dissolved metals and solids. In a number of installations cooling water and treated wastewater including rainwater is reused or recycled within the processes [tm 210, Copper Expert Group 1999]. The potential sources and relevance of potential emissions to water are shown in the following table and they are discussed later in this section

Emission Source	Suspended Solids	Metal Compounds	Oil
Surface Drainage	•••	••	•••
Cooling Water for direct cooling.	•••	•••	•
Cooling Water for indirect cooling.	•	•	
Granulating Water	•••	••	
Leaching (if not closed circuit)	•••	•••	•
Pickling	••	•••	•••
Tank House (if not closed circuit)		•••	
Scrubbing Systems	•••	•••	
Note. ••• more significant …………………..• less significant Open leaching circuits and open circuits in tank-houses are not used in the EU.			

Table 3.14: Significance of potential emissions to water from copper production processes

3.2.2.4.1 Suspended solids and metal compounds

These can be emitted from several stages of the process, the most significant can be wastewaters and rinses from pickling operations. The techniques for dealing with emissions from the raw materials handling and storage areas are covered in Chapter 2 and the application of these techniques are used to prevent and minimise these emissions. Surface water can result from either rainfall or from the wetting of stored material to prevent dust formation.

Potential sources of suspended solids and metal compounds are the cooling, granulating and leaching systems. In general these systems are either sealed and the water is re-circulated or are non-contact.

Wash waters, spent electrolyte and process effluents are also produced in the tank houses, pickling lines and from scrubbers. These effluents contain significant quantities of metal compounds in solution and are treated along with liquors bled from the sealed cooling and granulating systems before discharge to water [tm 28, WRC 1993]. System leakage can occur and monitoring arrangements are needed for the pipe work and storage tanks, specifically for pipelines outside the plant and in cases when they in areas without a collection system. Wastewater treatment processes are described in Chapter 2 and the method used depends on the contaminants that are present, the destination of the treated water and local environmental quality.

	Flow [m^3/a]	Main components [mg/l]					
		Cu	**Pb**	**As**	**Ni**	**Cd**	**Zn**
Process water	72000	0.01-0.2	0.001-0.04	0.01-0.1	0.004-0.15	0.0001-0.1	0.01-0.2
Surface run-off	322000	0.01-0.4	0.005-0.2	0.003-0.07	0.002-0.4	0.0002-0.1	0.03-0.4
Direct cooling water	11300000	0.01-0.25	0.001-0.1	0.001-0.1	0.002-0.06	0.0001-0.003	0.02-0.5
Cooling water (total)	82000000						

Note. Table refers to a combined primary/secondary copper smelter/ refinery complex located at a river close to the sea producing 370000 tonnes of Cu cathode per year.

Table 3.15: Example of the metal content in various waste waters after treatment [tm 124, DFIU Cu 1999]

Substance	Value kg/a
Cu	11
Ni	3
Zn	25
Pb	1
Cr	1
As	0.01
Cd	0.01
Hg	0.01
Sn	1
Note. Effluent discharge 35000m^3/a.	

Table 3.16: Annual loads discharged to water from a copper semis production plant [tm 124, DFIU Cu 1999]

Sludges from all of the processes are produced and these are usually sent for controlled disposal, in some cases they are returned to the smelter to recover the metallic fraction.

3.2.2.4.2 Oil

This can be present on secondary raw materials and can be washed from the storage areas. The techniques used for storage are covered in section 2. Waxes and oils are used in the coating and drawing processes associated with the production of rods and other shapes and their presence is taken into account to prevent contamination of water.

3.2.2.5 By-products, process residues and wastes

Some intermediate products generated during copper production may be covered by the Hazardous Waste List (Council Decision 94/904/EEC) shown in section 2.10.1. Most of these materials however contain recoverable quantities of copper and other non-ferrous metals and are therefore used as raw materials in their own right, for example slag from the production of tin from cassiterite is the main source of tantalum and niobium. Flue dusts from all sources can also be reused in the smelting process, to prevent dust formation during handling they are carefully handled, usually in specially designed systems or, already pre-treated for the further processing requirements. Some furnace linings can also be reused as tap-hole mass or in the process and may be incorporated in the slag, in other cases the linings are disposed.

Process Source	Intermediate Product, By-Product, Residue	End Use
Abatement Systems	Filter Dusts. Mercury compounds. Spent catalysts and acid. Sulphuric acid sludges. Weak acid.	Raw Material for Cu (returned to smelter), Pb, Zn and other metals. Raw material for Hg. Chemical Industry. Neutralisation Other uses e.g. leaching, decomposition for SO_2,
Smelter	Slag Furnace linings	To slag furnace or other separation – internal recycle. Recovered or disposed
Converter	Slag	To smelter – internal recycle.
Slag Furnace	Slag	Abrasive, construction material.
Refining (anode) furnace	Slag	To smelter – internal recycle.
Tank House	Electrolyte bleed Anode remnants Anode slime	Ni salts, Cu recovery, acid recovery or other use. Internal recycle: Converter (cooling) or anode furnace. Precious metals recovery.
Melting/smelting	Skimmings and slag	Raw material for metal recovery.
General	Oils	Oil recovery.
Hydro Metallurgy	Depleted electrolyte	Leaching.
Semis Production	Acid pickling solutions and rinses.	Disposal as waste if low in non-ferrous metals or sold for metal recovery.
Rod Production	Acid pickling solutions (if applied).	Recovery in separate electrolytic cell.

Table 3.17: Intermediate products, by-products and residues from the production of copper

Wastes destined for disposal are kept to a minimum and mainly consist of acid slimes from the sulphuric acid plants that are treated and sent for disposal or furnace linings some of which cannot be recovered in the process. In some cases tailings from the processing of smelter or converter slag by flotation are produced, these tailings are disposed of on site or at the mine site if it is close. Other wastes are either domestic or demolition wastes.

The above table shows the potential use of the process residues. Many of the residues are used as raw materials for the production of other metals or as materials recycled within the copper production route [tm 210, Copper Expert Group 1999]. The following tables show examples of the quantities of residues, intermediates and by-products generated by primary and secondary processes.

Process unit	**By-product residue**	**Amount [t/a]**	**Use/treatment option**
Primary plant: Annual cathode production: - primary copper 220000 t/a;			
Flash smelting furnace	Dust	100000	Internal use at the flash smelting furnace
	Slag	400000	Further processing in the electric furnace
Electric furnace	Dust	400	External use for Zn/Pb production
	Slag	400000	External use as construction material
Copper converter	Dust	4000	Internal recycling to the flash smelter or electric furnace (sec. plant)
	Slag	150000	Internal use at the flash smelting furnace
Anode furnace	Dust	200	Internal use at the flash smelting furnace
	Slag	20000	Internal use at the copper converter
Sulphuric acid plant	Sulphuric acid	656000	By-product for sale
Secondary plant: Annual cathode production: secondary copper 150000 t/a.			
Electric furnace	Dust	10000	By-product for sale to recover Zn
	Slag	40000	External use as construction material
Converter	Dust	400	Internal use at electric furnace
	Slag	10000	Internal use at electric furnace
Contimelt process	Dust	1000	Internal use at the flash smelter/electric furnace
	Slag	2000	Internal use at copper converter
Scrap converter/TLA plant	Dust	1000	Further processing in TLA plant
	Slag	2000	Internal use at the electric furnace
Others:			
Electrolysis	Anode slime (wet weight)	3000	Internal use at the chemical plant for the recovery of precious metals and Se, Te, Pb
	Final liquor	35000 m^3	Internal use at the chemical plant for the production of nickel sulphate, As_2O_3,H_2SO_4
Process waste water treatment plant	Sludge (wet weight)	1500	Disposal as hazardous waste
General	Household refuse	400	

Table 3.18: Example of the quantity of residues produced by a complex primary and secondary installation
[tm 124, DFIU Cu 1999]

Process unit	By-product, residue	Amount[t/a]	Use/treatment option
Blast furnace	Slag	30000 – 35000	Sold as construction material
	Oxide from after-burning chamber, boiler and cooler	700 – 800	Internal use at the blast furnace
	Filter oxide	1000 – 1300	External use to recover Zn, Pb etc
Converters	Slag	17000 – 19000	Internal use at the blast furnace
	Oxide from after-burning chamber	250 – 300	Internal use at the blast furnace
	Oxide from cooler	100	Internal use at the blast furnace
	Residues	300	Internal use at the blast furnace
	Filter oxide	3500 – 3700	External use to recover Zn, Pb etc
Anode furnace	Anode copper residues	7000 – 8000	Internal use at the blast furnace
	Filter oxide	150	Internal use at the blast furnace
	Residues from furnace	200	Internal use at the blast furnace
Electrolysis	Anode slime	360	External use
	Nickel sulphate	700	External use
General	Household refuse	n.a.	
Note. Annual production 60000 t/a cathode.			

Table 3.19: Example of the quantity of residues produced by a secondary installation [tm 124, DFIU Cu 1999]

Slags contain varying amounts of copper and many are re-used or treated to recover the metal content. Slag treatment is often carried out in a thermal process to produce an inert slag.

Component	Flash furnace	Peirce-Smith converter	Combined slag after electric furnace slag cleaning
	[wt.-%]		
Copper	1 – 2.5	3 – 5	0.3 - 0.8
Iron (total)	38 - 45	40 - 45	40 - 43
Silica	30 - 33	25	28 – 32
Magnetite	4 - 18	25	< 2

Table 3.20: Composition of some copper smelting slags before slag cleaning treatment [tm 124, DFIU Cu 1999]

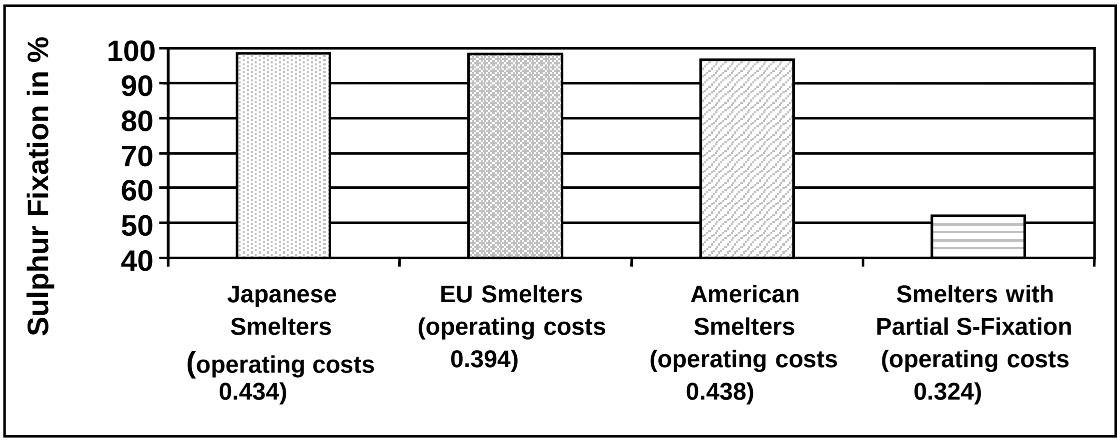
Many of the slags produced by slag treatment processes contain very low levels of leachable metals and are stable. They are frequently sold as products for the abrasive and construction industries as they have excellent mechanical properties, which are sometimes superior to those of competing natural minerals. Oils from various sources within the process can be recovered.

3.3 Techniques to Consider in the Determination of BAT

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2 "common processes" apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

The control of furnace operating parameters and the prevention of fugitive emissions from furnaces and the tapping and pouring processes is also important. Techniques used by other sectors are also applicable particularly those relating to the use of sulphur recovery systems.

The appropriate techniques on a site by site basis are strongly influenced by the raw materials that are to be processed, in particular the type and variability of the concentrate or secondary raw materials can be crucial to the choice of process. On a Worldwide basis some operations have a dedicated single source of raw material but the majority of the plants in Europe buy concentrate on the open market and need to maintain flexibility in processing a range of raw materials. In a similar manner the standard of collection and abatement systems used worldwide in the industry reflects local, regional or long-range environmental quality standards and direct comparison of the environmental performance of process combinations is therefore difficult. It is possible however, to judge how a particular process can perform with the appropriate, modern abatement equipment [tm210, Copper Expert Group 1999].



Note. Sulphur fixation: **-** Japanese 98.6%; European 98.3%; American 96.8%; Others 52%. (Costs based on 1€ = 1.06 $ (16-6-99))

Table 3.21: Average sulphur fixation vs operating cost in €/kg achieved by smelters worldwide
Source - Brook Hunt 1998 CRU Copper Studies 1997

Using the degree of sulphur fixation as an example, the above table illustrates the effects on environmental performance and the achievements of the European installations. The table shows that good sulphur fixation in EU can be achieved within economic boundaries. This is shown in terms of direct operating cost for plants with comparable, modern process technology but with variations in abatement.

3.3.1 Materials storage, handling and pre-treatment processes

3.3.1.1 Primary raw materials

The raw materials are concentrates, fluxes and fuel. Important aspects are the prevention of leakage of dust and wet material, the collection and treatment of dust and liquids and the control of the input and operating parameters of the handling and feeding processes.

The issues specific to this group are: -

- The potentially dusty nature of some concentrates and some fluxes (e.g. lime) means that enclosed storage, handling and treatment systems are techniques to consider in these instances. The dust generated by some slag crushing operations means that collection and abatement may be applicable for this process. Similarly slag granulation water may require settlement or other treatment prior to discharge.
- Concentrates are mixed with fluxes to produce a fairly constant feed therefore the general practice of sampling and analysis to characterise the concentrates and storage of individual concentrates separately so that an optimum blend can be prepared for smelting are techniques to be considered.
- Feed blends prepared from bedding plants or from dosing bin systems using weighing systems such as belt weighers or loss in weight systems are techniques to consider. They form a sandwich mix on the extraction belt. Final mixing and homogenisation takes place in the conveying and drying systems. Enclosed conveyors or pneumatic transfer systems are used. Hot gas rotary dryers, fluidised bed, flash or steam coil dryers etc can be used, steam coil dryers use waste heat from other parts of the process provided that the heat balance allows it. The drier and associated dust abatement stage therefore depends on site-specific conditions such as the reliability of the steam supply. Fabric or ceramic filters achieve better dust removal efficiencies than EPs.
- In some cases the dry material is reported to have an ignition temperature of between 300 and 400° C but this factor can be dealt with in a number of ways. For example the oxygen content of the gases in a hot air drier is low and the operating temperature is controlled at a maximum tolerable level, mostly by mixing with cold air, nitrogen may also be used, auto ignition may not be a problem in these cases. Similarly steam coil dryers can maintain a low temperature in the concentrate and a low airflow rate, this can achieve the same effect. Some techniques are also used to prevent auto ignition. Heat or spark detection can identify hot spots and these devices can be used to trigger nitrogen quenching. These are all techniques to be considered depending on the site.
- Storage of acid produced during the process in double walled tanks or tanks placed in chemically resistant bunds are techniques to be considered. The treatment of acid slimes from the sulphuric acid plant and weak acid from scrubbing systems depends on local processing or disposal requirements unless there is a local use for the material. Anode slimes and other metal containing residues that are destined for recovery off site should be stored drums or other suitable ways depending on the material.

EXAMPLE 3.01 RAW MATERIAL SAMPLING AND RECEPTION SYSTEM.

Description: Concentrate reception and sampling system. Enclosed vehicle tipping area, sealed transfer system and computerised sampling. Enclosed storage and blending area, enclosed conveyors.

Main environmental benefits: - Prevention of fugitive dust. Defined feed for the process.

Operational data: - Not available but visual indications are of a very high standard.

Cross media effects: - Positive effect - Reduction in energy usage, reduction of main emissions

Economics: - No data available but it can be concluded by common practice that these techniques are economically viable. Production efficiency increased.

Applicability: - Most primary processes.

Example plants: - Currently in use at installations in Spain, Belgium and Germany.

Reference literature :- [tm 106, Farrell 1998]

3.3.1.2 Secondary raw materials

There are a variety of secondary raw materials used for secondary production and they range from fine dusts to large single items. The copper content varies for each type of material and so does the content of other metals and contaminants. Size and copper content (low, medium and high) can be used to classify the materials. Techniques used for storage, handling and pre-treatment will vary according to the material size and the extent of any contamination. These factors vary from site to site and the techniques discussed in Chapter 2 are techniques to be considered. The site-specific issues that apply to this group are:

- The storage of fine dusts in enclosed buildings or in sealed packaging.
- The storage of secondary raw materials that contain water-soluble components under cover.
- The storage of non-dusty, non-soluble material in open stockpiles and large items individually in the open.
- Large items including lumps of slag, metal (blister etc) may damage concrete surfaces causing hidden cracks and the specific case influences the technique used.

Pre-treatment stages are often used to remove organic components such as cable insulation and printed circuit board remnants and to separate other metals e.g. tin or lead.

- The use of milling and grinding techniques with good dust extraction and abatement are techniques to consider. The fine dust that is produced may be treated to recover precious metals, pneumatic or other density separation techniques are used.
- Cryogenic techniques are also techniques to consider to make cable coverings friable and more easily separated.
- Thermal de-coating and de-oiling processes are also techniques to consider and will feature an after burning stage to destroy any organic material in the off gas.
- Fine dusts are stored and handled in a manner that prevents the emission of dust. They are often blended and agglomerated to provide a consistent feed to the furnace.

Raw Material	Storage	Handling	Pre-treatment	Comment
Coal or Coke.	Covered Bays, Silos.	Covered conveyors if non-dusty. Pneumatic.		
Fuel and other oils.	Tanks or drums in bunded areas.	Secure pipeline or manual system.		
Fluxes. If dust forming	Open on concrete or similar, floors. Enclosed (Silo) if required	Enclosed conveyors with dust collection. Pneumatic.	Blending with concentrates or other material.	
Concentrates.	Enclosed unless non-dust forming.	Enclosed with dust collection. Pneumatic.	Blending using conveyors. Drying.	
Copper Products – Cathodes, wire-rod, copper billets and cakes.	Open concrete area or covered storage.			
Fine dust.	Enclosed.	Enclosed with dust collection. Pneumatic.	Blending, Agglomeration.	
Coarse dust (raw material or granulated slag)	Covered Bays	Mechanical loader.	De-oiling if necessary	Oil collection if necessary
Lump (raw material or slag).	Open	Mechanical loader.		Oil collection if necessary
Whole Items	Open or Covered Bays	Mechanical loader.		Oil collection if necessary
Swarf	Covered storage	Charge skips	Swarf drying or de-oiling.	Oil collection if necessary
Cable.	Open	Mechanical loader.	De-coating.	
Circuit Boards.	Covered Bays	Mechanical loader.	Grinding + density separation.	Plastic content may provide heat input.
Process residues for recovery.	Open, covered or enclosed depending on dust formation.	Depends on conditions.		Appropriate drainage system.
Wastes for Disposal. (e.g. furnace linings)	Open covered or enclosed bays or sealed (drums) depending on the material.	Depends on conditions.		Appropriate drainage system.

Table 3.22: Storage, handling and pre-treatment techniques to consider for copper

3.3.2 Primary smelting processes

The copper smelting processes practised in the EU are [tm 92, Copper Expert Group 1998]: -

- Outokumpu flash smelting using high oxygen enrichment for normal copper concentrate to matte smelting. Matte conversion in Peirce-Smith converters to produce blister copper. Slag cleaning in electric furnace or by flotation.
- Partial roasting of concentrates in a fluid bed roaster, electric furnace smelting to matte. Matte conversion to blister copper in Peirce-Smith converters. Slag cleaning by fuming. The raw materials processed contain zinc and some lead as well as copper.
- Smelting and conversion to blister copper of primary and secondary lead/copper and some zinc containing raw materials in an ISA Smelt furnace. Lead production by slag cleaning in a blast furnace.

These are all techniques to be considered.

The Outokumpu flash furnace produces a high-grade matte that assists and simplifies the process of conversion.

In some instances the furnace can produce blister copper directly without a converting stage. The use of the Outokumpu Flash furnace in this manner is characterised by blister copper production in one smelting step when using specific low iron containing or very high grade concentrates (low slag fall) [tm 137, Cu Expert Group 1998]. For example this process is used in Poland for direct blister production from concentrate with a low iron content.

The Outokumpu flash smelting process features heat recovery in the form of steam and electricity and also the collection and recovery of sulphur dioxide as sulphuric acid. Furnace lining life is approximately 5 to 10 years (depending on various factors, like furnace size, production rate and operating parameter practised etc.).

In addition to those above, several other furnaces are used for the smelting stage worldwide [tm 137, Copper Expert Group 1998] and several of these can also be considered. The use of the reverberatory furnace for primary copper concentrates is not included as a technique to be considered.

There is a distinction between these processes as two of the processes, the Mitsubishi and Kennecott/Outokumpu processes, combine the smelting and converting stages. The Mitsubishi processes uses three interconnected furnaces with gravity flow of molten material between the furnaces. The Kennecott/Outokumpu process uses a matte granulation and grinding process between the smelting and conversion flash furnaces so that the unit operations are uncoupled.

All of the furnaces mentioned have been described earlier and are listed in the following table, which summarises the advantages and disadvantages of the various processes.

Furnace	Applied Capacity x1000 t/a	Gas Collection	Advantages	Disadvantages	Comments
Smelting process.					
Outokumpu Flash Smelting	~ 150 to 370 (mostly 200 to 300)	Sealed Furnace	High smelting rate. High quality matte. Long furnace lining life.	Comparatively higher investment but lower operating cost.	Vast process knowledge available.
Electric (with partial roasting)	~ 40 to 220	Sealed Furnace	Primary and secondary. Compact.	Two-stage process	
ISA Smelt	~ 170 to 230	Hooded	Primary and secondary. High smelting rate. Variety of fuels	Requires a settler to separate matte and slag.	Moist feed can increase gas volumes
Noranda and El Teniente (for 1 unit)	~ 120 to 150 / and 70 to 190	Hooded.	Compact. Lower cost.	Furnace lining life ~ 2 years	Processes are developing rapidly and their status will improve in time.
Inco Flash	~ 120 to 200	Sealed Furnace	High smelting rate. High quality matte.	Autogeneous 100% O_2 used resulting in narrow operating window.	
Contop	~ 120	Sealed Furnace	High Bi and Zn removal.	Low throughput	Only one plant.
Vanyucov process	~ 100 or more	Hooded	Similar to Noranda		Too little data to assess.
Baiyin process	~ 70	Hooded	Similar to Noranda. Divided furnace to give integral settler		Too little data to assess.

Table continued on following page

Furnace	Applied Capacity x1000 t/a	Gas Collection	Advantages	Disadvantages	Comments
Continuous, Coupled Process					
Mitsubishi	~ 120 to 240	Sealed Furnace	Can also melt purchased and anode scrap. High smelting rate. No ladle transfer	Some limitation in feed. Coupled unit operation with effect on efficiency of the complete line. Sulphur content of blister copper.	3rd plant being constructed.
Continuous Uncoupled Process					
Kennecott/ Outokumpu Flash Smelting and converting process	~ 300	Sealed Furnaces	Surge storage of ground matte. No ladle transfer.	Comparatively higher investment cost but lower direct operating costs.	2nd plant ordered. The only process concept with uncoupled unit operation. Operation at different sites possible

Table 3.23: Overview of Primary Copper Smelting furnaces

3.3.3 Sulphur dioxide removal

The sulphur dioxide produced during the smelting and converting stages can have a severe environmental impact and is removed from the gases in either a sulphuric acid plant or by recovery as sulphur dioxide. The various processes used for sulphur dioxide removal are described in Chapter 2 of this document. The process used depends on local markets for liquid sulphur dioxide, generally conversion to sulphuric acid is used [tm 92, Copper Expert Group 1998]. There are several factors that are specific to the copper industry. These are all techniques to consider in the determination of BAT.

The use of oxygen enrichment in copper smelters results in a high sulphur dioxide content in the smelting furnace gases. Although this is subsequently diluted to 14% SO_2 for conversion, the gas volume reduction allows significant savings to be made in the size of ducts, blowers and abatement plant [tm 140, Finland Cu 1999; tm 107, Ullmanns 1996]. The other factor that is present with high gas strength is the potential to use the excess heat present in the gas particularly after the catalysis stages, which are strongly exothermic; however that may reduce the flexibility to accept variations of gas flow and composition. The dilution of the gas mentioned before also has to provide sufficient oxygen for the catalytic process.

The other factor affecting the sulphur dioxide content is the variable content of gases from the copper converter, which is described above. This variation of SO_2 content means that the design of the acid plant needs to take this into account in the scrubber and heat transfer stages and in the choice of catalyst. As reported earlier the choice of catalysts is now greater and caesium oxide doped catalysts may be capable of improving performance.

The performance of a metallurgical acid plant is dependent on the performance of the gas cleaning section. If the cleaning system is not effective in removing impurities from the incoming gas, the performance of the contact section will deteriorate. Although the design of wet gas cleaning systems may differ widely, they have the following requirements and features in common:

- Solid contaminants must be removed, giving a final gas quality of < 1 mg solid/Nm^3 (optically clear).
- Sulphur trioxide content of the gas to be reduced to the level of 15 - 25 mg/Nm^3.
- Fluorides and chlorides must be removed to prevent damage to downstream tower brickwork and converter catalyst.
- The gas must be cooled to a temperature satisfying the acid plant water balance. The temperature is dependent on the SO_2 concentration of the gas and the concentration of the acid produced. A gas with 4 - 6% SO_2 requires cooling to temperatures below 30 °C while a gas with SO_2 contents of well above 10% can tolerate gas temperatures of approximately 35 - 40 °C, when producing 98.5% grade acid.

The rate of conversion of sulphur dioxide to sulphur trioxide is generally reported for these processes and can be in the range 99.5 to 99.9% for the gases produced from primary copper smelting and converting. There are however, several factors that affect the conversion rate and these must be taken into account at a local level. The factors are: -

- Input gas cleanliness to reduce poisoning of the catalyst e.g. mercury removal depending on the content in the feed.
- Input gas strength and consistency. Higher strength gases and more consistent SO_2 concentrations tend to enable higher conversion efficiencies to be achieved. This is due in part to the consistent inter-pass gas cooling that can be achieved when there are few variations in concentration.
- Choice of catalyst. Caesium oxide doped catalysts tend to increase conversion rates provided that the other factors are controlled to prevent poisoning. Routine catalyst changes may allow improvements to be made to the catalyst during maintenance but to be fully effective must be accompanied by improvements in other areas.
- Correct input gas temperature, oxygen content and water balance (see above).
- Effective adjustment of gas conditions, in particular the temperature, between the catalyst passes.

Conversion rates therefore vary with time and steady state values can be misleading however the following examples illustrate the performance that can be achieved by well designed plants operating with different input gas characteristics.

EXAMPLE 3.02 SULPHURIC ACID PLANT OPERATING UNDER VARYING GAS CONDITIONS

Description: - Gas cleaning and washing section. 3 lines of Lurgi double contact sulphuric acid plant, 4 and 5 passes, modern catalyst. Weak acid to neutralisation ~ 12 – 15 m³/h with 5% H_2SO_4, as well as thermal decomposition of acid bleed with higher (~ 50%) acid concentration.

Main environmental benefits: - High conversion rate for sulphur dioxide More than 99.6% achieved with a recent installation.

Operational data:-

Component	Measured Values	
Off-gas volume:	320000	Nm³/h
SO_x	100 – 1100	mg/Nm^3
SO_3	20 – 40	mg/Nm^3
NO_x (as NO_2)	20 – 45	mg/Nm^3
Cl^- (as HCl)	2 – 7	mg/Nm^3
F^- (as HF)	1 – 4	mg/Nm^3
Average – residual dust:	< 2	mg/Nm^3
Range – residual dust :	1 – 7	mg/Nm^3
Range – components:		
Cd	< 0.01 – 0.02	mg/Nm^3
Hg	< 0.01 – 0.07	mg/Nm^3
Tl	< 0.01 – 0.02	mg/Nm^3
As	< 0.01 – 0.1	mg/Nm^3
Se	< 0.01 – 0.02	mg/Nm^3
Sb	< 0.01 – 0.03	mg/Nm^3
Pb	< 0.01 – 0.15	mg/Nm^3
Cu	< 0.01 – 0.09	mg/Nm^3
PCDD/PCDF	0.001 – 0.01	ng ITE/Nm^3

Table 3.24: Performance data of a sulphuric acid plant operating under varying gas conditions

Cross media effects: - Positive effect – Reduction of main emissions of sulphur dioxide by conversion to sulphuric acid, recovery of the heat from the gases and evolved during conversion.

Economics: - 55 million € installed for 1 acid plant line. See also appendix on cost

Applicability: - Off gases from primary smelter (SO_x concentration > 6%; combination with off gases from secondary smelter is possible). These features can also be applied to most existing installations.

Example plants: - Currently in use by a plant in Germany

Reference literature :- [tm 124, DFIU Cu 1999; tm 210, Copper Expert Group 1999].

EXAMPLE 3.03 SULPHURIC ACID PLANT OPERATING UNDER IDEAL CONDITIONS

Description: - Double contact sulphuric acid plant, 4 passes modern caesium catalyst. Monsanto Enviro Chem 3:1 IPA process

Main environmental benefits: - Maximum recovery of sulphur dioxide.

Operational data: - Treatment of combined FSF and FCF gases with 30 –40% SO_2, diluted to 14% at contact plant inlet at an annual average flow of 171300 Nm^3. Up to 99.9% conversion achieved. Plant relies on a high, constant sulphur dioxide feed, sophisticated gas cleaning and inter-pass cooling and Cs doped catalyst. Sulphur dioxide emission in the tail gas (as annual average) is around 150 mg/Nm^3.

Cross media effects: - Positive effect - Reduction of main emissions of sulphur dioxide, recovery of energy.

Economics: - Not assessed but the process has been recently installed and is operating economically.

Applicability: - Specific case for ideal feed gas conditions.

Example plants: - In operation in a plant in USA.

Reference literature : - [tm 140, Finland Cu 1998].

The other factor that is important when high strength gases are used in a sulphuric acid plant is the residual SO_2 content in the exhaust gases. Most European plants achieve a conversion efficiency in the range 99.5 to 99.8% and with an input concentration of 8.4, 10, 11 or 13% SO_2 at the contact plant. The% conversion excludes the period during start up and shutdown operations and emergency events.

3.3.4 Secondary smelting processes

The range of secondary materials and the variation in copper content and degree of contamination has lead to the development of a range of smelters for secondary materials [tm 137 Copper Expert Group 1998]. In Europe the Mini Smelter, blast furnace, the ISA Smelt furnace, the TBRC and the sealed submerged arc electric furnace are used for a wide range of materials. They are all techniques to consider depending on the type of raw material.

The Mini Smelter is used for secondary materials and slag using iron and high iron content scrap as a reductant. The converter is used for the treatment of iron containing black copper from the smelting furnaces and for the smelting of alloy scrap. The reverberatory hearth furnace is used for refining of converter copper and scrap with higher copper contents.

Table 3.24 gives an overview of the advantages and disadvantages of the secondary smelting furnaces for lower grade feed materials.

Several of the techniques described in Chapter 2 are applicable to fume extraction and abatement and the process control systems used by these furnaces. These techniques are not routinely used by all installations at the time of writing. The process control system for the blast furnace is considered to be suitable for development and its potential inclusion is subject to this factor.

Gases from secondary smelters usually contain little or no sulphur dioxide provided sulphidic material is avoided but can contain significant quantities of the more volatile metals such as lead and zinc etc. They can also contain VOCs, dioxins, CO and dust and so the abatement stages for secondary smelting involves gas cooling (with heat/energy recovery), after-burning to destroy organic carbon and dioxins, coarse particle separation if necessary and fabric filtration. The collected dusts are recycled to recover these metals.

EXAMPLE 3.04 DESTRUCTION OF DIOXINS

Description: - Oxygen injection in upper zone of blast furnace. The process concerned has no room to allow an afterburner to be fitted. There are some restrictions in the degree of gas mixing achieved but the overall performance is acceptable. Control systems for the system may be developed.

Main environmental benefits: - Destruction of dioxins. Destruction of CO and other carbon.

Operational data: - Dioxins < 0.5 ng/Nm^3 TEQ achieved.

Cross media effects: - Overall positive effect - Reduction of main emissions. Energy cost of producing oxygen.

Economics: - Not available but the technique is a low cost modification and is operating viably.

Applicability: - Most hot top blast furnaces and maybe other processes.

Example plants: - Currently in use by plants in Germany.

Reference literature : - [tm 124, DFIU Cu 1999].

Furnace	Capacity Range	Gas Collection & Abatement Requirement	Advantages	Dis-advantages	Comments
Blast Furnace	~150 to 200 tonnes per day per furnace.	Semi Sealed. Gas cooling* after-burning and cleaning (fabric filter)	Low grade material.	Lack of process control development.	Improvement in process control for inclusion. Production rate depends on type of feed and copper content.
Submerged Arc Electric Furnace	For a 8 MVA furnace: 8 - 25 tonnes per hour melting rate	Sealed. After-burning, gas cooling and cleaning**	Established for computer scrap. Low gas volume.	Some feed restrictions.	CO formed burns in the furnace to provide heat. Production rate depends on type of feed copper content and furnace rating.
Mini Smelter		Enclosed. Gas cooling and cleaning (fabric filter)	High smelting rate. Compact.	Some feed restrictions.	
TBRC	Up to ~ 40 to 70 tonnes per batch	Enclosed Gas cooling* and cleaning (fabric filter)	Range of material. High smelting rate. Compact. Rotation.	Expensive.	
ISA Smelt	~ 30000 to 40000 tonnes per year.	Hoods Gas cooling* & cleaning**	Range of material. High smelting rate.	Developing.	Not proven for lower grade material under reducing conditions. Commissioning stage for batch processing sulphur containing feed producing matte and matte converting
Converter	~15 to 35 tonnes per batch per converter	Hooded. Gas cooling and cleaning** (fabric filter)			For treatment of black copper from melting furnaces and smelting of copper alloys.
Hearth Shaft Furnace	~ 250 t/d	Sealed and hooded, after-burning, cooling & cleaning (fabric filter)	Use for melting and refining of metal, good energy efficiency	Some feed restrictions	Fire refining of higher grade scrap, anode and blister copper.
Contimelt process	50 – 100 t/h	After-burning (reduction furnace), WHB, cleaning (fabric filter).	High production rate, high energy utilisation.	Some feed restrictions	Fire refining of higher grade scrap, anode and blister copper.
Reverberatory hearth furnace	~ 250 to 400 tonnes per day	Semi Sealed and hooded. Gas cooling* after-burning and cleaning (fabric filter)	Use for converting and refining.	Sealing. Some feed restrictions.	Can use Tuyeres along with tilting system. Fire refining of higher grade scrap, and blister copper.

Note. *) If the temperature level is high enough waste heat recovery may be considered; for cleaning in fabric filters further cooling is required.

**) In the EU plants the off-gas may contain sulphur dioxide during certain campaigns and therefore is treated in a scrubber or sent to in an acid plant at these times.

Table 3.25: Overview of secondary smelting furnaces

3.3.5 Converting

3.3.5.1 Primary copper converters

The converting stage used in Europe is the Peirce-Smith (or similar) Converter. It is also commonly used Worldwide [tm 92, Copper Expert Group 1998]. This type of converter has a very robust and efficient level of performance. They are capable of a high level of metallurgical treatment and can be used to fume off included metals such as lead and zinc which can then be recovered. The heat generated during processing is also available to melt copper scrap (e.g. anode scrap) and this factor is an important advantage. They suffer from the disadvantage that they rely on the feed and transfer of material by ladle, skip or mould.

This is a potential source of fugitive fume that contains dust, metals and sulphur dioxide. The ladle or skip used for feeding can interfere with the efficient positioning of the fume collector hoods. Good operation of the converter therefore relies on the use of primary and secondary fume collection hoods during charging and pouring to collect as much fugitive fume as possible. Dusts, fluxes, carburant, scrap etc. can be added through the hood. Automatic controls can prevent blowing during the periods that the converter is “rolled out” or “rolled in” again.

These processes and the techniques for control and fume collection are suitable for use with new and existing installations and are techniques to consider.

Other converter processes are also used worldwide [tm 137 Copper Expert Group 1998] and are also techniques to consider. The converter stages that are used in the continuous Mitsubishi and Outokumpu/Kennecott flash smelting/flash converting processes do not require ladle transfer and therefore remove this source of secondary fume. Both of these processes however, still require some fume collection at launders and tap-holes and the flash converting process is dependent on furnace matte and converting slag granulation matte grinding and handling, which may be a potential source of some emissions to air and water. Nevertheless these processes are inherently cleaner and emission control does not rely as much on maintenance and operator care. In the Mitsubishi converting furnace matte is flowing into a molten copper bath and reacts by forming slag and metal; due to this reaction the blister copper leaving the converting and entering the anode furnace is high in sulphur. The off-gases are therefore comparatively higher in sulphur dioxide and require SO_2 removal at fire refining stage.

The gases collected from the converting cycles are cooled, cleaned and sent to a sulphur recovery system. As reported earlier, the SO_2 content of gases from converter operation is variable between 6 – 12% throughout the converting cycle, the gases are mixed with the strong gases from the smelting stage. The continuous converting processes have strong, constant concentrations of SO_2 and therefore enable comparatively smaller gas handling, cleaning and cooling systems and somewhat smaller sulphur conversion stages to be used

The ISA Smelt furnace is also used in a combined process of batch-wise smelting and copper/lead matte converting to blister copper.

Converter	**Capacity Range**	**Gas Collection**	**Advantages**	**Disadvantages**	**Comments**
Batch Converters.					
Peirce-Smith (or similar)	~ 100 to 250 (primary) and ~ 15 to 35 (secondary) tonnes per batch copper	Primary and secondary hoods.	Simple Proven Technology. Melting of anode and other scrap. Robust and flexible. Good metallurgical performance. Fuming of some metallic inclusions.	Relies on ladle transfers.	Vast process knowledge available. Use in primary and secondary production. Though hood charging is used.
Hoboken	~ 50 – 100 tonnes per batch of copper	Siphon for primary gas collection.	Gas collection easier.	Blockages in goose neck. Ladle transfer.	Mainly primary. Use also for copper/lead matte conversion.
TBRC	~ 40 – 70 tonnes per batch of copper	Enclosed.	Secondary smelting of scrap.		Use in secondary production.
ISA Smelt	~40000 tonnes per year	Hoods, gas cooling and cleaning			Primary and secondary. Not generally proven. Applied at the time of writing for batch-wise conversion of Cu/Pb matte.
Integrated converters.					
Mitsubishi	Up to ~ 240000 tonnes per year of copper	Sealed	High SO_2.	Difficult arrangement in existing plants. Closely coupled with smelting process.	Primary only. Practices additional Cu scrap treatment. May be applicable to other smelters.
Kennecott/ Outokumpu	~ 300000 tonnes per year of copper	Sealed	High SO_2 conc. Surge storage of Matte.	Melting of anode scrap not yet available. To date only applied in one smelter and a second under construction.	Primary only.

Table 3.26: Overview of converters for primary and secondary copper production

3.3.5.2 Secondary copper converters

As reported [tm 137, Copper Expert Group 1998], the most common converting stage for secondary production uses the Peirce-Smith (or similar converters), the TBRC and the ISA Smelt furnace. The TBRC, when used as a converter, is compact and is normally totally enclosed allowing collection of the secondary fume. Copper alloy scrap additions are made to the converter. Carbon additions are made for heat balancing and for the separation of elements like zinc or tin by volatilisation under reducing conditions. The same remarks apply to the fume collection systems that are used in primary copper production. Good operation of the converter therefore relies on the use of primary and secondary fume collection hoods during charging and pouring to collect as much fugitive fume as possible, dusts such as fluxes and carburant can be added through the hood. Automatic controls can prevent blowing during the periods that the converter is “rolled out”. Gases from the conversion of secondary copper secondary processes are treated by gas cooling (with heat/energy recovery if practicable), coarse particle separation and sulphur dioxide removal if necessary and fabric filtration.

These processes and the techniques for control and fume collection are suitable for use with new and existing installations and are techniques to consider.

3.3.6 Fire refining

Fire refining is described earlier. Rotary furnaces, reverberatory hearth furnaces, hearth shaft furnaces and the Contimelt process are all techniques to consider for primary and secondary smelters. They feature gas additions via tuyeres or lances. The hearth shaft furnace and the Contimelt process are designed for solid feed. The reverberatory hearth furnace takes solid and molten copper feed and the rotary furnace takes mainly molten copper feed. Molten copper feed normally requires the use of ladle transfer for filling and some fugitive emissions may have to be considered as potential problems at this point. Additions of scrap to refining furnaces can give rise to fugitive fume and scrap that is contaminated with organic material should be avoided. The rate of addition of scrap can be controlled.

Fume collection systems are used for the fire refining furnaces, the abatement system required will vary depending on the material used. The gas and fumes from the furnace are collected, after-burnt during the reduction stage, cooled and cleaned in fabric filters or scrubbers. Depending on the sulphur carry over from the converter, sulphur dioxide may need to be removed, e.g. by caustic scrubbing. For example when fire-refining blister copper from the Mitsubishi converting furnace, the off-gases can be comparatively higher in sulphur dioxide and require SO_2 removal.

Heat recovery from the refining furnace off-gas is a technique to consider at units melting solid material at high rates.

Casting of molten copper from the anode furnace into a casting wheel or continuous caster are techniques to consider.

The processes and the techniques for control, fume collection and sulphur dioxide removal are suitable for use with new and existing installations.

3.3.7 Electro-refining

Electro-refining processes that feature optimised cell dimensions (spacing, cell size etc), and use stainless steel cathode blanks or copper starter sheets are techniques to be considered. For existing tank houses the expense of conversion to stainless steel pre-formed cathodes may not be appropriate and copper starter sheets will be used in these instances. Mechanised (and automatic) harvesting and stripping as well as more elaborate short circuit detection is also worth considering depending on the scale of the operation.

The recovery of copper from solutions involves electro winning and in these cases gases are evolved at the anode and may produce an acid mist. Collection and removal of these mists is a technique to consider.

Sealed tank-house drainage systems and the recirculation of all solutions collected, the recovery of anode slimes and electrolyte bleed are also techniques to be considered.

3.3.8 Slag treatment processes

There are various sources of slag produced in the process. Their techniques to consider depends on the source but essentially smelter slags and some converter slags can be treated in slag treatment furnaces (electric) when carbon is added and the slag is decopperised to produce matte and clean slag. Some slags that are rich in copper such as converter slag can be returned to the smelting furnace or can be slow cooled and a copper rich portion separated, for example in a concentrate flotation unit. Slag cleaning by the injection of coal into the slag bath using a rotary furnace is also a technique to consider, slag fuming and slag re-circulation into the first stage smelting furnace (reduction or matte smelting stage) are also techniques to consider.

Decopperised slag has a very low leachable metal content and has several useful properties that allow its use in civil engineering and as a shot-blasting medium. The use or the recycling of slags and the recycling of filter dusts is considered to be part of the process.

3.3.9 Hydrometallurgical processes

The hydrometallurgical treatment of copper oxide and low grade sulphide ores is not practised in Europe at the time of writing but may have future uses for example at a mine site. The basic process outlined earlier and in Chapter 2 can have several variants depending on the characteristics of the ore. The background reports should be consulted [tm 130, Chadwick 1994; tm 137, Cu Expert Group 1998].

Because the hydrometallurgical processes involve leaching, solvent extraction and electrolytic stages adequate disposal of leached material needs to be considered as well as the containment of the solvent extraction mixers and settlers. The techniques discussed in Chapter 2 to prevent emissions to water for example by containing drainage systems are relevant as are the techniques to recover VOCs and to use of benign solvents.

3.3.10 Tin and other metals

The processes that were discussed earlier as available techniques are all considered being techniques to consider in the determination of BAT. The specific feed materials will influence the final process choice. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes.

3.3.11 Copper wire-rod

The processes that were discussed earlier as available techniques are all considered being techniques to consider in the determination of BAT. The use of advanced controls on the burners of a shaft furnace to optimise combustion and maintain minimum levels of CO while maintaining product quality should be considered.

3.3.12 Ingots, tubes and semi-finished products

The specific feed materials and the final products will influence the choice of process and the factors discussed under wire-rod will apply. If copper alloys are used in the process the melting temperature should be controlled, any fume produced during melting and casting should be collected efficiently and treated in a fabric filter, ZnO can be recovered from the fume. The techniques for temperature and process control discussed in Chapter 2 should also be considered in conjunction with these processes.

3.3.13 Fume/gas collection and abatement

The gas collection and abatement techniques discussed in section 2.7 and 2.8 of this document are techniques to be considered for the various process stages involved in the production of copper etc.

The identification of any organic contamination of secondary raw materials is particularly important to consider so that the most appropriate pre-treatment, furnace and abatement combination can be used to prevent fugitive emissions and destroy dioxins and other organic components in the off-gas.

The use of secondary hoods is also a technique to be considered the use of intelligent systems for the targeting of fume collection can reduce the energy demand of these systems. There are several site-specific issues that will apply and some of these are discussed in 3.3.1.1 of this chapter. The design of hooding systems needs to take account of access for charging and other furnace operations and the way the source of process gases change during the process cycle. Essentially the process technologies discussed in this chapter, combined with suitable abatement will meet the demands of stringent environmental protection.

Source	Component in off gas	Treatment Method
Poor combustion, organic material in feed	CO, VOC, dioxins	Process control Afterburner. Activated carbon injection,
Sulphur in fuel or raw material	Sulphur dioxide	Wet or semi-dry scrubber system, lime injection.
Combustion conditions	NO_x	Process control, correct use of oxygen. Catalytic reduction.
Furnace and handling molten materials	Dust Metal oxide fume	Scrubber and/or fabric filter.

Table 3.27: Abatement methods to consider

EXAMPLE 3.05 TARGETED SECONDARY FUME TREATMENT

Description: - Treatment of secondary fume and ventilation gases by SO_2 absorption and fabric filter.

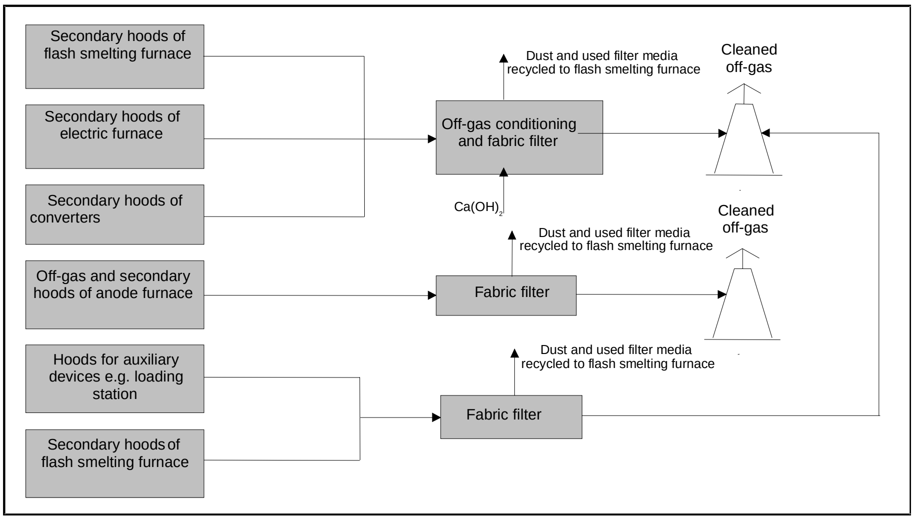


Figure 3.12: General arrangement of the system

Secondary gases from ventilation area:	Converter secondary hoods, electric slag cleaning furnace hoods, electric slag cleaning furnace off-gases, ventilation systems at flash furnace, anode furnaces, reverts handling and preparation.
Inlet Conditions:	
Max design volume :	580000 Nm^3/h
Volume variation:	~ 350000 to 550000 Nm^3/h
Absorbent for SO_2 removal:	Slaked lime
Average dust & absorbent content:	1500 mg/Nm^3
Range dust :	1 – 5 g/Nm^3
SO_2 inlet range :	100 – 1500 mg/Nm^3
Outlet conditions:	
Volume variation:	~ 350000 to 550000 Nm^3/h
Average residual dust:	< 2 mg/Nm^3
Range residual dust :	1 - 7 mg/Nm^3
Range components:	
Cd	< 0.01 – 0.1 mg/Nm^3
As	< 0.01 – 0.8 mg/Nm^3
Ni	< 0.01 – 0.3 mg/Nm^3
Se	< 0.01 –0.9 mg/Nm^3
Sb	< 0.01 – 0.5 mg/Nm^3
Cu	< 0.02 – 2 mg/Nm^3
Sulphur absorption	~50 to 70 %

Table 3.28: Performance data of the system

The installation uses a system of 3 secondary hoods in addition to the main hood. These hoods can be connected either to the sulphuric acid plant (hood 1) or to the secondary cleaning system (hoods 2 & 3). During filling and pouring operations the individual hoods are motor-driven to the positions that ensure optimal collection efficiency. Intelligent controls are used. The converter hood arrangement is shown below: -

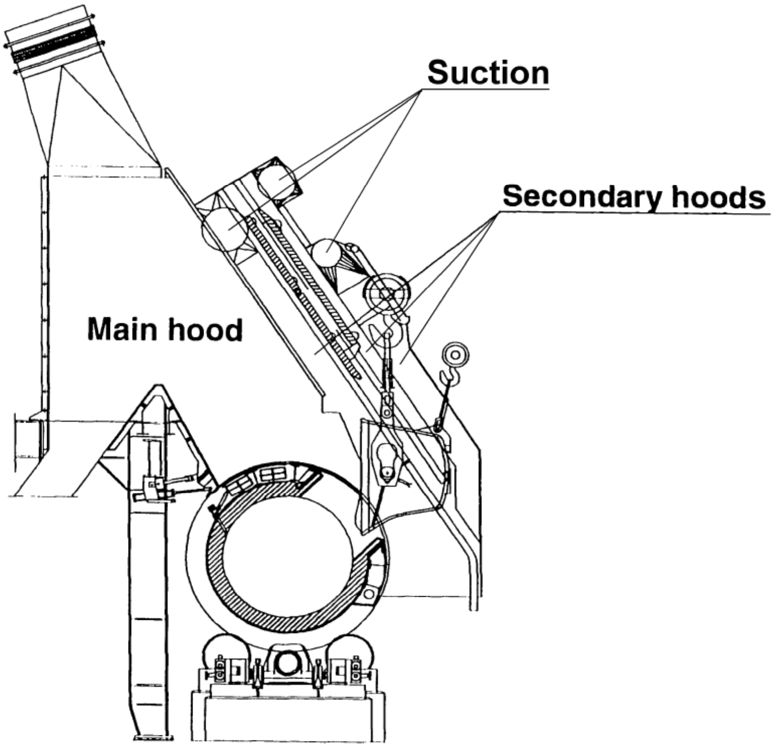


Figure 3.13: Targeted secondary fume capture system
[tm 201, Velten 1999]

Main environmental benefits:- Collection and treatment of fugitive emissions. Minimisation of energy use.

Operational data: - 99% fume capture achieved

	Dust emission kg/a	
	Before additional secondary gas collection (1992)	**After additional secondary gas collection (1996)***
Anode production t/a	220000	325000
Fugitive emissions: -		
Total Smelter	66490	32200
Smelter roofline	56160	17020
Controlled emissions (Primary smelter): -		
Smelter/acid plant	7990	7600
Secondary hoods stack	2547	2116
Note. * Emissions after an investment of 10 million Euros to give an improved fugitive gas capture and treatment system. Additional energy = 13.6 GWh/a		

Table 3.29: Performance of secondary fume capture improvements

Cross media effects: - Positive effect - Reduction in energy usage compared to total ventilation air capture, reduction of main emissions

Economics: - 23 million DM for complete system including hooding, ducts, controls. Energy consumption 13.6 GWh/a. See also appendix on cost data.

Applicability: - Most converter processes. Applicable to a range of furnaces such as the El Teniente and Noranda furnaces.

Example plants: - Germany.

Reference literature : - [tm 161, Petersen 1999]; [tm 92, Cu Expert Group 1998].

EXAMPLE 3.06 COLLECTION OF VENTILATION GASES AT THE ROOF LINE

Description: - Converter aisle fume collection system to treat the ventilation gases. All of the ventilation gases are collected at the roofline. They are treated to remove dust, metals and sulphur dioxide.

Main environmental benefits: - Collection of fugitive emissions from the converter aisle.

Operational data: - 99.9% fume capture achieved from smelter/converter building producing 170000 t/a anodes, gases are cleaned in combination with dryer gases. Limited SO_2 removal possible with current system using EP.

Emissions	**Emission point**		
	Primary capture 200000 Nm^3/h	**Secondary capture 1000000 Nm^3/h**	**Fugitive**
Sulphur dioxide.	523 t/a	2242 t/a	147 t/a

Table 3.30: Performance of gas treatment after roofline capture

Cross media effects: - Overall positive effect – Very energy intensive but a reduction of total emissions

Economics: - Not available but 2 plants are operating viably.

Applicability: - Most converter processes.

Example plants: - Sweden, Finland

Reference literature: - [tm 140, Finland Cu 1999]; [tm 106, Farrell 1998].

The use of hoods for tapping and casting is also a technique to consider. Tapping fume will consists of fumes from oxygen lancing, dust from drilling, fumes from the vaporised slugs if a tapping gun is used and fumes from all exposed metal and slag surfaces. These fumes will consist mainly of oxides of the metals that are involved in the smelting process.

The furnace gases that are collected are usually very hot and cooling or energy recovery is used to prevent damage to abatement equipment. Conversion to sulphuric acid or production of sulphur dioxide is the technique for primary copper. Fabric filters and /or scrubbers are used for secondary copper and for the drying and fire refining stages, scrubbing or dry gas de-sulphurisation methods to remove lower concentrations of sulphur dioxide are techniques to consider.
The following two examples illustrate the use of after-burning, cooling, neutralisation and filtration.

EXAMPLE 3.07 AFTER-BURNING, GAS COOLING AND FABRIC FILTER

Description: - Post combustion chamber and gas treatment comprising coke/lime treatment followed by fabric filter. Post combustion system used for a blast furnace producing 15200 t/a black copper. Gas volume 32000 Nm^3/h.

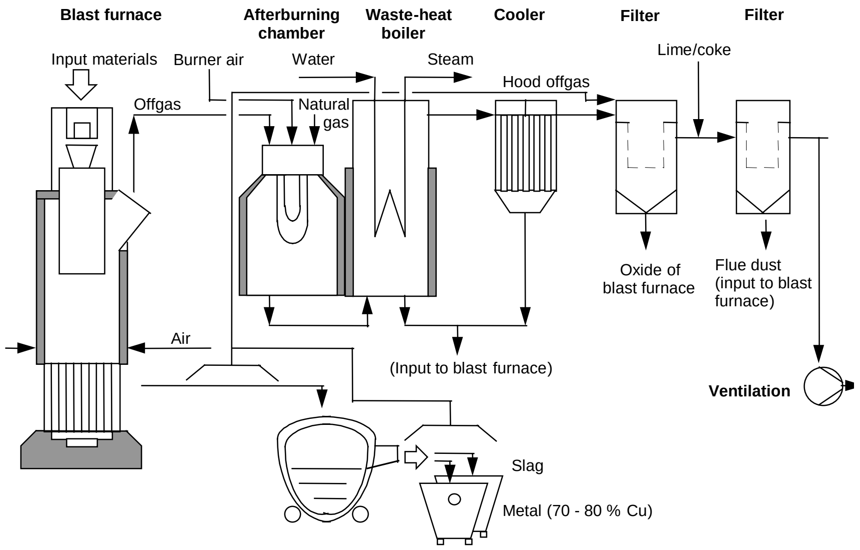


Figure 3.14: General arrangement of an afterburner system

Main environmental benefits: - Destruction of dioxins. Destruction of CO and other carbon.

Operational data: - Dioxins < 0.1 ng/Nm^3 TEQ achieved.

Cross media effects: - Positive effect - Reduction of main emissions. Recovery of other metals.

Economics: - Installed cost of afterburner and fabric filter ~ 1.5 million €. See also Appendix on costs.

Applicability: - Most blast furnaces, applicable to other furnaces with the same requirement to cool gases and remove CO, SO_2 and dust.

Example plants: - In use in plants in Austria and Germany.

Reference literature: - [tm 124, DFIU Cu 1999], [tm 160, Winter Cu 1999], [tm 226, VDI 2102 1999]

EXAMPLE 3.08 GAS COOLING AND FABRIC FILTER

Description: - Gas cooling system and fabric filter. Incorporates lime addition if sulphur dioxide is present in the gases.

Main environmental benefits: - Treatment of gases from converter and fire refining furnaces to remove dust and metals.

Operational data: - Dust - 1 - 3 mg/Nm^3. Cu+Pb+Zn < 0.2 mg/Nm^3

Cross media effects: - Positive effect - Efficient reduction of dust and metals. Recovery of Zn and Pb etc.

Economics: - Not available but viable operation established. Similar process in appendix on costs.

Applicability: - Most converter and anode furnaces. Applicable to dryers.

Example plants: - In use at a plant in Austria.

Reference literature: - [tm 160, Winter Cu 1999]

3.3.14 Process control and management

The principles of process control and management such as the use of ISO 9000 systems discussed in Chapter 2 are applicable to the production processes used in this Group. Some of the furnaces and processes are capable of improvement by the adoption of many of these techniques. Temperature control of furnaces used for melting copper alloys is a technique to consider. Operator training, provision of operational instruction and the management systems to implement these factors are vital. Systems for preventative maintenance should also be considered where justified or required.

3.3.15 Wastewater

This is a site-specific issue, existing treatment systems are reported to be to a high standard. All wastewater should be treated to remove dissolved metals and solids. The techniques listed in Chapter 2 are the techniques to consider. In a number of installations cooling water and treated wastewater including rainwater is reused or recycled within the processes. Run-off water, if collected and kept separately, should be treated by settlement and/or pH adjustment before release.

EXAMPLE 3.09 WASTEWATER TREATMENT

Description: - Treatment of weak acid from the sulphuric acid plant, various acidic wash waters using lime and iron sulphate.

Main environmental benefits: - Minimum wastewater discharge, reduction in water consumption.

Operational data:

Inlet Conditions:		
Flow:	35	m^3/h
Content:		
H_2SO_4	60	g/l
Cu	2100	mg/l
Hg	15	mg/l
As	2200	mg/l
Pb	2600	mg/l
Ni	7	mg/l
Cd	110	mg/l
Suspended solids	200	mg/l
Effluent water*:		
Flow	31.2	m^3/h
pH	9.5	
Cu	0.2 - 0.5	mg/l
Hg	0.05	mg/l
As	0.1	mg/l
Pb	0.2	mg/l
Ni	0.5	mg/l
Cd	0.1	mg/l
Gypsum sludge: - Amount:	6 – 7	t/h
: - Composition	40 – 50	%moisture
	~ 30 - 35	%$CaSO_4$
	~ 1	%As (as arsenic compound),
	~ 1	% Cu,
	~ 1 – 2	% Fe,
	~ 0.01	% Hg,
	~ 1	Pb,
	~ < 0.1	% Ni,
	~ < 0.1	% Cd.

* Design data taking variations in effluent into account.

Table 3.31: Performance data for the treatment of weak acid

Cross media effects: - Positive effect - Reduction of main discharges to water, possible re-use of waste-waster and sludge.

Economics: - Equipment cost 2.5 million Euros, installed costs 4.5 to 5.2 million Euros. Electricity 200kw. Milk of lime (10%); 15 m^3/h. H_2SO_4 (10%); 0.8 m^3/h. $FeSO_4.7H_2O$; 80 kg/h

Applicability: - Most process water systems.

Example plants: - Project under construction in EU.

Reference literature : - [tm 210, Cu Expert Group 1999]

EXAMPLE 3.10 WASTEWATER TREATMENT AND REUSE

Description: - Surface water and process effluent collection and treatment system. Includes treatment with NaHS followed by settlement and sand filter. Water is re-used within the process and for stock yard watering.

Main environmental benefits: - Minimum waste-water discharge, reduction in water consumption.

Operational data: - Maximum water re-use achieved. 110000 m^3/a discharged.

Component	Secondary copper process water after treatment with NaHS, settlement and sand filtration
Cu mg/l	0.04
Pb mg/l	0.04
Ni mg/l	0.07
Zn mg/l	0.13
As mg/l	< 0.01
Cd mg/l	0.004
Suspended solids mg/l	1.0

Table 3.32: Performance data for a treatment system using NaHS

Cross media effects: - Positive effect - Reduction of main discharges to water, re-use of waste-waster.

Economics: - Not available but in operation and economically viable.

Applicability: - Re-use of rainwater for damping scrap area.

Example plants: - Belgium.

Reference literature: - [tm 106, Farrell 1998].

EXAMPLE 3.11 COOLING WATER TREATMENT

Description: - Treatment of direct cooling water bleed applied in an anode casting system.

Main environmental benefits: - Minimum waste-water discharge, reduction in water consumption.

Operational data:

Type of treatment:	**Settling, pH adjustment and precipitation**	
Raw water: Quantity:	~ 350000 m^3/a	
Main components:	Before treatment	In effluent
pH		8.5 – 9.5
mg/l Cu,	< 30	0.01 – 0.25
mg/l Pb,	< 2.5	0.001 – 0.1
mg/l As	< 2.0	0.001 – 0.1
mg/l Ni	< 0.5	0.002 – 0.06
mg/l Cd,	< 0.01	0.0001 – 0.003
mg/l Zn	< 1.0	0.02 – 0.5

Table 3.33: Performance data for a cooling water bleed treatment system

Cross media effects: - Positive effect - Reduction of main discharges to water.

Economics: - Not available but the system is operating viably.

Applicability: - Re-use of rainwater for damping scrap area.

Example plants: - In use in a plant in Germany.

Reference literature: - [tm 210, Cu Expert Group 1999]

3.3.16 Process residues

The available techniques comprising the recovery of metals from the residues and the minimisation of waste for final disposal are the techniques to consider.

3.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector; which for the production of copper are SO_2, dust, metal oxide fume, organic compounds, wastewater, residues such as furnace linings, sludge, filter dust and slag. Dioxin formation during treatment of secondary copper materials is also an issue;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous section. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this section are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

Best Available Techniques are influenced by a number of factors in this sub-sector and a methodology of examining the techniques is needed. The approach that has been used is given below.

- First of all the choice of process depends strongly on the raw materials that are available to a particular site. The most significant factors are the composition, the presence of other included metals, their size distribution (including the potential to form dust) and the degree of contamination by organic material. There may be primary materials available from single or multiple sources, secondary raw materials of varying quality or a combination of primary and secondary raw materials.

- Secondly the process should be suitable for use with the best gas collection and abatement systems that are available. The fume collection and abatement processes used will depend on the characteristics of the main processes, for example some processes avoid ladle transfers and are therefore easier to seal. Other processes may be able to treat recycled materials more easily and therefore reduce the wider environmental impact by preventing disposal.

- Finally, the water and waste issues have been taken into account, in particular the minimisation of wastes and the potential to reuse residues and water within the process or by other processes. Energy used by the processes and abatement is also a factor that is taken into account in the choice of processes.

The choice of BAT in a general sense is therefore complicated and depends on the above factors. The varying requirements mean that BAT is influenced mainly by the raw materials available to the site and the required throughput of the plant, the issues are therefore site specific. There are advantages for some primary process that are capable of accepting some secondary materials.

The following points summarise the recommended methodology that has been used in this work: -

- Is the process industrially proven and reliable?
- Are there limitations in the feed material that can be processed? -e.g. In primary smelting some processes are suited for “clean” concentrate and others for complex feed smelting.
- The type of feed and other metals contained in it (e.g. Pb, Zn) influences process selection.
- Are there production level constraints? - e.g. a proven upper limit or a minimum throughput required to be economic.
- Can latest and efficient collection and abatement techniques be applied to the process?
- Can the process and abatement combinations achieve the lowest emission levels? The associated emissions are reported later.

- Are there other aspects such as safety that are related to processes?

At the time of writing several process and abatement combinations could be operated to the highest environmental standards and meet the requirements of BAT. The processes vary in the throughput that can be achieved and the materials that can be used and so several combinations are included. All of the processes maximise the reuse of residues and minimise emissions to water. The economics of the processes vary. Some need to operate at a high throughput to achieve economic operation, while others are not able to achieve high throughputs.

The collection and abatement techniques used with these processes were discussed in Chapter 2 and under techniques to consider in the determination of BAT in this chapter and when applied in combination with the metallurgical process will result in a high level of environmental protection.

As indicated in the general preface to this document, this section proposes techniques and emissions that are considered to be compatible with BAT in general. The purpose is to provide general indications of the emission and consumption levels that might be considered as an appropriate benchmark of BAT based performance. This is done by quoting achievable levels in ranges that are generally applicable to both new and upgraded plants. Existing installations may have factors, such as space or height limitations that prevent full adoption of the techniques.

The level will also vary with time depending on the condition of the equipment, its maintenance and the process control of the abatement plant. The operation of the source process will also influence performance as there are likely to be variations in temperature, gas volume and even the characteristics of the material throughout a process or batch. The achievable emissions are therefore only a basis from which actual plant performance can be judged. Process dynamics and other site-specific issues need to be taken into account at a local level. The examples given in the section on techniques to consider in the determination of BAT give the concentrations associated with some existing processes [tm 137 Cu Expert Group 1998].

3.4.1 Materials handling and storage

The conclusions drawn for Best Available Techniques for the materials handling and storage stages are given in section 2.17 of this document and are applicable to the materials in this chapter. These techniques are:

- The use of liquid storage systems that are contained in impervious bunds that have a capacity capable of containing at least the volume of the largest storage tank within the bund. Various guidelines exist within each Member State and they should be followed as appropriate. Storage areas should be designed so that leaks from the upper portions of tanks and from delivery systems are intercepted and contained in the bund. Tank contents should be displayed and associated alarms used. The use of planned deliveries and automatic control systems to prevent over filling of storage tanks.

- Sulphuric acid and other reactive materials should also be stored in double walled tanks or tanks placed in chemically resistant bunds of the same capacity. The use of leak detection systems and alarms is sensible. If there is a risk of ground water contamination the storage area should be impermeable and resistant to the material stored.

- Delivery points should be contained within the bund to collect spilled of material. Back venting of displaced gases to the delivery vehicle should be practised to reduce emissions of VOCs. Use of automatic resealing of delivery connections to prevent spillage should be considered.

- Incompatible materials (e.g. oxidising and organic materials) should be segregated and inert gases used for storage tanks or areas if needed.

- The use of oil and solid interceptors if necessary for the drainage from open storage areas. The storage of material that can release oil on concreted areas that have curbs or other containment devices. The use of effluent treatment methods for chemical species that are stored.

- Transfer conveyors and pipelines placed in safe, open areas above ground so that leaks can be detected quickly and damage from vehicles and other equipment can be prevented. If buried pipelines are used their course can be documented and marked and safe excavation systems adopted.

- The use of well designed, robust pressure vessels for gases (including LPG's) with pressure monitoring of the tanks and delivery pipe-work to prevent rupture and leakage. Gas monitors should be used in confined areas and close to storage tanks.

- Where required, sealed delivery, storage and reclamation systems can be used for dusty materials and silos can be used for day storage. Completely closed buildings can be used for the storage of dusty materials and may not require special filter devices.

- Sealing agents (such as molasses and PVA) can be used where appropriate and compatible to reduce the tendency for material to form dust.

- Where required enclosed conveyors with well designed, robust extraction and filtration equipment can be used on delivery points, silos, pneumatic transfer systems and conveyor transfer points to prevent the emission of dust.

- Non-dusty, non-soluble material can be stored on sealed surfaces with drainage and drain collection.

- Swarf, turnings and other oily material should be stored under cover to prevent washing away by rainwater.

- Rationalised transport systems can be used to minimise the generation and transport of dust within a site. Rainwater that washes dust away should be collected and treated before discharge.

- The use of wheel and body washes or other cleaning systems to clean vehicles used to deliver or handle dusty material. Local conditions will influence the method e.g. ice formation. Planned campaigns for road sweeping can be used.

- Inventory control and inspection systems can be adopted to prevent spillages and identify leaks.

- Material sampling and assay systems can be incorporated into the materials handling and storage system to identify raw material quality and plan the processing method. These systems should be designed and operated to same high standards as the handling and storage systems.

- Storage areas for reductants such as coal, coke or woodchips need to be surveyed to detect fires, caused by self-ignition.
- The use of good design and construction practices and adequate maintenance.

The summary table for material handling and storage is reproduced below.

Raw Material	Storage	Handling	Pre-treatment	Comment
Coal or Coke.	Covered Bays, Silos.	Covered conveyors if non-dusty. Pneumatic.		
Fuel and other oils.	Tanks or drums in bunded areas.	Secure pipeline or manual system.		
Fluxes. If dust forming	Open on concrete or similar, floors. Enclosed (Silo) if required	Enclosed conveyors with dust collection. Pneumatic.	Blending with concentrates or other material.	
Concentrates.	Enclosed unless non-dust forming.	Enclosed with dust collection. Pneumatic.	Blending using conveyors. Drying.	
Copper Products – Cathodes, wire-rod, copper billets and cakes.	Open concrete area or covered storage.			
Fine dust.	Enclosed.	Enclosed with dust collection. Pneumatic.	Blending, Agglomeration.	
Coarse dust (raw material or granulated slag)	Covered Bays	Mechanical loader.	De-oiling if necessary	Oil collection if necessary
Lump (raw material or slag).	Open	Mechanical loader.		Oil collection if necessary
Whole Items	Open or Covered Bays	Mechanical loader.		Oil collection if necessary
Swarf	Covered storage	Charge skips	Swarf drying or de-oiling.	Oil collection if necessary
Cable.	Open	Mechanical loader.	De-coating.	
Circuit Boards.	Covered Bays	Mechanical loader.	Grinding + density separation.	Plastic content may provide heat input.
Process residues for recovery.	Open, covered or enclosed depending on dust formation.	Depends on conditions.		Appropriate drainage system.
Wastes for Disposal. (e.g. furnace linings)	Open covered or enclosed bays or sealed (drums) depending on the material.	Depends on conditions.		Appropriate drainage system.

Table 3.34: Summary of handling and storage techniques for copper

3.4.2 Process selection

It is not possible to conclude that a single production process can be applied to this group of metals. The techniques for the following process stages are considered to be BAT for the raw materials that are available.

3.4.2.1 Primary copper smelting

Taking these factors into consideration the following combinations, when used with appropriated collection and abatement techniques, are considered to be BAT for the production of copper.

- The continuous processes from Mitsubishi and Outokumpu/Kennecott are considered to be BAT for the smelting and converting stage in primary copper production. While at the moment the Outokumpu/Kennecott system processes primary raw materials only, the Mitsubishi system also treats copper secondary raw material and scrap but may have a higher sulphur dioxide emission from the anode furnace. These processes use sealed furnaces, do not depend on ladle transfer of molten matte and other materials and are therefore inherently cleaner. The collection and treatment of fume from granulating stages and from launders remains a potential source as well as the separate melting of (anode) scrap, where this is required. These processes have different capital costs, operating costs and capacities and the final choice depends on local conditions such as the raw material that are available and the desired throughput.

- Similar environmental performance, using concentrate blends from various sources, can be achieved using the Outokumpu Flash Smelting Furnace. For smaller throughputs the ISA Smelt furnace has been proven at the mine site. These furnaces are used in combination with the Peirce-Smith (or similar) converter.

- The combination of partial roasting in a fluid bed roaster, electric furnace matte smelting and Peirce-Smith converter offers advantages for the treatment of complex feed materials allowing recovery of other metals contained in the concentrate like zinc and lead.

- The use of the Outokumpu Flash Smelting Furnace for direct smelting to blister copper using specific concentrates with a low iron content or very high grade concentrates (low slag fall).

To achieve a high environmental standard, the converter stage for the non-continuous processes i.e. the Peirce-Smith (or similar) converter, needs to be provided with advanced primary and secondary gas collection systems. The hooding systems should be designed to allow access for the ladle transfers while maintaining good fume collection. This can be achieved by the use of a system of intelligent control to target fume emissions automatically as they occur during the cycle without the high-energy penalty of continuous operation. An example is shown in techniques to consider in the determination of BAT. The blowing cycle of the converter and the fume collection system should be controlled automatically to prevent blowing while the converter is rolled out. Additions of materials through the hood or tuyeres should be used if possible. This combination provides potentially greater flexibility, allows the use of both primary and secondary raw materials and utilises the heat generated by the converting process for scrap melting.

The Noranda, El Teniente converter and Contop furnaces listed as techniques to consider may also achieve the same environmental performance as those listed above. They are currently operated under lower environmental standards but given good gas collection and abatement systems these processes may offer advantages in energy efficiency, cost, throughput and ease of retrofitting. The INCO flash furnace may also have advantages but operates with 100% oxygen resulting in a narrow operating window.

The information available for the Baiyin and the Vanyucov processes is limited. At the moment it does not allow an evaluation to be made in regard to their potential as BAT [tm 137, Copper Expert Group 1998].

Gases from the primary smelting and converting processes should be treated to remove dust and volatile metals, to recover heat or energy and the sulphur dioxide converted to sulphuric acid in a double contact sulphuric acid plant designed in accordance with the techniques to consider in the determination of BAT. Liquid sulphur dioxide production in combination with a contact plant to convert the residual sulphur dioxide into acid is BAT if a local market exists for the material.

Applied Technique	Raw Materials	Abatement Techniques	Comments
Outokumpu Flash Smelting/ Peirce-Smith Converter	Concentrate and copper scrap	Process gas: Acid plant Collection and cleaning techniques for fumes; Water treatment plants	The standard smelter concept with a high level of maturity, flexibility and environmental performance in combination with adequate abatement techniques. Capacities proven up to 370000 t/a copper.
Partial Roasting /Electric Furnace/ Peirce-Smith Converter	Normal and complex concentrates, lower grade secondary material, copper scrap.	Process gas: Acid plant Collection and cleaning techniques for fumes; Water treatment plants	Proven process concept, capacity practised up to 220000 t/a copper. For zinc recovery the process is combined with slag fuming.
Mitsubishi Continuous process.	Concentrate and copper scrap.	Process gas: Acid plant Collection and cleaning techniques for fumes; Water treatment plants.	To date two plants in operation and two more under construction. Capacities proven up to 240000 t/a copper.
Outokumpu - Kennecott Flash Smelting/Flash Converting process.	Concentrate.	Process gas: Acid plant Collection and cleaning techniques for fumes; Water treatment plants	In this combination only in one plant with single feed source in operation., capacity (flash converter) ~ 300000 t/y copper. A second plant on similar basis under construction.
ISA Smelt Furnace/Peirce-Smith Converter.	Concentrate and secondary.	Process gas: Acid plant Collection and cleaning techniques for fumes; Water treatment plants	Two plants in operation. Capacities proven up to 230000 t/a copper.
Noranda and El Teniente process /Peirce-Smith Converter	Copper concentrate, copper scrap (Noranda)	Process gas: Acid plant Collection and cleaning techniques for fumes; Water treatment plants	El Teniente widely used in Southern America, mainly for single source concentrates. Capacities proven up to 190000 t/a copper reached.
Contop /Peirce-Smith Converter	Copper Concentrate.	Process gas: Acid plant Collection and cleaning techniques for fumes; Water treatment plants	Only one plant. Potential for complex feed material. Capacity reached: 120000 t/a copper.
Inco Flash / Pierce Smith Converter	Copper Concentrate	Process gas: Acid plant Collection and cleaning techniques for fumes; Water treatment plants	So far in use in plants with mainly single source concentrate feed. Capacities proven up to 200000 t/a copper.

Table 3.35: Primary copper smelters considered as BAT

3.4.2.2 Secondary copper smelting

For the production of copper from secondary raw materials the variation in feed stock and the control of quality also has to be taken into account at a local level and this will influence the combination of furnaces, pre-treatment and the associated collection and abatement systems that are used. The processes that are considered to be BAT are Blast Furnaces, mini-smelter, TBRC, Sealed Submerged Arc Electric furnace, ISA Smelt, and the Peirce-Smith converter.

The submerged arc electric furnace is a sealed unit and is therefore inherently cleaner than the others, provided that the gas extraction system is adequately designed and sized. At the time of writing the electric furnace is also used for secondary material containing sulphur and is connected during such operation to a sulphuric acid plant. The gas volume produced is reported to be lower than the other furnaces [tm 92, Cu Expert Group 1998] and the size of the abatement plant could therefore be smaller.

For high grades of copper scrap without organic contamination, the reverberatory hearth furnace, the hearth shaft furnace and Contimelt process are considered to be BAT in conjunction with suitable gas collection and abatement systems.

3.4.2.3 Primary and secondary converting

The converting stage that can be used with these furnaces is any of the techniques that are listed as techniques to consider. If batch operated converters such as the Peirce-Smith converters (or similar) are used they should be used with total enclosure or efficient primary and secondary fume collection systems.

This can be achieved by the use of a system of intelligent control to target fume emissions automatically as they occur during the cycle without the high-energy penalty of continuous operation. An example is shown in figure 3.13. The blowing cycle of the converter and the fume collection system should be controlled automatically to prevent blowing while the converter is rolled out. Additions of materials through the hood or tuyeres should be used if possible. This combination provides potentially greater flexibility, allows the use of both primary and secondary raw materials and utilises the heat generated by the matte converting process for scrap.

The ISA Smelt furnace can be operated batch-wise. Smelting is carried out in a first stage followed by conversion of matte to blister or after secondary smelting under reducing conditions, for oxidisation of iron and eliminating zinc or tin in a second stage is also considered as BAT.

Applied Technique	Raw Materials	Abatement Technique	Comments
Blast Furnace.	Oxidic material.	After-burning, gas cooling * and cleaning** (fabric filter)	High energy efficiency. Capacity normally 150 - 250 t/d.
Mini Smelter (Totally enclosed).	Secondary inc. Fe, Pb & Sn	Gas cooling and cleaning (fabric filter)	Integrated with TBRC secondary process.
TBRC (Totally enclosed).	Secondary (most grades).	Gas cooling and cleaning (fabric filter)	Converter stage – TBRC (Totally enclosed). Capacity up to 70 tonnes /batch.
Sealed Submerged Arc Electric Furnace.	Secondary inc. Sn & Pb (except very low grade).	After-burning, gas cooling and cleaning**	Converter stage – Peirce-Smith (with primary and secondary fume collection). Capacity up to 25 t/h melting rate.
ISA Smelt. (Not proven for lower grade material under reducing conditions.)	Secondary (most grades).	Gas cooling * and cleaning **	Converter stage – Peirce-Smith or Hoboken (with primary and secondary fume collection). Capacity for sulphidic material ~40000 t/a.
Reverberatory hearth furnace	Secondary (higher grades). Blister copper, black copper.	After-burning, gas cooling and cleaning (fabric filter)**	Used for fire refining and smelting higher grades of secondary material.
Hearth shaft furnace.	Secondary (higher grades). Blister copper, black copper.	After-burning, gas cooling and cleaning (fabric filter)**	Used for melting and fire refining.
Contimelt	Secondary (higher grades). Blister copper	After-burning(reduction furnace), WHB and cleaning (fabric filter)**	Used for melting and fire refining.
Peirce-Smith (or similar) Type Converter.	Copper alloy scrap, black copper from blast furnace.	Gas cooling and cleaning** (fabric filter).	Ability to fume off other metals. Capacity 15 - 35 tonnes/batch.

Note. *) If the temperature level is high enough waste heat recovery may be considered; for cleaning in fabric filters further cooling is required.

**) The off-gas may contain sulphur dioxide during certain campaigns and can be treated in a scrubber or an acid plant at these times.

Table 3.36: Secondary copper smelters considered as BAT

3.4.2.4 Other processes and processing stages

Applying the methodology outlined above for the other process stages gives the following conclusion.

The other processes that are considered to BAT are: -

- The drying of concentrate etc in directly fired drum and flash dryers, in fluid bed and steam dryers.
- Slag treatment by electric furnace slag cleaning, slag fuming, crushing/grinding and slag flotation.
- Fire refining in rotary or tilting reverberatory furnaces. Anode casting in pre-formed moulds or in a continuous caster.
- Electrolytic copper refining by optimised conventional or mechanised permanent cathode technology.
- The hydro-metallurgical processes outlined in 3.1.1.2 are considered to be BAT for oxidic ores and low grade, complex and precious metal free copper sulphide ores. Techniques are emerging rapidly.
- The processes for the production of wire-rod, semis etc. by the Southwire, Contirod, Properzi & Secor, Upcast, Dip Forming, continuous casting and similar processes, form the basis of BAT for the production of these materials provided a high standard of abatement is achieved.
- The processes for the production of ingots, tin etc. that are described as techniques to consider form the basis of BAT for the production of these materials provided a high standard of abatement is achieved.

The particular technique used depends on the raw materials and other facilities available on or near the installation.

3.4.3 Gas collection and abatement

Best Available Techniques for gas and fume treatment systems are those that use cooling and heat recovery if practical before cleaning. Fabric filters that use modern high performance materials in a well-constructed and maintained structure are applicable. They feature bag burst detection systems and on-line cleaning methods. Gas treatment for the fire refining stage can include a sulphur dioxide removal stage and/or after-burning if this as considered necessary to avoid local, regional or long-range air quality problems.

Fume collection systems follow the best practice out lined in techniques described in earlier in this chapter and in section 2.7. Fume production from secondary raw materials can be minimised by the choice of the furnace and abatement systems. Some raw materials are contaminated with organic material and can be pre-treated before smelting to minimise fume production.

The fume collection systems used can exploit furnace-sealing systems and can be designed to maintain a suitable furnace depression that avoids leaks and fugitive emissions. Systems that maintain furnace sealing or hood deployment should be used. Examples are through hood additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems.

Process Stage.	Component in Off – gas.	Abatement option.
Raw Materials Handling	Dust and metals.	Correct storage, handling and transfer. Dust collection and fabric filter
Raw materials thermal pre-treatment	Dust and metals. Organic material* and carbon monoxide.	Correct pre-treatment. Gas collection and fabric filter Process operation, after-burning and correct gas cooling.
Primary Smelting	Dust and metals. Sulphur dioxide. Hg.	Process operation and gas collection, gas cleaning followed by gas cooling/final cleaning and sulphuric acid plant or sulphur dioxide recovery (normally followed by sulphuric acid plant). If high in feed: removal after SO_2 gas cleaning.
Secondary Smelting	Dust and metals. Organic material* and carbon monoxide. Sulphur dioxide. **	Process operation and gas collection, cooling and cleaning by fabric filter Process operation, after-burning if necessary and correct gas cooling. Scrubbing if necessary.
Primary Converting	Dust and metals. Sulphur dioxide.	Process operation and gas collection, gas cleaning followed by sulphuric acid plant
Secondary Converting	Dust and metal vapour or compounds. Organic material. * carbon monoxide. *** Sulphur dioxide. **	Process operation and gas collection, cooling and cleaning by fabric filter. Process operation, after-burning if necessary and correct gas cooling. Scrubbing if necessary.
Fire Refining	Dust and metals Organic material. * carbon monoxide. **** Sulphur dioxide**	Process operation and gas collection, cooling and cleaning by fabric filter or scrubber. Process operation, after-burning (if necessary during poling) and correct gas cooling. Scrubbing if necessary.
Melting and Casting	Dust and metals Organic material. * carbon monoxide.	Process operation and gas collection, cooling and cleaning by fabric filter. Process operation, after-burning if necessary and correct gas cooling.
Anode casting and slag granulation.	Water vapour	Wet scrubber or de-mister if necessary.
Pyro-metallurgical slag treatment processes	Dust and metals Carbon monoxide Sulphur dioxide	Process operation and gas collection, cooling and cleaning by fabric filter. After-burning if necessary. Treatment for removal
Note. * Organic materials include VOC reported as total carbon (excluding CO) and dioxins, the exact content depends on the raw materials used. ** Sulphur dioxide may be present if sulphur containing raw materials or fuels are used. Carbon monoxide may be produced by poor combustion, the presence of organic material or deliberately to minimise oxygen content. *** For batch process, CO only at start of the blow **** CO only when not after-burning		

Table 3.37: Summary of the abatement methods for components in off-gases

Secondary fume collection is expensive and consumes a lot of energy but is needed in the case of some batch converters and for the ventilation of tap-holes, launders etc. The use of an intelligent system capable of targeting the fume extraction to the source and duration of any fume is more energy efficient.

The table 3.37 summarises the options considered to be BAT for abatement processes for the components likely to be present in the off-gases. There may be raw material variations that influence the range of components or the physical state of some components such as the size and physical properties of the dust produced, these should be assessed locally.

3.4.3.1 Emissions to air associated with the use of BAT

Emissions to air comprise the captured/abated emissions from the various sources, plus the fugitive or uncaptured emissions from these sources. Modern, well operated abatement systems result in efficient removal of pollutants and the information at the time of writing indicates that the fugitive emissions can be the largest contributor to the total emissions to air.

a) For primary copper the total emissions to air are based on the emissions from:
  - The material reception, storage, blending and sampling.
  - The smelting, converting and fire refining furnaces and anode casting with the associated metal transfer and hot gas handling and cleaning system.
  - The slag cleaning furnace, slag granulation and slag handling system.
  - The wet gas cooling and cleaning section and the sulphuric acid plant.
  - The electrolytic copper refinery.

b) For secondary copper the total emissions to air are based on the emissions from:
  - The material reception, storage, blending and sampling.
  - The smelting, converting and fire refining furnaces and anode casting with the associated metal transfer and hot gas handling and cleaning system.
  - The slag handling system.
  - The electrolytic copper refinery.

c) For copper wire-rod fabrication the total emissions to air are based on the emissions from:
  - The melting, refining (if applied) and holding furnaces with the associated hot gas handling and cleaning system.
  - The casting machinery, the rod mill and auxiliary equipment.

d) For copper semis fabrication and ingot production the total emissions to air are based on the emissions from:
  - The material reception and storage.
  - The melting, refining and holding/casting furnaces with the associated hot gas handling and cleaning system and ladle transfer system.
  - The casting machinery, the fabrication units and auxiliary equipment.

Fugitive emissions can be highly significant and should be assessed locally. They can be predicted from the furnace gas capture efficiency and can be estimated by monitoring (see section 2.7).

The following tables summarise the captured emissions associated with the use of best available techniques for collected emissions.

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
SO_2 – rich off-gas streams (> 5%)	> 99.7% conversion factor	Double contact sulphuric acid plant (Tail gas SO_2 content depends on feed gas strength). A de-mister may be appropriate for the final removal of SO_3.	Very low levels for other air-borne pollutants will be reached due to intensive gas treatment prior to the contact plant (wet scrubbing, wet EP and, if necessary, mercury removal) to ensure H_2SO_4 product quality
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used. > 99.9% conversion factor has been achieved in a plant with a high, constant sulphur dioxide feed, sophisticated gas cleaning and inter-pass cooling.			

Table 3.38: Emissions to air from primary smelting and converting associated with the use of BAT in the copper sector
Lower strength gases may be produced from complex metallurgical processes used to produce copper, lead and precious metals. Data is provided in the lead and precious metal chapters

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Acid mists	< 50 mg/Nm³	De-mister, Wet scrubber.	A de-mister or water scrubber will allow the collected acid to be reused.
VOC or solvents as C	< 5 - 15 mg/Nm^3	Containment, condenser, carbon or bio filter.	
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 3.39: Emissions to air from hydrometallurgical and electro-winning processes associated with the use of BAT in the copper sector
There are no acid mists from Electro-refining processes

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 - 5 mg/Nm^3	Fabric filter.	The characteristics of the dust will vary with the raw materials and affect the value achieved. High performance fabric filters can achieve low levels of heavy metals. The concentration of heavy metals is linked to the concentration of dust and proportion of the metals in the dust.
SO_2	< 50 - 200 mg/Nm³	Alkali semi-dry scrubber and fabric filter. Wet alkali or double alkali scrubbers using lime, magnesium hydroxide, sodium hydroxide. Combinations of sodium or alumina/aluminium sulphate in combination with lime to regenerate the reagent and form gypsum.	Potential cross-media effects from energy use, wastewater and solid residues together with the ability to re-use scrubber products will influence the technique used.
NO_x	< 100 mg/Nm^3 < 100 - 300 mg/Nm^3	Low NO_x burner. Oxy-fuel burner.	Higher values are associated with oxygen enrichment to reduce energy use. In these cases gas volume and mass emission is reduced.
Total organic carbon as C	< 5 - 15 mg/Nm^3 < 5 - 50 mg/Nm^3	Afterburner. Optimised combustion.	Pre-treatment of secondary material to remove organic coatings if necessary.
Dioxins	< 0.1 - 0.5 ng TEQ/Nm^3	High efficiency dust removal system (i.e. fabric filter), afterburner followed by quenching.	Other techniques are available (e.g. adsorption on activated carbon: - carbon filter or by injection with lime/carbon). Treatment of a clean de-dusted gas is required to achieve low levels.

Note. Collected emissions only.
Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period.
For the abatement system used, the characteristics of the gas and dust be taken into account in the design of the system and the correct operating temperature used. For SO_2 or total carbon removal, the variation in raw gas concentration during batch processes may affect the performance of the abatement system. For example converter "blows" will produce peak raw gas concentrations and consequently the number cycles per day influence the associated range (given as a daily average), a similar effect may be seen with other batch process stages. Peak concentrations in the treated gas may be up to 3 times the reported range. For NO_x, the use of highly efficient processes (e.g. Contimelt) requires a balance to be established locally between energy use and achieved value.

Table 3.40: Emissions to air from secondary smelting and converting, primary and secondary fire refining, electric slag cleaning and melting associated with the use of BAT in the copper sector

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 - 5 mg/Nm^3	Fabric filter with lime injection (for SO_2 collection/filter protection).	Dust re-circulation may be used for fabric protection/fine particle capture. The concentration of heavy metals is linked to the concentration of dust and proportion of the metals in the dust.
SO_2	< 500 mg/Nm^3 < 50 - 200 mg/Nm^3	Fabric filter with dry lime injection into a cool gas. Alkaline wet scrubber for SO_2 collection from hot gases (from dryer gases after dust removal).	There are potentially significant cross media effects using wet or semi-dry scrubbing systems with a cool gas.
Dioxins	< 0.1 - 0.5 ng TEQ/Nm^3	Fabric filter with lime injection for filter protection.	Treatment of a clean de-dusted gas is required to achieve low levels.
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 3.41: Emissions to air from secondary fume collection systems and drying processes associated with the use of BAT in the copper sector

The metal content of dust varies widely between processes. In addition, for similar furnaces there are significant variations in metal content due to the use of varying raw materials and the use of the furnaces to separate minor elements for subsequent collection and enrichment for further processing. It is therefore not accurate to detail specific achievable concentrations for all metals emitted to air in this document.

The issue is site specific but the following table gives some indication of the effects on the contents of metals in dust that will be encountered locally.

Component	Concentrate to matte smelting furnace EP dust	Blast furnace dust	Scrap converter dust	Matte converter EP dust	Electric slag cleaning furnace dust	Anode furnace dust
Pb%	0.1 – 5	5 – 40	5 – 30	2 – 25	2 - 15	2 – 20
Zn%	0.1 – 10	20 – 60	25 – 70	5 – 70	25 - 60	5 – 40
Sn%	0.1 – 1	0.2 – 5	1 – 20	0.1 – 4		
Cu%	5 – 30	2 – 12	2 - 15	10 – 25	0.5 – 2.5	15 – 25
As%	0.1 – 4					0.5 – 10
Ni%	0.1 – 1	0.1 - 1		0.1 - 1		

Table 3.42: Metal content of some dusts from various copper production processes

Some metals have toxic compounds that may be emitted from the processes and so need to be reduced to meet specific local, regional or long-range air quality standards. It is considered that low concentrations of heavy metals are associated with the use of high performance, modern abatement systems such as a membrane fabric filter provided the operating temperature is correct and the characteristics of the gas and dust are taken into account in the design.

3.4.4 Wastewater

This is a site-specific issue, existing treatment systems are reported to be to a high standard. All wastewater will be treated to remove solids and oils/tars, absorbed acid gases (e.g. sulphur dioxide, HCl) should be reused if possible or neutralised if necessary. The sources of the emissions to water are: -

a) For primary and secondary copper the total emissions to water are based on:
- The slag treatment or granulating system.
- The electrolytic copper refinery with the electrolyte purification circuit and anode slime leaching section.
- The wastewater treatment system and run-off water.
- The weak sulphuric acid from the SO_2 gas cooling and cleaning in combination with wastewater treatment.

b) For copper wire-rod, semis and ingot production the total emissions to water are based on:
- The wastewater treatment system.

Examples of wastewater treatment applied in several processes are given in the section on techniques to consider in the determination of BAT above and for process waters comprise treatment with hydroxide or sulphide precipitants depending on the metals contained followed by sedimentation and, if necessary, filtration. The examples show the concentrations associated with these processes. The performance associated with the correct treatment of wastewater is shown below.

	Main components [mg/l]					
	Cu	**Pb**	**As**	**Ni**	**Cd**	**Zn**
Process or direct cooling water	<0.1	<0.05	<0.01	<0.1	<0.05	<0.15
Note: The associated emissions to water are based on a qualified random sample or a 24-hour composite sample. The extent of wastewater treatment depends on the source and the metals contained in the wastewater.						

Table 3.43: Associated concentration range of metals from a variety of copper wastewater streams

3.4.5 Process residues

The use or recycling of slags, slimes and filter dusts is considered to be part of the processes. The production processes in this sector have been developed by the industry to maximise the re-use of the majority of process residues from the production units or to produce residues to enrich minor elements in a form that enables use in other non-ferrous metal production processes.

Process Source	**Intermediate Product, By-Product, Residue**	**End Use**
Abatement Systems	Filter Dusts. Mercury compounds. Spent catalysts and acid. Sulphuric acid sludges Weak acid.	Raw Material for Cu (returned to smelter), Pb, Zn and other metals. Raw material for Hg. Chemical Industry. Neutralisation sludge for disposal. Decomposition for SO_2 recovery, neutralisation (sludge for disposal), other uses e.g. as leaching media.
Smelter	Slag Furnace linings	To slag furnace or other separation – internal recycle. Recovered or disposed
Converter	Slag	To smelter – internal recycle.
Slag Furnace	Slag	Abrasive, construction material.
Refining (anode) furnace	Slag	To smelter – internal recycle.
Tank House	Electrolyte bleed	Ni salts, Cu recovery, acid recovery or other use.
Melting/smelting	Skimmings and slag	Raw material for metal recovery.
General	Oils	Oil recovery.
Hydro Metallurgy	Depleted electrolyte	Leaching.
Semis Production	Acid pickling solutions and rinses.	Disposal as waste if low in non-ferrous metals or sold for metal recovery.
Rod Production	Acid pickling solutions (if applied).	Recovery in separate electrolytic cell.

Table 3.44: Potential uses of intermediate products, by-products and residues from the production of copper

The quantity of residues and by-products obtained is strongly dependent on the raw materials in particular the iron content of primary materials, the content of other non-ferrous metals in primary and secondary materials and the presence of other components such as silica etc. The emissions to land are therefore very site and material specific and depend on the factors discussed earlier. It is therefore not possible to produce a realistic, typical table of quantities that are associated with the use of BAT without detailing the raw material specification, this can only be considered locally. The principles of BAT include waste prevention and minimisation and the re-use of residues whenever practical. The above table gives an overview of the potential use of residues from the processes used to produce copper, the list is not exhaustive and in addition some options may not be available due to the absence of suitable facilities.

3.4.6 Costs associated with the techniques

Cost data has been compiled for a variety of process variations and abatement systems. The cost data is very site specific and depends on a number of factors but the ranges given may enable some comparisons to be made. The data is provided in an appendix to this note so that costs for processes and abatement systems over the whole of the non-ferrous metal industry can be compared.

3.5 Emerging Technologies

- It has been reported [tm 137 Cu Expert Group 1999] that development activity is taking place in the development and improvement of bath smelting techniques. Bath smelting can offer low cost installations because of the potential high reaction rates in modern plant coupled with sealed or semi-sealed furnaces. Plant reliability needs to be proven in the long term and data from some of the Chinese and Russian installations using Baiyin or Vanyucov furnaces should be examined if it becomes available.

Technique	Comments
Continuous smelting/converting: Combination Noranda reactor and Mitsubishi converter furnace	Results of commissioning in 1999 to be awaited for evaluation.
Noranda continuous converter	Results of commissioning to be awaited for evaluation.

Table 3.45: Emerging bath smelting technology

- ISA Smelt for reduction/oxidation is not industrially proven but is emerging.

- The use of hydro-metallurgical processes is also emerging and they are suitable for mixed oxidic/sulphidic ores that contain low concentrations of precious metals. Iron and sulphide oxidising bacteria may be used to assist leaching. Some processes are being developed for concentrates and dust treatment based on leaching for example:-leach: solvent extraction: electro-win (L:SX:EW) processes. [tm 137, Cu Expert Group 1999; tm 56, Kojo 1998].

Developments in other industrial sectors may also be seen as emerging for copper production processes. Particular developments are: -

- The use of modern fabrics for bag filters mean that more effective and robust fabrics (and housing design) can allow bag life to extended significantly, improving performance and reducing costs at the same time.

- The capture of fugitive emissions can be achieved in a number of ways. The use of intelligent damper controls can improve fume capture and reduce fan sizes and hence costs. Sealed charging cars or skips are used with a reverberatory furnace at a secondary aluminium smelter and reduces fugitive emissions to air significantly by containing emissions during charging.

4 PROCESSES TO PRODUCE ALUMINIUM FROM PRIMARY RAW MATERIALS AND SECONDARY RAW MATERIALS

4.1 Applied Processes and Techniques

4.1.1 Primary aluminium

4.1.1.1 Production of alumina

Alumina is produced from bauxite in the well-established Bayer process. This process is normally carried out close to the mine site but there are sites in Europe where bauxite is converted to alumina at the same site as an aluminium smelter or at stand alone alumina refineries.

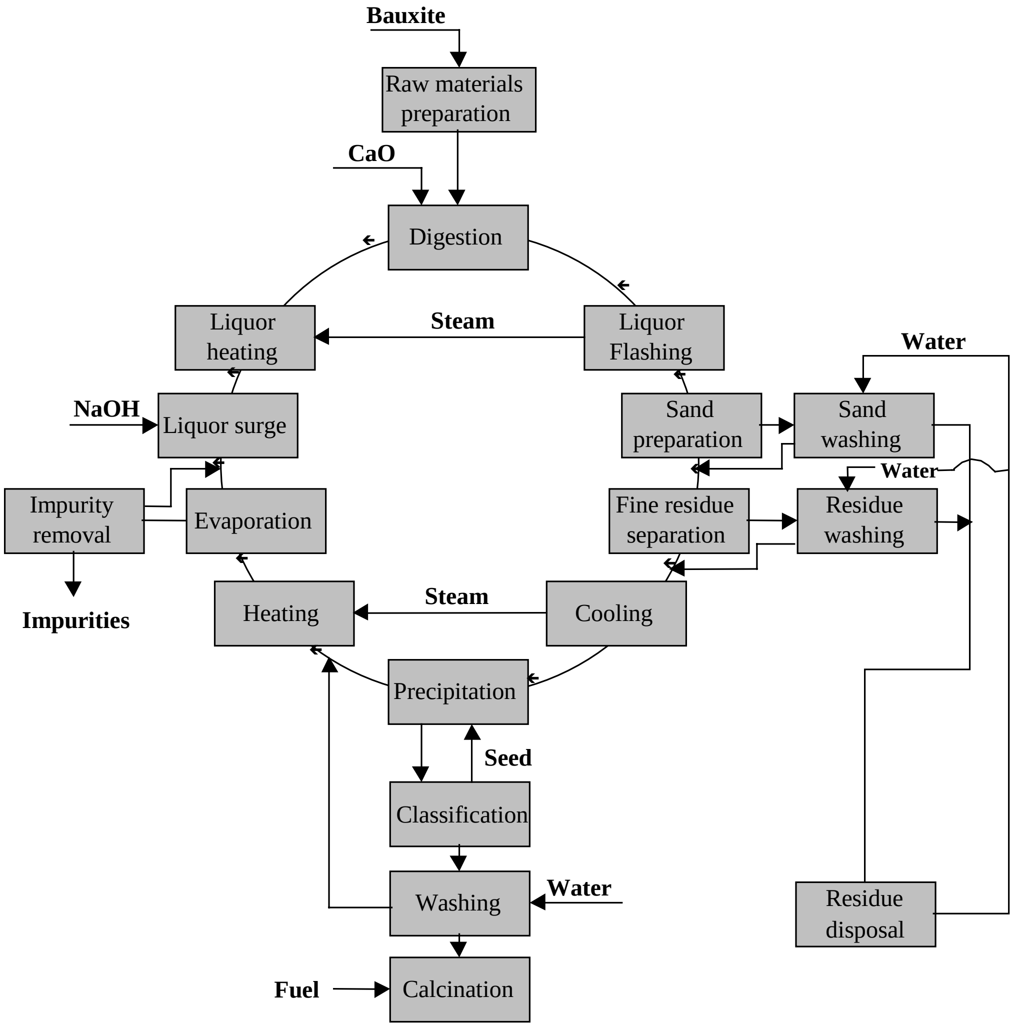


Figure 4.1: Alumina production – Bayer process

The overall process is standard for all sites and uses caustic soda to extract alumina from bauxite at elevated temperatures and pressures in digesters. Slurry is produced, which contains dissolved sodium aluminate and a mixture of metal oxides called red mud that is removed in thickeners. The aluminate solution is cooled and seeded with alumina to crystallise hydrated alumina [tm 30, Irish EPA 1996]. The crystals are washed and then calcined in rotary kilns or fluid bed/fluid flash calciners before use or shipping [tm 77, Al Expert Group 1998; tm 90 Al Expert Group 1998]. Other metals such as vanadium may be present and can also be recovered from the liquor.

Although the basic process is standard across the industry there are variations in the equipment used in particular the digesters and calciners. These variations mainly affect the energy used in the process [tm 77, Al Expert Group 1998]. This is shown later.

4.1.1.2 Aluminium production by electrolysis

Aluminium is produced from primary materials by the electrolytic reduction of aluminium oxide (alumina) dissolved in a molten bath of mainly sodium aluminium fluoride (cryolite) at a temperature of approximately 960 °C [tm 6, HMIP Al 1993; tm 100, NL Al 1998].

The electrolytic cells comprise a carbon cathode, insulated by refractory bricks inside a rectangular steel shell, and a carbon anode suspended from an electrically conductive anode beam. The cells are connected in series to form an electrical reduction line (potline). A direct current is passed from a carbon anode through the bath to the cathode and thence, by a busbar, to the next cell [tm 6, HMIP Al 1993; tm 100, NL Al 1998].

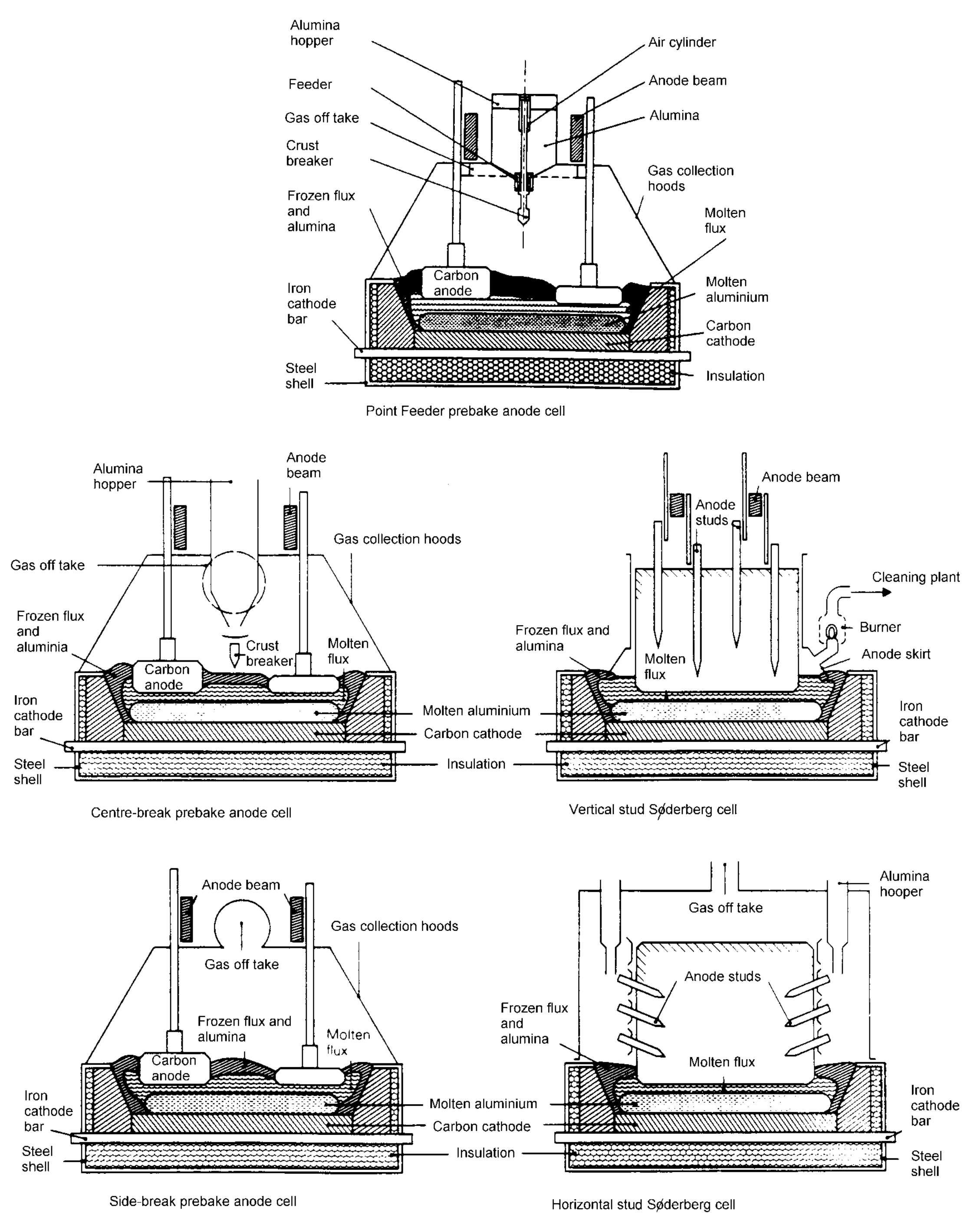
Alumina is added to the cells to maintain an alumina content of 2 - 6% in the molten bath, computer controlled additions are used in modern plant. Fluoride compounds are added to lower the bath melting point, enabling the cells to be operated at a lower temperature. Aluminium fluoride (AlF_3), the most common additive, also neutralises the sodium oxide present as an impurity in the alumina feed. Most cells are now operated with the AlF_3 content of the bath significantly in excess of the stoichiometric cryolite composition, however, fluoride emissions increase as the excess AlF_3 in the bath is increased [tm 6, HMIP Al 1993; tm 77 Al Expert Group 1998; tm 100, NL Al 1998].

Liquid aluminium is deposited at the cathode in the bottom of the cell and oxygen combines with the carbon anode, to form carbon dioxide. The carbon anodes are therefore continuously consumed during the process.

Cell systems vary according to the type of anode and the method used to feed alumina, as illustrated in fig 4.2 [tm 6 & 17, HMIP Al 1993; tm 100, NL Al 1998]. There are two main types of electrolytic cells, Søderberg and Prebake.

a) Søderberg anodes are made in situ from a paste of calcined petroleum coke and coal tar pitch, which is baked by the heat arising from the molten bath. The current is fed into the Søderberg anode through studs that have to be withdrawn and re-sited higher in the anode as the anode is consumed. As the anode is consumed, more paste descends through the anode shell, thus providing a process that does not require changing of anodes. Alumina is added periodically to Søderberg cells through holes made by breaking the crust of alumina and frozen electrolyte which covers the molten bath. Automatic point feeding systems are used in upgraded plants, eliminating the need for regular breaking of the crust. A gas skirt is attached to the lower part of the anode casing for gas collection. Fumes are collected and combusted in burners to reduce the emission of tars and PAHs. Pot-room ventilation gases may also collected and treated.

b) Prebaked anodes are manufactured from a mixture of calcined petroleum coke and coal tar pitch, which is formed into a block and baked in a separate anode plant. The anode production plant is often an integrated part of the primary aluminium plant and should be included in the definition of installation for such facilities, the contribution of anode production to the total emissions should also be included. Chapter 12, carbon and graphite, covers this process in more detail. The anodes are suspended in the cells by hanger rods attached to anode beams, which also serve as the electrical conductor. The anodes are gradually lowered as they are consumed and are replaced before the rods are attacked by the molten bath. The remnants of the anodes, which are known as anode butts, are cleaned of bath material and recycled through the anode plant.



Point Feeder prebake anode cell

Centre-break prebake anode cell

Vertical stud Søderberg cell

Side-break prebake anode cell

Horizontal stud Søderberg cell

Figure 4.2: Primary aluminium electrolytic cells

Prebake cells normally have 12 - 40 individual anodes, which are changed at regular intervals. In a large pot room, anode changing is a frequent occurrence and involves the removal of the cell cover shields. Although there is usually little leakage from the cell being maintained (depending on the rating of the extraction system), the overall extraction rate from other cells is reduced. This results in an increase in fugitive emissions if several covers are removed at the same time.

Prebake cells can be one of two types depending on how alumina is added.

- Side-worked prebaked anode cells (SWPB), alumina is fed into the cells after the crust is broken around the circumference. The gas collection hoods over the length of the cells have to be opened during this operation.

- Centre-worked prebaked anode cells (CWPB) are fed with alumina after the crust is broken, along the centreline or at selected points on the centreline of the cell (point feeder – pf). These feeding methods can be carried out without opening the gas collection hoods.

The gas collection system extracts the process gases to an abatement system that uses dry alumina scrubbers to remove and reclaim HF and fluorides. The scrubber also removes residual tars but does not remove sulphur dioxide. The alumina leaving the scrubbers is removed in bag filters or EPs and is usually fed directly to the cells. Pot-room ventilation gases may also be collected and treated in a wet scrubber system.

The cathode is not consumed in the process but the cathodes deteriorate with time. Carbon blocks absorb electrolyte and after 5 - 8 years have to be replaced due to swelling and cracking which results in penetration of molten electrolyte and aluminium to the cathode conductor bar and steel shell. Small amounts of cyanides are formed through a reaction between nitrogen and carbon. The cathode residue is known as spent pot lining, several disposal and recycling routes for this material are used [tm 42, Ausmelt 1998; tm 77 Al Expert Group 1998; tm 100, NL Al 1998] and are described later in section 4.2.1.4.

Molten aluminium is periodically withdrawn from the cells by vacuum siphon into crucibles. The crucibles are transported to the casting plant and the aluminium emptied into heated holding furnaces. Alloying additions are made in these furnaces and the temperature is controlled. Skimmings formed by the oxidation of molten aluminium on the surface of the melt are skimmed off, sealed containers can be used to minimise further oxidation of the skimmings, and nitrogen or argon blanketing is also used [tm 106, Farrell 1998].

Throughout this chapter the term skimmings refers to both skimmings and drosses.

4.1.1.3 Refining

The metal is refined at this stage to remove impurities such as sodium, magnesium, calcium oxide particles and hydrogen. This refining stage is performed by the injection of a gas into the molten metal usually in an in-line reactor. The treatment gas used varies depending on the impurities, argon or nitrogen is used to remove hydrogen and mixtures of chlorine and argon or nitrogen is used to remove metallic impurities. Aluminium fluoride is also used to remove magnesium. The metal is then filtered before casting.

Alloy adjustments are also made in the holding furnace by the addition of the required metal (Si, Cu, Mg, Pb, Sn, Zn) or a master alloy of the metal with aluminium (Ti, Cr, Fe, Mn, Ni) [tm 116, Secondary Al Expert Group 1998].

Other additions are also made to refine the grain of the metal, titanium or titanium boride are the most common.

Skimmings are produced at this stage and are removed from the surface of the molten metal and are recycled by the secondary aluminium industry.

4.1.1.4 Casting

Slabs, T-bars or billets are cast in vertical direct chill casting machines that use water-cooled metal moulds and holding table at the bottom part of the moulds. The table is lowered as the ingot is formed. Other casting methods include the use metal moulds (static or continuously moving) and the continuous casting of thin sheets and the continuous casting of wire rod [tm 6, HMIP Al 1993]. Additional small quantities of skimmings are also produced at this stage and are removed from the surface of the molten metal.

4.1.2 Secondary aluminium

4.1.2.1 Production processes

The main feature of secondary aluminium production is the diversity of raw materials encountered and the variety of furnaces used [tm 116, ALFED 1998]. The type of raw material and its pre-treatment is therefore used to judge the best type of furnace to be used for a particular type of scrap with its size, oxide content and degree of contamination among others [tm 145, Winter 1998]. These factors also influence the choice of fluxes associated with the process to maximise the recovery of aluminium [tm 2, HMIP Al 1993; tm 77 & 116, ALFED 1998]. The choice of process technology used will vary from plant to plant. The number of factors that impact upon the choice of process mean that there is the potential for many viable strategies which can address similar circumstances.

Rotary or reverberatory furnaces are used for melting a wide range of secondary raw materials, rotary furnaces can incorporate a tilting mechanism and this is reported to reduce the amount of flux needed [tm 145, Winter 1998]. Induction furnaces and the Meltower process are used to melt the cleaner aluminium grades. Reverberatory furnaces often include a side well. A pumping system (mechanical or electromagnetic) is sometimes used to convey molten metal through the side well and a charging well to assist melting of small particles. Electromagnetic pumps have no moving parts and rely on an external coil to induce the electromagnetic force, stirring is induced in the charging well and in the furnace. Other pumps, which have heat resistant internal parts and metal “spinners” are also used [tm 145, Winter 1998].

Reverberatory furnaces may also use a sloping hearth in the metal feed area where, items containing large pieces of iron can be placed. Aluminium is melted off the iron substrate, which remains on the hearth. Contamination of the melt by iron is therefore minimised [tm 77, Al Expert Group 1998; tm 116, ALFED 1998]. Details of some of the furnaces are given in 2.5.2.

Typical sources of aluminium scrap are process scrap, used beverage cans (UBCs), foils, extrusions, commercial scraps, turnings, and old rolled or cast metal. In addition to this aluminium is also recovered from skimmings and salt slags. Various contaminants may be present and this is taken into account in the choice of pre-treatment or in the design of the furnace [tm 77, Al Expert Group]. Scrap is sometimes sorted first into alloy types to produce the desired alloy with the minimum of reprocessing [tm 116, ALFED 1998; tm 121, Hoogovens 1998].

Scraps such as UBCs and turnings are major sources of material feedstock and may be contaminated. These sometimes require to be de-coated or de-oiled prior to melting to improve melting rate (and thermal efficiency) and to reduce the potential for emissions [tm 121, Hoogovens 1998; tm 122, ETSU 1998]. The melting of cleaned material can save energy and reduce Skimmings generation. The pre-treatment processes are outlined in table 4.24.

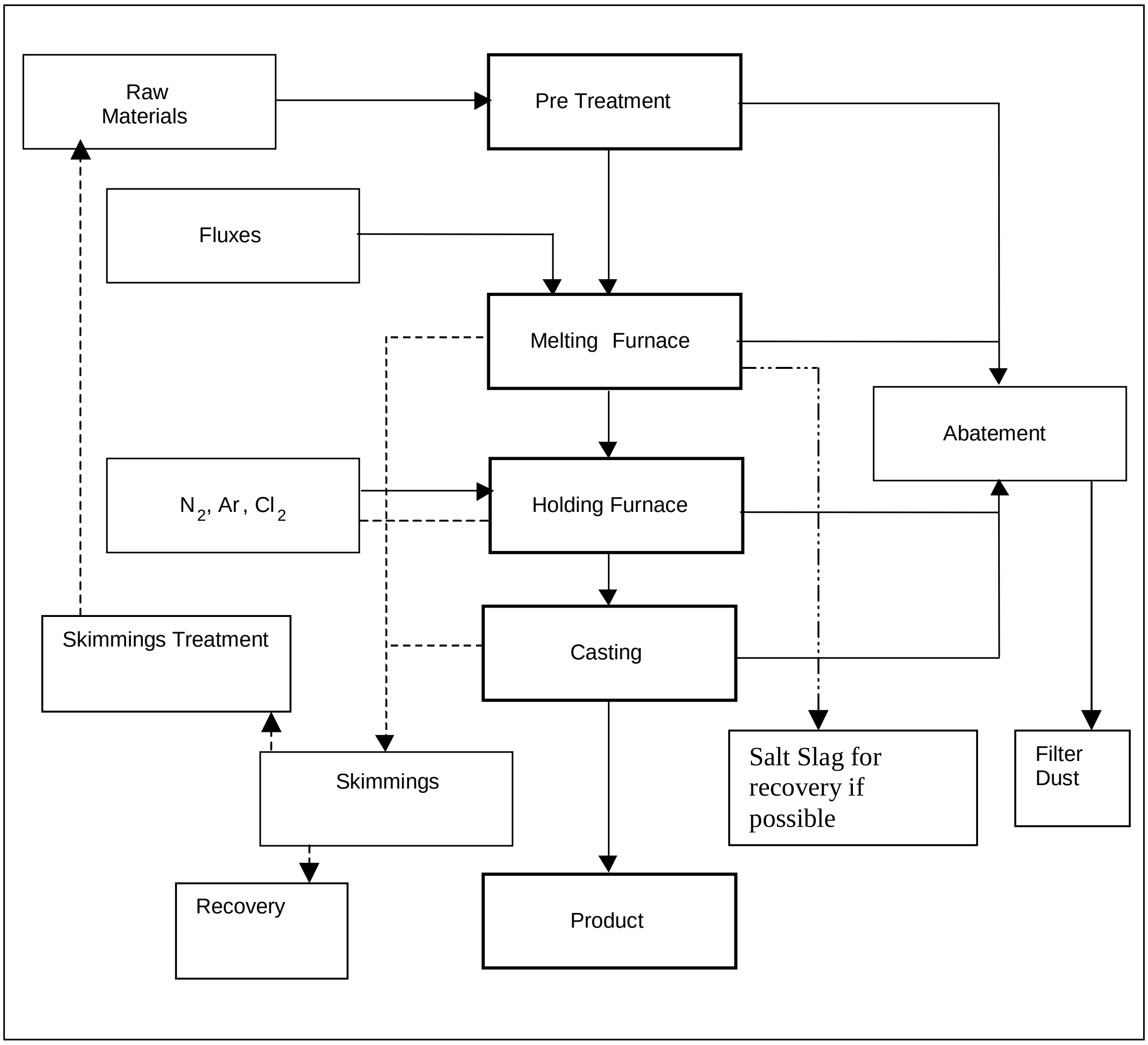


Figure 4.3: Secondary aluminium generic process

A range of different fluxes is used within the secondary industry to assist in the processing of the metal in a number of ways. An example is the use of fused salt (a mixture of sodium and potassium chlorides and some fluorides) to prevent oxidation and absorb impurities. Furnace gases contain chlorides and HCl produced from the salt. Refractory fluxes and fluorinated fluxes are also used. Salt slag is tapped after the metal. There are variations in the quantity of salt flux used and this depends on the furnace used and the oxide content of the raw material. Pre-treatment of the feed material can reduce the salt usage by half (Example 4.06). It has also been reported that up to 1.8 kg of salt per kg non-metallic constituents is used for a static rotary furnace and < 0.5 kg per kg for a tilting rotary furnace [tm 145, Winter 1998].

The use of a side-well reverberatory furnace with a charging well and pumping system can increase the number of grades of scrap, including foil and small turnings that can be melted in these furnaces. It can also reduce the loss of metal by oxidation without using large quantities of salt or other flux [tm 121, Hoogovens 1998; tm 122 & 123 ETSU 1998].

4.1.2.2 Refining and casting processes

Metal may be tapped from the melting furnace where alloy additions are made either directly to a casting system or via a transfer system into a holding furnace (where other alloying additions can be made). The metal is then refined either in the holding furnace or in an inline reactor, to remove gases and other metals generally in the same manner as primary aluminium. Magnesium can be present in secondary aluminium and may need to be reduced. Treatment of molten aluminium with chlorine gas mixtures is used to remove magnesium although sodium aluminium fluoride and potassium aluminium fluoride are also used [tm 116, Al Expert Group 1998; tm 34, US EPA 1995]. The latter material is a by-product of the production of some master alloys.

Large ingots, billets and slabs are cast in the same way as primary aluminium and a range of smaller ingots may also be produced (e.g. for supplying the casting industry) may also be produced in a large variety of alloys depending on the final application. It is also possible to transport molten aluminium by road in special thermally insulated containers to end-users.

4.1.2.3 Skimmings and slags

Aluminium is easily oxidised and this is a significant factor in the production processes. The melting of aluminium without a protective flux produces an oxide layer known as skimmings. This is skimmed from the metal surface before casting. Skimmings that have been removed from a furnace contain between 20 - 80% aluminium. Skimmings are sometimes treated as soon as they are removed from the furnace to reduce emissions and further oxidation of the metal present. Methods include inert gas cooling, hot pressing to remove molten aluminium and cooling in purpose built coolers.

Cold skimmings are treated by a number processes to recover aluminium. For example by smelting in rotary furnace under a salt flux or by using separation techniques such as milling and processing to separate oxide from the metal [tm 116, ALFED 1998]. In the latter case the metal can be re-melted in relevant furnaces and the fine fraction can be further processed e.g. recycled in the steel industry or in the salt slag recovery process. It has been reported that the ultimate generation of salt slag and waste is reduced and the use of energy is lower due to a lower burden of inert material in the furnace [ALSA 1999].

Rotary furnaces are used to recover aluminium from skimmings and the metallic fraction produced from the treatment of skimmings. A salt flux is usually used to facilitate this process, the salt reduces oxidation and promotes the removal of some impurities (e.g. Mg, Ca, Li). Several installations exist where salt slag can be recovered using a washing and crystallisation process. The processes can produce recycled aluminium granules and salt. It is reported [tm 90, Al Experts 1998] that the metal oxide fraction (mainly oxides of aluminium, calcium and magnesium) can be further processed and washed to produce fine aluminium oxide that has been sold to the cement industry.

4.1.2.4 Salt slag recovery

The large blocks of salt slag are crushed to manageable size and sieved to recover metallic aluminium granules (typically up to 10%). The finely crushed material is then dissolved in water so that the chlorides go into solution producing brine, leaving the insoluble aluminium oxide and the finest metallic particles of aluminium, which is not normally economically recyclable as the metal. Gases are evolved from this stage of the process and mainly contain ammonia, methane, hydrogen and phosphine. There is also the potential for major dust emissions during the crushing stages. It is possible to use these gases as a fuel for other parts of the process [tm 116, ALFED 1998]. The brine is filtered removing the insoluble oxides and the solution is then sent for evaporation and crystallisation from which the original sodium and potassium chlorides can be recovered. These chlorides are then re-used as flux in the melting process.

The residual metal oxides comprise calcium, magnesium and aluminium oxides (up to 65% Al_2O_3) and also contains, sulphates, chlorides and nitrates [tm 206, TGI 1999]. In cases where the oxide fraction has potential markets further washing is necessary to reduce these anions to manageable levels. The brine solution from the washing can be returned to the dissolution stage. It has been reported that in some cases it is possible to achieve complete recovery of the materials present in the salt slag [tm 90, Al Experts 1998].

4.2 Present Emission and Consumption Levels

4.2.1 Primary aluminium

Besides CO_2 which is inherently linked to the process, there are potential emissions to air of dust, SO_2, HF, particulate fluorides, CO, PFCs and PAHs from the pot gas extraction system and the pot room ventilation system. There are potential emissions to air of dust, metals, chlorides and combustion products from the holding and treatment furnaces in the cast house [tm 6, HMIP Al 1993; tm 100, NL Al 1998].

To water/sea there are potential emissions of particulate matter, SO_2, fluorides and PAH from wet scrubbers and storm water run off.

The main sources of waste is spent pot lining materials (SPL).

PAHs emitted to water should be reported as the 6 compounds in the Borneff list and those emitted to air as B(a)P [tm 29, PARCOM 1997; tm 128, Nordheim 1997].

The production of anodes is covered, along with the production of graphite, in Chapter 12 of this document. The use of anode butts from the production of aluminium as part of the raw material input to this process contributes fluorides.

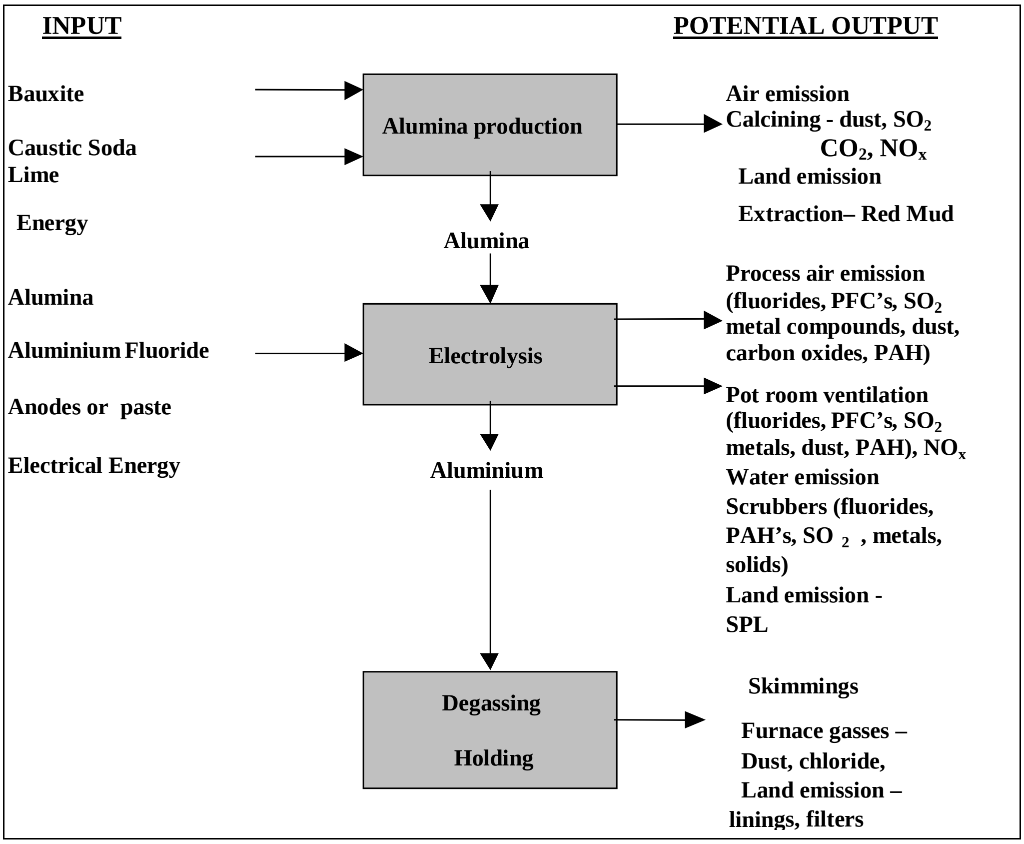


Figure 4.4: Input and output from primary aluminium production

4.2.1.1 Energy and other inputs

The material and energy inputs to the process are significant. Approximately 2 tonnes of bauxite are required to produce 1 tonne of alumina, which in turn produces about 0.53 tonnes of aluminium. The carbon anodes are consumed, approximately 0.4 to 0.45 tonnes of carbon is used per tonne of aluminium produced. The energy costs are also high and could account for approximately 30% of the production costs.

The production of alumina requires energy for digestion and calcination. The energy use is influenced mainly by the origin and chemical composition of the bauxite, the type of digesters used and the type of calciners used. The range of energy used in European plants is 8.0 to 13.5 GJ per tonne with a mean value of 11 GJ per tonne [tm 90, Al Expert Group 1998]. The quantities of NaOH and CaO used are also linked to the composition of the bauxite.

Parameter	**Typical Range kg/t Alumina**
Bauxite	1970 – 2250
NaOH (50%)	33 – 160
CaO	35 – 110
Water	1000 – 6000
Energy GJ/t	8.0 – 13.5

Table 4.1: Input Ranges for alumina production

The reduction of energy demand is mainly influenced by the use of tube digesters, which are able to operate at higher temperatures using a fused salt heat transfer medium. These plants have an energy consumption of less than 10 GJ per tonne.

The electrolysis stage has a high energy use ranging from 53 GJ per tonne for the best operated CWPB cells (including anode production) to 61 GJ per tonne for some traditional Søderberg cells.

Parameter	**Pre Bake**	**Søderberg**
Alumina – kg/t Al	1900 – 1940	1900 – 1940
Anodes nett – kg/t Al	400 – 440	
Anode Paste – kg/t Al		500 – 580
Al F_3 - kg/t Al	15 - 25	15 - 25
Cathode Life – years	5 – 8	5 – 8
Power for Electrolysis – kWh/kg Al	12.9 – 15.5	14.5 – 17.0
Rodding Plant Cast Iron – kg/t Al	1.0 – 3.0	
Ramming and Collar Paste – kg/t Al	0 – 25	
Electrical Power Total – kWh/kg Al *	14.0 – 16.5	15.0 – 18
Note. * Including rectifier loss, pollution control and auxiliary consumption. Energy data is produced based on the conventions used by the Industry. Anode production accounts for 5500 MJ/t.		

Table 4.2: Input Ranges for Electrolysis

The production of aluminium from recycled metal uses down to 5% of the energy of primary production [tm 29, PARCOM 1997].

Parameter	Range
Skimmings Produced – kg/t Al	10 – 25
Fluxes - kg/t Al	0 – 1.5
Gases – kg/t Al	0 – 6.0
Swarf etc – kg/t Al	0 – 3
Water – kg/t Al	200 – 12000
Homogenisation energy MJ/t Al	500 – 1200
Cast House Energy – MJ/t Al	800 – 1900 *
Note. * Not including re-melting of cold metal.	

Table 4.3: Cast House Consumption data

4.2.1.2 Emissions to air

There are five distinct sources within the process: -

- Gases from calcining and heating for the production of alumina;
- process gases from anode baking;
- process gases from electrolytic cells;
- pot room ventilation.
- degassing and casting.

The potential releases from the electrolysis stage are: -

- fluorides;
- perfluorocarbons (PFCs);
- tars and poly-aromatic hydrocarbons (PAHs);
- sulphur dioxide (SO_2) and other sulphur compounds;
- dust;
- metal compounds;
- oxides of nitrogen (NO_x);
- carbon monoxide (CO);
- carbon dioxide (CO_2).

The emission that takes place from the electrolytic cells and via the pot room ventilation are related to each other by the efficiency in which the flue gases from the cells are captured [tm 29, PARCOM 1997; tm 100, NL Al 1998].

4.2.1.2.1 Capture of gases

a) Prebake

CWPB cells are totally enclosed and have a fume extraction system. A typical value for CWPB cells for the efficiency of capturing the flue gases within the process air is 95 to > 99% depending on the design of the extraction system, the effectiveness of the cell covers and the arrangement of the extraction and filter systems. The capture efficiency depends on a good rate of extraction, well designed hoods and good operating practice to ensure that the minimum number of hoods are open at a time. Open hoods or hoods that are not well sealed allow air ingress into the extraction system and therefore reduce the efficiency of extraction at the remaining cells.

SWPB cells are usually partially enclosed and a capture efficiency of about 85 to 95% is achieved. This is due to the poor hooding arrangements and the reliance on the frozen alumina layer to contain the gases. Some SWPB cells are fully hooded but need to be opened more frequently for alumina additions, anode change and maintenance.

b) Søderberg

For conventional VSS Søderberg electrodes the situation is similar to SWPB. The crust breaker and the alumina feeder are mounted on vehicles and the cells are only partly hooded. There is a low degree of automation and consequent problems with controlling accurate alumina feeding to the bath with this pot system.

During crust breaking and alumina feeding, emissions of air pollutants to the pot room atmosphere increase. The steel contact bolts (studs) that support the anodes and conducting the electricity must be pulled out at regular intervals and replaced in a higher position. During this operation higher levels of PAHs are emitted. The gas collection skirt surrounding the anode casing is connected to a simple gas burner leading to a gas exhaust tube, this burner aims to burn CO and hydrocarbons that are emitted [tm 6, HMIP 1993].

Several improvements have been made to the conventional Søderberg electrode system. The objectives were to reduce anode effects and emissions from the pots to a level comparable with the total emission from prebaked pots, including anode baking. The main features are: -

- Automatic alumina point feeding and control of electrolysis;
- Complete skirt coverage of bath crust;
- The use of "Dry Paste" with a lower pitch content.
- Improved burner for incineration of PAHs and other hydrocarbons in pot exhaust gas;
- Complete hood coverage of the anode top, which is connected to a separate gas exhaust and dry alumina scrubber or dry anode top in combination with stud hole paste and increased anode height depending on effectiveness.

These improvements result in a significant increase in the capture of gases [tm 29, PARCOM 1997]. The range that is encountered in typical VSS Søderberg Plants is 65 to 95% capture efficiency depending on the degree of modification [tm 77, Al Expert Group 1998]. HSS Søderberg Plants have a similar performance to SWPB cells.

The uncontrolled emissions to the pot room from SWPB and Søderberg cells are therefore significant and these processes often have wet scrubbing systems such as sea water scrubbers to remove fluoride and PAHs from cell room ventilation gases. CWPB cells are inherently more efficient at capturing process gases but rely on good design, maintenance and operating procedures. The following table shows the concentration of several components in the cell gases.

Type of cell	Total fluoride mg/Nm^3	Dust mg/Nm^3	Sulphur dioxide mg/Nm^3
VSS Søderberg	700 - 1700	500 - 1800	500 - 2000
Hooded Prebake	75 - 500	150 - 500	50 - 400

Table 4.4: Untreated primary aluminium cell gas concentrations
[tm 29, OSPARCOM 1997]

4.2.1.2.2 Fluorides

Airborne gaseous and solid fluorides are emitted from the pots during electrolysis. The main pollutant (50 to 80%) is gaseous hydrogen fluoride (HF), whilst the rest is solid fluorides (mainly aluminium fluoride and cryolite). HF is formed by reaction of aluminium fluoride and cryolite with hydrogen, introduced to the pot as fixed water in aluminium oxide, as residual hydrogen in anodes and as moisture in the air. As modern pots are often operated with a high stoichiometric excess of AlF_3 (12 - 13%), the fluoride generation has increased over the years and fume capture has become more important [tm 100, NL Al 1998].

The total fluoride emission from the pots varies between 20 and 40 kg F per tonne aluminium. With a capture efficiency of > 98%, and cleaning efficiency of > 99.5 to 99.9% in the dry scrubbing installations, the stack emission can be 0.02 to 0.2 kg total F per tonne aluminium. Alumina is used as the scrubbing medium. The alumina is normally collected in a bag filter or EP, and is then used directly in the electrolysis cells. The fluorides collected in the alumina form aluminium fluoride and sodium fluoride (after reaction with any sodium oxide present in the alumina) and contribute to the amount of Cryolite in the cell bath. Several plants that operate alumina scrubbers produce excess cryolite from the reaction of fluorides with the sodium content of the alumina and this is sold as “excess bath”.

Uncaptured emissions are discharged to the pot room atmosphere and emitted through the ventilation system. This can represent 0.4 – 0.8 kg per tonne of aluminium as calculated by PARCOM, giving a total fluoride emission in the range 0.4 – 1.0 kg F per tonne aluminium [tm 29, PARCOM 1997].

Most of the Søderberg plants operating in Scandinavia use wet scrubbers (using seawater or caustic soda) in addition to the dry scrubber to remove sulphur dioxide (SO_2) from the exhaust gases. [tm 29, PARCOM 1997; tm 100, NL Al 1998]. Some plants also use seawater scrubbers for ventilation air to remove fluorides, sulphur dioxide and dust from the pot-room ventilation air.

Fluorides and chlorides are also emitted during the degassing and refining stages. The quantity and components of the emission depends on the degassing and refining agents used.

4.2.1.2.3 PFCs

PFCs as tetra-fluoro methane (CF_4) and hexa-fluoro ethane (C_2F_6) are formed during the anode effects. They are emitted in the ratio CF_4:C_2F_6 approximately 10:1. They cannot be removed from the gas stream with existing technology once they are formed [tm 29, PARCOM 1997].

An anode effect occurs when the alumina content of the electrolyte falls below 1 – 2% and a gas film is formed at the anode. This stops the production of the metal and increases the cell voltage from 4 – 5 to 8 – 50 volts. Factors that influence the generation of PFCs are the frequency and duration of “anode effects” and the operating current of the cell. The control of cell voltage and alumina additions is a major factor in controlling anode effects [tm 6, HMIP 1993].

The PFC emission of modern plants can be minimised by the use of semi-continuous point feeding of alumina and improved process control. These CWPB plants can be operated with an anode effect frequency of < 0.1 to 0.5 per pot per day, resulting in an emission ranging from 0.02 to 0.1 kg PFCs per tonne Al [tm 77, Al Expert Group 1998; tm 100, NL Al 1998]. Many older plants used anode effects as a control for bath alumina content and consequently PFC emissions can be much higher. The use of modern control systems and automatic point feeding of alumina in both Prebake and Søderberg cells minimises the number and duration of anode effects [tm 29, PARCOM 1997; tm 77, Al Expert Group]. An automated anode effect killing system can also be used in conjunction with the control system for example the use of anode height differential or compressed air.

Emissions of PFCs are a key environmental issue for the aluminium industry and extensive research is under way to improve the presently incomplete knowledge of the problems and possible solutions.

4.2.1.2.4 Tars and PAHs

The emissions of tar and PAH during electrolysis in prebake plants are negligible due to the fact that the anodes are baked in a separate operation. Very small amounts of tar and PAHs may be emitted from a limited number of prebake plants using carbon paste for anode pin connection and for protection collars. Measurements at start up of new cells and from plants using collar paste indicate emissions are negligible. [tm 100, NL AL 1998].

Installations that include an anode production plant will have a source of tars and PAHs from this part of the process. The production of anodes is covered in Chapter 12 of this document but the emissions from an integrated process are relevant to this chapter. There are examples where the process gases from an anode plant share the same alumina scrubber and fabric filter as the electrolysis process. The results from these plants show no difference in performance of the abatement plant when anode process gases are included. It can be concluded that the alumina scrubber is efficient at removing PAHs and tars from an anode plant or from Søderberg cells. Spent alumina from the scrubbers is used as feed to the cells (but not for covering the bath). EPs are also used to remove tar [see Chapter 12]. Wet scrubbers for the ventilation gases will also remove some PAHs particularly the particulate fraction.

At Søderberg plants tar and PAHs are emitted during the electrolysis due to the self baking anode. Emissions occur by evaporation from the carbonisation of the paste. Stud pulling is the operation giving the most significant emissions. Emissions depend on the anode design, the paste quality, and the operating practises. Generally the use of dry scrubbers removes tar and PAHs effectively from the pot gases [tm 29, PARCOM 1997, tm 77, Al expert group]. The use of dry anode paste and colder anode tops help to reduce the PAH emissions from the anode.

4.2.1.2.5 Sulphur dioxide and sulphur compounds

The anodes used currently have a sulphur content ranging from 1 to over 3.5%. The sulphur will react with oxygen resulting in an emission of sulphur dioxide or carbonyl sulphide - COS. Due to the differences in the sulphur content of the anodes, the emission of sulphur dioxide can range from about 8 to over 30 kg per tonne Al, based on an anode consumption of 0.4 tonne per tonne Al (sulphur content ranging from 1 to over 3.5%). For COS it has been reported that ~ 10% of sulphur in the anode is formed into COS or 2 kg/t of Al for anodes containing 2.5% S.

The emission of SO_2 via the pot room ventilation of will range from 0.2 to 0.6 kg per tonne (concentration: 0.1 to 3 mg/Nm^3). The emission via the process air from the cells has a typical concentration ranging from 50 to 400 mg/Nm^3 [tm 29, PARCOM 1997; tm 100, NL Al 1998]. Where the process gas is wet scrubbed, the concentration range in the emission to air will typically be 5 - 40 mg/Nm^3.

It has been reported that sulphur in the anodes may have a beneficial effect in suppressing the adverse effects of sodium contained in the anode butts for recycling [tm 77 Al Expert Group 1998].

4.2.1.2.6 Dust

Alumina and cryolite are the principal dusts emitted during electrolysis. Alumina used to remove fluorides from the exhaust gases (so-called secondary alumina) is also emitted if the dust collection system is not efficient. This secondary alumina will contain some HF adsorbed on the surface.

Total dust generation varies and depends on the type of process applied and the type of alumina, but ranges from 0.6 to 10 kg per tonne Al. Typical dust concentrations for pot room ventilation are 0.5 to 5 mg/Nm^3 whereas the dust concentration in the process air ranges from 150 - 500 mg/Nm^3 before abatement and from 1 - 20 mg/Nm^3 after abatement [tm 100, NL Al 1998].

Casting is another source of dust (and metals) and cast-house fume is usually collected and treated in a fabric filter. Some studies have been carried on the presence of dioxins in fume from the casting process as the use of chlorine for degassing and the presence of carbon from combustion gases may lead to their formation. All measurements from primary smelter cast houses show levels significantly below 1 g/year.

4.2.1.2.7 Metals

Metals are known to occur in trace concentrations in alumina and aluminium fluoride and can therefore be emitted during electrolysis. Tellurium is extracted from alumina produced at one installation and is therefore a potential contaminant. Other, volatile metals are also present and can be emitted from the pot room and the cast house. A limited amount of data is available about the environmental impact but trace metals are not considered to be a significant release [tm 100, NL Al 1998].

4.2.1.2.8 Oxides of nitrogen

Oxides of nitrogen (NO_x) are produced during electrolysis due to the presence of nitrogen in the anode, which can be oxidised to NO_x. The nitrogen content in the anodes generally ranges from 0.2 to 0.4%. When the nitrogen is completely converted into NO_x the emission may be 0.5 to 2 kg NO_2 per tonne Al (concentrations of 5 - 20 mg/Nm^3in the stack). The actual amount of NO_x released is still subject of discussion. Control measurements at two prebake plants in Norway showed an emission level of 0.1 to 0.2 kg NO_2 per tonne Al [tm 100, NL Al 1998]. The combustion gases from the burners used in holding and melting furnaces in the cast house will contain oxides of nitrogen.

4.2.1.2.9 Carbon monoxide

Carbon monoxide (CO) is produced during electrolysis by the back reaction of aluminium metal dissolved in the electrolyte with the CO_2 produced at the anode ($2\,Al + 3\,CO_2 \rightarrow Al_2O_3 + 3\,CO$), this lowers the cell efficiency. In a modern smelter the generation of CO before any re-oxidation to CO_2 is in the order of 100 to 150 kg per tonne Al. The production of CO also increases during an anode effect [tm 6, HMIP Al 1993; tm 100, NL Al 1998].

4.2.1.2.10 Carbon dioxide

Carbon dioxide (CO_2) is formed during electrolysis by the reaction of the carbon anode with the oxygen formed by electrolysis and by a secondary reaction with air. An efficient prebake plant consumes about 0.4 tonnes of carbon anodes per tonne aluminium, corresponding to 1.4 to 1.7 tonnes of CO_2 per tonne aluminium. This emission is however far less than the emission of CO_2 by combustion of fossil fuels when used for the generation of the electric power required for electrolysis [tm 77, Al Expert Group 1998]. Carbon dioxide is also emitted from burners used in the holding and melting furnaces.

4.2.1.2.11 Summary of main air pollutants

A summary of the relevance of the main air pollutants and their emission sources, as discussed above and based on literature findings, is given in the following table.

Component	Flue gases from electrolysis cells	Pot room ventilation	Degassing and Holding
Fluorides – gaseous and total F	•	•••	• (chlorides)
PFCs	•••	•	
Tars and PAHs	•**	•• **	
SO_2 (without scrubbers)* and COS	••*		•
Carbon dioxide	••		
Dust	•	•	•

Note. * Wet scrubbers are generally used after dry scrubbing in Scandinavia to remove SO_2 and are usually associated with the use of seawater as the scrubbing medium.
** Tars and PAHs are relevant to Søderberg processes and pre-bake processes that have an integrated electrode production process. They can also be relevant for the small number of plants using paste for anode pin connection protection collars.
••• More significant…………..• less significant

Table 4.5: Significance of potential emissions from primary aluminium

Parameter	Pre Bake	VS
HF –kg/t Al	0.15 – 2.0	0.2* – 3.5
Total Fluoride -kg/t Al	0.3 – 4.0	0.5* – 4.0
Dust –kg/t Al	0.6 – 7.0	1.5* – 10.0
SO_2 –kg/t Al	10 – 30	10 – 30
SO_2 –kg/t Al if wet scrubbing is used	1.0 – 3.5	1.0 – 3.5
CF_4/C_2F_6 – kg/t Al	0.02 – 1.0	0.2 – 1.0
Carbon dioxide – t/t Al	1.4 – 1.6	1.6 – 1.9
B(a)P -g/t Al	-	5 – 20

Note. * With wet scrubbing for ventilation.

Table 4.6: Total air emissions from primary aluminium smelters

The relevance of the uncontrolled emissions by the pot room ventilation is based on 98% fume capture from the cells. Regular CWPB cells can achieve this efficiency but when a lower efficiency is achieved, for example in SWPB or Søderberg cells, the relevance of the pot room ventilation increases [tm 77, Al Expert Group 1998; tm 100, NL Al 1998].

Gases emitted from ventilation air in Primary Smelters have been calculated [tm 29, PARCOM 1997]. The calculation was based on the concentration of the components in the cell gases and the capture efficiency of the hood and extraction system. This calculation is relevant in establishing the significance of uncaptured emissions but draws the same conclusion as the importance of the efficiency of the fume capture system and this factor is deemed to the most relevant for this work. Most smelters will also have a regular monitoring of this.

Parameter	Emission kg/tonne of Al
Dust	0.02 – 0.3
NO_x	< 0.1 – 0.4
SO_2	0 – 3

Table 4.7: Primary aluminium cast house - emissions to air

4.2.1.2.12 Climate gases

The production of primary aluminium results in emission of CO_2 as an inherent product of the electrolytic process (from carbon based anodes) and from the combustion of fuel to produce alumina and generation of electricity where this is based on fossil fuels. In addition to this poly-fluorinated carbons (PFC's) like CF_4 and C_2F_6 are produced during the anode effect in the electrolysis cells. Both gases are powerful climate gases with 100 year Global Warming Potential's of 6500 and 9200 respectively.

Calculations for European primary aluminium smelters shows that the total quantity of PFC gases emitted, calculated as CO_2 equivalent emission were about 15 million tonnes in 1990. Improvements in controlling the electrolysis process have significantly reduced the number of anode effects and the duration of the each anode effect. The PFC emission has therefore been considerably reduced over the past 10 years and calculations show that the CO_2 equivalent emission below 6 million tonnes in year 2000 will be achieved.

Efficiency improvements in other parts of the process have also contributed to a reduction in direct CO_2 emissions, reducing the total emission of climate gases. The specific PFC emissions from different technologies are given in table 4.5. The improvements and further reductions are discussed under techniques to consider in the determination of BAT.

Work is still progressing at a pilot stage, to develop an inert anode material so that carbon dioxide would not be produced during electrolysis and is reported as an emerging technique. The elimination of a carbon anode would also prevent the formation of PFCs.

4.2.1.3 Water emissions

The production of primary aluminium is inherently a dry process. Discharge of wastewater is usually limited to cooling water, rainwater run-off from surfaces and roofs and sea water scrubbers for pot room ventilation gases. The rainwater run-off can be contaminated by open storage of raw materials and deposited solids. Typical values for this contamination are < 0.03 kg/tonne Al for suspended solids and < 0.02 kg/tonne Al for dissolved fluoride. In addition, considerable amounts of wastewater can be discharged when wet systems are used for air pollution control [tm 100, NL Al 1998].

The anode production can account for a production of wastewater consisting of cooling water, used to cool the green anodes or the flue gases. The cooling process can be performed using indirect water systems, resulting in a discharge of cooling water. Indirect water systems can also be used to cool the flue gases, to make them suitable for abatement with regular techniques (bag filters, electrostatic precipitators) [tm 100, NL Al 1998].

The production of alumina from bauxite is a process that eliminates water releases by operating a closed system. Water that is contained in the red mud or used to transport it to the disposal site is highly alkaline and is pumped back to the plant and re-used [tm 77, Al Expert Group 1998].

The electrolysis stage is a dry process and no wastewater is produced directly. Rain water contamination is prevented by good practice outlined in section 2.9.

Parameter	Pre Baked	Søderberg
Fluoride – kg/t Al	0 – 3.0	0 – 5.0
Suspended Solids – kg/t Al	0 - 6.0	0 – 6.0
PAH (Boneff 6) – g/t Al	0 - 0.01	8 – 15

Table 4.8: Emissions to water from the primary aluminium electrolysis plants

4.2.1.4 Process residues and waste

The production of metals is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). The most important process specific residues are listed below.

4.2.1.4.1 Red mud

Red mud produced during the extraction of alumina from bauxite is a significant waste and has a major disposal requirement. The mud is generally alkaline from the extraction process and contains 3 to 12 kg of NaOH per tonne of alumina produced. It therefore requires careful handling. Current practice is to deposit red mud on or near the site in specially designed, sealed ponds. Excess water from the ponds is normally returned to the process.

A salt containing vanadium may also be produced during the removal of impurities from the liquor produced during digestion. This salt is a major source of other metals such as vanadium and tellurium.

4.2.1.4.2 Spent Pot Lining

With a cathode lifetime of 5 - 8 years, which is common for modern plants, the quantity of Spent Pot Lining (SPL) generated is 20 - 30 kg/t aluminium produced. The SPL is normally considered to consist of two distinct fractions, the carbon part and the refractory material. The carbon part is the actual cathode from the electrolysis cell and the remainder is varying types of insulating material.

The two fractions are often separated when dismantling the cathode. The spent cathode also contains some bath material, steel bars used to conduct electricity to the carbon cathode, and often flakes of aluminium metal from metal penetration into the cathode. These parts are either reused directly at the plant or in the case of steel bars sent outside the plant for recycling. The carbon part is relatively homogeneous, while the refractory part can be composed of a number of different types of refractory materials or other types of insulation.

The following table gives a typical analysis of SPL [tm 134, EAA 1998].

Compound	Carbon lining	Insulation
	Range wt%	
Al_2O_3	0 – 10	10 – 50
C	40 – 75	0 – 20
Na	8 – 17	6 – 14
F	10 – 20	4 – 10
CaO	1 - 6	1 - 8
SiO_2	0 - 6	10 – 50
Metallic Al	0 - 5	0
CN	0.01 – 0.5	0 - 0.1
CN, free	0 – 0.2	0 – 0.05
Others		

Table 4.9: Composition of Spent Pot Lining

The problem constituents linked to this material are soluble fluoride and soluble cyanide. In addition any wetting of this material will produce an alkaline leachate and liberate minor quantities of NH_3 and PH_3. PAH is not considered to be a problem since the carbon lining has already been carbonised at temperatures above 1250° C and any ramming paste has been heated to above 900° C in the electrolytic cell. The problem constituents mentioned are mainly linked to the carbon part of the SPL and the refractory parts in immediate contact with this. As can be seen from the tables, the content of these constituents is lower in the refractory part.

Spent pot lining can be re-used, treated or disposed of [tm 134, EAA 1998].

Re-use

Re-use in pyrometallurgical furnaces.
Reuse for Cryolite Production.
Re-use in the cement industry.
Re-use as a fuel.

Treatment processes

Reynolds Metals rotary kiln process.
Elkem pyro-hydrolysis process (also produces cryolite).
Comalco Comtor process.
Vortec/Ormet process.
Alcoa/Ausmelt process

Deposit practises

Seashore deposit.
Landfill deposit as hazardous waste.

4.2.1.4.3 Other materials

Skimmings from the holding and treatment processes represent 15 to 20 kg per tonne of aluminium produced. This material contains 30 to 80% aluminium and cooling under an inert gas blanket prevents oxidation. They are used as a raw material in the secondary aluminium industry. Spent filters from metal treatment are usually disposed of. Solid wastes produced by gas cleaning installations (dust and sludge) can be reused [tm 77 & 90, Al Expert Group 1998].

Anode butts from some plants are also disposed if they fail to meet quality standards. Furnace linings from the casting process and anode baking process may be recovered or disposed.

Good waste management practice and the use of recovery methods makes it possible to reduce waste for landfill. See examples.

Source	Use/treatment options
Al skimmings	Recovery.
Filter dust	Re-use in process.
SPL	Carburant, flux and furnace linings.
Bricks	From anode furnaces, reuse.
Steel	Recovery.
Carbon dust (anode plant)	Reuse.

Table 4.10: Options to reduce waste for a primary aluminium smelter

Source	Quantity kg per tonne Al
Al Skimmings	15 – 25
SPL	20 – 30
Other Hazardous Waste	7 – 15
Non Hazardous Waste	12 – 14

Table 4.11: Specific waste quantities from primary aluminium production

Steel from the anode plant is normally re-melted in an induction furnace and re-cast for use in the process. The melting of steel that is contaminated with fluorides is a further potential source of these emissions and appropriate collection and abatement is required.

4.2.2 Secondary aluminium

There are potential emissions to air of dust, metal compounds, chlorides, HCl and products of poor combustion such as dioxins and other organic compounds from the melting and treatment furnaces. The formation of dioxins in the combustion zone and in the cooling part of the off-gas treatment system (de-novo synthesis) may be possible. The emissions can escape the process either as stack emissions or as fugitive emissions depending on the age of the plant and the used technology. Stack emissions are normally monitored continuously or periodically and reported by on-site staff or off-site consultants to the competent authorities.

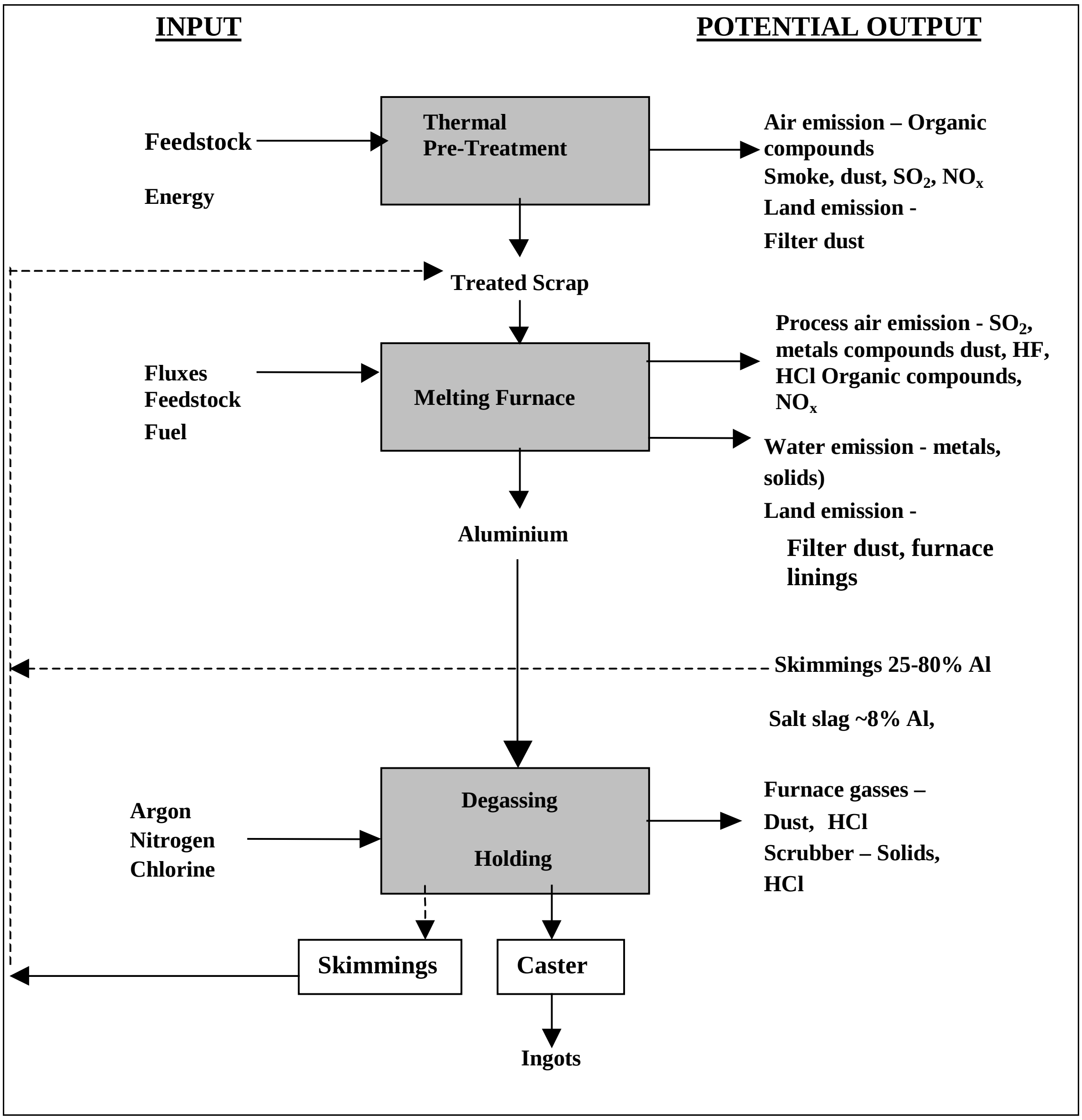


Figure 4.5: Input and output from secondary aluminium production
NB smoke and dust can be associated with organic compounds such as VOC and dioxins

Ammonia and other gases can be emitted from the improper storage, treatment and transport of skimmings [tm 33, Mantle 1988]. Dust will also arise from the handling and treatment of the skimmings. There are potential releases to water of suspended solids, metals and oils from the improper product and material storage.

The type and quality of scrap has a major influence on the significance of the releases. This is discussed in detail in the section dealing with techniques to consider.

There are potential sources of emissions from the pre-treatment, melting, degassing and holding stages.

Pre-treatment processes are covered in section 2.5, the secondary aluminium industry mainly uses swarf drying and thermal de-coating to pre-treat scrap and millings and other mechanical process and concentration methods for skimmings and salt slags.

Salt slags arise when mixtures of sodium and potassium chloride are used to cover the molten metal to prevent oxidation, increase yield and increase thermal efficiency. These slags are generally produced in rotary furnaces and can have an environmental impact if they are deposited on land. The quantity of salt slag produced varies considerably and is dependent on the type of material, the furnace and the degree of contamination of the aluminium etc. There are options available for salt free melting in some furnaces using many types of feed materials and there are options for recycling of salt slag.

4.2.2.1 Emissions to air

The potential releases to air are: -

- dust and smoke;
- metal compounds;
- organic materials (VOC, and dioxins) and CO;
- oxides of nitrogen (NO_x);
- sulphur dioxide.
- chlorides, HCl and HF.

A significant proportion of the emission of these substances is produced by the fuel used and by contamination of the feed material. Some dust is produced by fine dusty scrap and by salt fume [tm 77 & 90, Al Expert Group 1998].

Component	Pre Treatment	Melting	Refining and de-gassing
HCl, HF and chlorides	•	••	•••
Metals and compounds	••	••	••
Oxides of nitrogen	•	••	• (combustion gases)
SO_2	• (with suitable fuel)	• (with suitable fuel)	• (combustion gases)
Organic compounds (VOC, dioxins)	•••	•••	
Dust	•••	•••	••
Note. ••• More significant…………..• less significant			

Table 4.12: Significance of potential emissions to air

In addition there are potential releases of dust and phosphine from the treatment of salt slag that may need to be considered as a cross-media effect.

4.2.2.1.1 Capture of gases

Chapter 2.7 covers the techniques used. Fume extraction is an important element in secondary aluminium production as dust and smoke can be formed from contaminants on the feed as well as from the combustion and melting stages [tm 33, Mantle 1988]. The presence of several possible emission points on a furnace is also significant, and the collection of the emissions from such points needs to be addressed. In addition various systems may be employed to reduce fugitive emissions during the charging phase of the process. For example docking cars that seal against the charging door can be used to prevent emissions during charging.

The other important factor is the combustion of organic coatings in the pre treatment or melting furnace and the extraction and abatement systems can all be designed to cope with the treatment of these emissions. Fugitive emissions can be significant unless the fume collection systems are well designed.

4.2.2.1.2 Dust and metals

These are associated together and are produced from the combustion gases or from the scrap or fluxes used. Some metals, which are present as contaminants, will be fumed off during melting and will form dusts. The production of smoke due to the presence of organic carbon and the presence of chloride may lead to the formation of dioxins that will also be associated with the particles. After burning is used to destroy organic materials that escapes the combustion zone, injection of treatment materials such as lime, sodium bi-carbonate and carbon is also practised. Most installations then use (high efficiency) bag filters or ceramic filters to remove dust and emissions can lie in the range 0.6 to 20 mg/Nm^3. A spark arrester or cooling chamber often precedes them to provide filter protection. Energy recovery can be practised, most commonly re-cuperative burners are used.

Contents	Typical value (%)	Range (%)
CaO	25	0 - 50
Al_2O_3	15	6 - 25
NaCl, KCl	35	20 - 50
Carbon	6	1 - 6
Heavy metals *	-	0.01 - 10
Al, metal.	3	2 - 7
PCDD/F	5 µg/kg	3 - 10 µg/kg
Note. * Zn, Pb, Cu, Mn, V, Cr, Ni, Sn, (in traces Co, As, Tl, Be, Sb)		

Table 4.13: Typical composition of filter dust from secondary aluminium

Although salt slag processing may not be a process that is included in a permit for aluminium production, the potentially significant emission of dust from the crushing stages of an off-site process is an issue that can be taken into account locally.

4.2.2.1.3 Organic materials (VOC, dioxins) and CO

Poor combustion of fuel or the organic content of the feed material can result in the emission of organic materials. The provision of effective burner and furnace to controls is used to optimise combustion. Peak combustion rates from included organic materials needs to be taken into account if they are fed to the furnace. It is reported that pre-cleaning of scrap removes much of the organic material and improves the melting rate [tm 122, ETSU 1998]. The use of chlorine mixtures for de-gassing and magnesium removal and the use of chlorides (salt flux) will provide a source of chlorine for the potential formation of dioxins.

Afterburners are used to destroy organic material produced in the furnace or pre-treatment stages. Carbon may be added and efficient dust filtration used to remove organic material and dioxins that are associated with particulate matter.

4.2.2.1.4 Sulphur dioxide and oxides of nitrogen

Both of these compounds are produced as a result of the combustion systems used in the furnaces. The emissions are generally not significant. Low NO_x burners and low sulphur fuels can be used to minimise emissions. The use of oxy fuel burners can reduce the formation of thermal NO_x but there is a possibility that oxygen enrichment might have the opposite effect due to higher operating temperatures, higher concentrations are however associated with lower gas volumes and overall quantities. Reported emissions are in the range 10 to 900 grams of NO_x per tonne of metal depending on the furnace [tm 116, ALFED 1998].

4.2.2.1.5 HF, HCl and Chlorides

Chlorine may be used to treat the molten aluminium before casting to remove hydrogen and magnesium (de-magging). One possible use of rotary furnaces is for magnesium removal without any further use of chlorine. If an excess of chlorine is used it could be emitted as aluminium chloride and this can hydrolyse in contact with air to produce HCl. Some sites use wet scrubbers and others used dry or semi-dry scrubbing to remove these compounds. Their formation can be minimised by good control and the use of mixtures of chlorine and inert gases. The use of salt fluxes in a melting furnace can also result in the emission of very fine fume that contains metal chlorides. The use of fluorides for de-magging or as a flux can result in the release of HF and fluorides in small quantities.

4.2.2.1.6 Summary of emissions to air

Emissions	**Range**
Particulate mg/Nm^3	< 5 - 50
HF mg/Nm^3	< 5
Chlorides mg/Nm^3	< 5
HCl mg/Nm^3	3 - 40
SO_2 mg/Nm^3	15 - 530
NO_2 mg/Nm^3	40 - 420
Dioxins ng/Nm^3	< 0.1 - 1
VOC's mg/Nm^3	10 - 57
Energy Consumption MJ/t swarf	3500 - 5200

Table 4.14: Swarf drying

Emissions	**Range**
Particulate mg/Nm^3	< 1 - 35
HF mg/Nm^3	0.1 - 5
Chlorides mg/Nm^3	1 - 5
HCl mg/Nm^3	0.1 - 40
Dioxins ng/Nm^3	< 0.1 - 1
Energy Consumption MJ/t	2000 - 8000

Table 4.15: Induction furnace melting (abated)

Emissions	Range
Particulate mg/Nm^3	1 - 30
HF mg/Nm^3	0.1 - 5
Chlorides mg/Nm^3	< 1 - 5
HCl mg/Nm^3	0.1 - 40
SO_2 mg/Nm^3	5 - 520
NO_2 mg/Nm^3	50 - 450
Dioxins ng/Nm^3	< 0.1 - 1
VOCs mg/Nm^3	5 - 90
Energy Consumption MJ/t Al	4000 - 12000

Table 4.16: Rotary furnace melting (abated)

Emissions	Range
Particulate mg/Nm^3	< 0.1 - 35
HF mg/Nm^3	0.1 - 5
Chlorides mg/Nm^3	< 1 - 5
HCl mg/Nm^3	0.5 - 40
SO_2 mg/Nm^3	0.5 - 515
NO_2 mg/Nm^3	15 - 450
Dioxins ng/Nm^3	< 0.1 - 1
VOC's mg/Nm^3	2 - 55
Energy Consumption MJ/t Al	3300 - 8000

Table 4.17: Reverberatory and side-well furnace melting (abated)

Emissions	Range
Particulate mg/Nm^3	< 5 - 50
HF mg/Nm^3	< 5
Chlorides mg/Nm^3	1 - 5
HCl mg/Nm^3	30 - 40
SO_2 mg/Nm^3	10 - 530
NO_2 mg/Nm^3	20 - 420
Dioxins ng/Nm^3	< 0.1 - 1
VOC's mg/Nm^3	5 - 57
Energy Consumption MJ/t	2300 - 3800

Table 4.18: Sloping hearth furnace melting (abated)

4.2.2.2 Water emissions

The production of aluminium from secondary raw materials is essentially a dry process. Discharge of wastewater is usually limited to cooling water, which is often re-circulated and rainwater run-off from surfaces and roofs. The rainwater run-off can be contaminated by open storage of raw materials such as oily scrap and deposited solids. Typical values for this contamination are < 0.03 kg/tonne Al for suspended solids. In addition, considerable amounts of wastewater can be discharged when wet systems are used for air pollution control.

4.2.2.3 Process residues and waste

Skimmings from the holding and treatment processes represent 15 to 20 kg per tonne of aluminium produced. This material contains a significant amount of aluminium and the pre-treatment of the skimmings e.g. by pressing or cooling under an inert gas blanket reduces oxidation. During storage, Skimmings can react with moisture (from the air) to produce ammonia and other gases. Skimmings are used as a raw material in other parts of the secondary aluminium industry and are sometimes pre-treated by milling and air classification to separate aluminium from aluminium oxide.

Spent filters from metal treatment are usually disposed. In some cases when sodium bicarbonate is used for gas cleaning, solid residues can be recovered with the salt flux [tm 2, HMIP Al 1993; tm 33, Mantle 1988; tm 145, Winter 1998]. Alternatively filter dust can be treated thermally to destroy dioxins.

Furnace linings and dust can be recovered in the salt slag treatment processes or disposed.

Residue	Origin	Volume	Treatment	Comments on treatment
Salt slag	Melting in rotary drum furnace	Up to 500 kg/t Al	Recovery via dissolution and crystallisation techniques. Production of reusable substances if possible Al-granulate, mixed salt, Al_2O_3.	Aim to prevent landfill.
Filter dust	Exhaust gas cleaning	Up to 35 kg/t Al (0.1 - 10 kg/t Al*)	Disposal with pre-treatment or underground site, Partly reconditioned with salt slag or Used in the steel industry	Ban on surface disposal in some countries, thermal treatment possible (neutralisation with $NaHCO_3$ or Na_2CO_3 → use with salt slag)
Furnace lining	Melting furnace	~ 2 kg/t Al	Potential for reconditioning with skimmings, otherwise Leaching + landfill	No surface disposal in some countries. Production of injection moulding compounds reported
Skimmings	All furnaces not using salt, Cleaning of smelter, foundries	~ 25 kg/t Al 40 - 80 kg/t Al*)	Smelting in rotary furnace. Recovery, pellets used in rotary drum furnace, dross dust used in the recovery of salt slag	Aim to prevent landfill
Note. * using Closed Well furnace ** Non metallic products (oxide proportions from Al scrap)				

Table 4.19: Typical residues from secondary aluminium production

Emissions	Range
Particulate mg/Nm^3	10 - 40
* Dust kg/t	300 - 700
Energy Consumption MJ/t	300 - 800
Note. * The quantity of dust depends on the metallic content of the original Skimmings.	

Table 4.20: Skimmings preparation

Proprietary salt flux is a mixture of NaCl, KCl and calcium fluoride. Some fluoride may also be added up to 5%. When the used flux is tapped from the furnace (at this stage called salt slag) it contains large amounts of aluminium oxide, which the flux has separated from the raw materials. Up to 8 - 10% of the total weight of salt slag is metallic aluminium. The aluminium, sodium and potassium chlorides can be recovered for further use using separation and crystallisation processes. In some plants the oxide portion can be sold after a washing stage or can be used as cover in landfill sites.

Contents	Typical value (%)	Range (%)
Al, metallic	8	5 - 20
Water soluble parts *	37	20 - 40
Water insoluble parts **	55	45 - 75
PCDD/F	5 ng/kg	< 10 ng/kg
Note: * Water soluble salts. ** Metal oxides, non-recovered metal and insoluble salts.		

Table 4.21: Typical composition of salt slag

Emissions	Range
Particulate mg/Nm^3	15 - 40
Ammonia mg/ m^3	30 - 40
Phosphine mg/ m^3	0.1 – 0.5
Hydrogen sulphide ppm	50 - 100
Energy Consumption MJ/t	300 - 800

Table 4.22: Typical collected air emissions from salt slag recycling (excluding boiler exhaust - if fitted)
Fugitive emissions of dust from the crushing of salt slag can be highly significant

4.3 Techniques to Consider in the Determination of BAT

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2 "common processes" apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

Techniques used by other sectors are also applicable particularly those relating to the removal of tars and PAHs.

The techniques to consider on a site by site basis are strongly influenced by the raw materials that are available to a site, the process in place and in particular the type and variability of secondary raw materials. For example the metals they contain can be crucial to the choice of process.

The applied processes described above are applied to a wide range of secondary raw materials of varying quantity and composition and are also representative of those used worldwide. Primary processes have developed in recent times and control of the operating conditions and feeding techniques for cells have improved as have the containment and extraction systems. The techniques have been developed by the Companies in this sector to take account of this.

4.3.1 Materials storage, handling and pre-treatment processes

The storage of raw materials depends on the nature of the material described above. The storage of fine dusts in enclosed buildings, silos or in sealed packaging is used. The storage of non-dusty, non soluble material in open stockpiles and large items individually in the open is used.

4.3.1.1 Primary raw materials

The raw materials are bauxite, caustic soda, lime, chlorine mixtures, alumina, fluxes, anode material, secondary material and fuel. Other important materials are products, Skimmings, slags and process residues. Important aspects are the prevention of leakage of dust and wet material, the collection and treatment of dust and liquids and the control of the input and operating parameters of the handling and feeding processes. The issues specific to this group are: -

- The potentially dusty nature of bauxite, alumina and fluxes means that enclosed storage, handling and treatment systems may be appropriate in these instances. Closed conveyors, pneumatic transfer systems and storage silos are techniques to be considered.
- The dust generated by some milling and separation operations means that collection and abatement may be applicable for this process.
- Fabric or ceramic filters achieve better dust removal efficiencies than EPs.

Material	Storage	Handling	Pre-treatment	Comment
Coal or coke.	Covered bays, Silos.	Covered conveyors. Pneumatic.		
Fuel other oils and pitch.	Tanks or drums in bunded areas.	Secure pipeline or manual system.	Heated storage and pipelines	Back venting of displaced gases
Bauxite and alumina	Enclosed if dust forming.	Enclosed with dust collection. Covered conveyor.		
Chlorine gas or mixtures containing chlorine	Approved pressure vessels	Approved methods		
Products – Slab, billets, sheets and ingots	Open storage.			
Process residues for recovery e.g. skimmings.	Covered or enclosed depending on dust formation.	Depends on conditions.		Salt slag and skimmings kept dry. Appropriate drainage system.
Wastes for disposal.	Covered or enclosed bays or sealed (drums) depending on the material.	Depends on conditions.		Appropriate drainage system.

Table 4.23: Primary materials storage, handling and pre-treatment methods for aluminium

Skimmings and other metallic residues that are destined for recovery off site should be cooled preferably under an inert atmosphere and stored in dry conditions or other suitable ways depending on the material e.g. size reduction.

4.3.1.2 Secondary raw materials

There are a variety of secondary raw materials and they range from fine dusts to large single items. The metal content varies for each type of material and so does the content of other metals and contaminants.

Secondary raw materials that contain oil or contain water-soluble components are stored under cover. Skimmings can hydrolyse to produce ammonia gas. The techniques used for storage, handling and pre-treatment will therefore vary according to the material size and the extent of any contamination. These factors vary from site to site and the techniques discussed in section 2.4 will be applied on a site and material specific basis. The specific issues that apply to this group are:

- Pre-treatment stages are often used to remove oil or coatings or to separate aluminium from oxides. The removal of oil and coatings by thermal means for example in a swarf drier is a technique to consider.

- Other pre-treatment stages may also include granulation, media separation and magnetic separation to remove ferrous contamination. These are techniques to consider.
- Skimmings treatment by milling and grinding techniques when used with good dust extraction and abatement is also a technique to consider. The fine dust that is produced may be treated to recover other metals.
- The use of pneumatic or other density separation techniques is a technique to consider.
- Fine dusts storage and handling in a manner that prevents the emission of dust is a technique to consider.

Material	Storage	Handling	Pre-treatment	Comment
Fuel other oils	Tanks or drums in bunded areas.	Secure pipeline or manual system.	Heated storage and pipelines	Back venting of displaced gases
Fluxes and salt.	Enclosed (Silo) if dust forming.	Enclosed conveyors with dust collection.		
Fine dust (Skimmings) etc.	Enclosed if dust forming.	Enclosed with dust collection.	Milling and density separation.	
Swarf	Covered bays if soluble or emulsified oil.	Mechanical loader.	Swarf dryer. Centrifuging	Oil collection if necessary
Coarse dust	Open or covered bays	Mechanical loader.	Swarf dryer if necessary.	Oil collection if necessary
Lump (raw material or slag).	Open	Mechanical loader.		Oil collection if necessary
Whole Items, foils and sheets.	Open or covered bays	Mechanical loader.		Oil collection if necessary
Chlorine gas or mixtures containing chlorine	Approved pressure vessels	Approved methods		
Products – Slab, billets, sheets and ingots	Open storage.		Pre-heating	
Process residues for recovery e.g. skimmings, salt slag and linings.	Covered or enclosed depending on dust formation.	Depends on conditions.	Separation by milling and/or dissolution. - Potentially very dusty.	Skimmings and salt slag need to be kept dry. Appropriate drainage system.
Wastes for disposal.	Covered or enclosed bays or covered containers for transport depending on the material.	Depends on conditions.		Appropriate drainage system.

Table 4.24: Secondary materials storage, handling and pre-treatment methods for aluminium

4.3.2 The production of alumina from bauxite

The Bayer process is the standard technique to consider. There are several process variations and they should be considered in the determination of BAT. They are: -

- Handling, storage and grinding of bauxite, lime and other materials to minimise dust.
- Design and operation of digesters to minimise energy use e.g. the use of tube digesters and thermal heat exchanger oils to allow maximum heat recovery and higher digestion temperature.
- The use of fluidised bed calciners with preheating to use the heat content of the off gases. The use of fabric filters or EPs to remove calcined alumina and dust.
- Disposal of red mud in sealed areas with the reuse of transport and surface water from the ponds.

4.3.3 Primary aluminium smelting processes

The electrolysis cells detailed in the section on applied techniques are techniques to be considered in conjunction with the following features to minimise environmental impact: -

- Automatic multiple point feeding of alumina.
- Computer control of the electrolysis process based on active cell databases and monitoring of cell operating parameters.
- Complete hood coverage of the cell, which is connected to a separate gas exhaust and filter system. The use of robust cell covers and adequate extraction rates taking account of fluoride evaporation and carbon burn off.
- 98 to > 99% fume collection from the cells on a long term basis. If a lower collection efficiency is achieved the collection and treatment of ventilation gases should be considered.
- Minimisation of the time for changing anodes and other actions that need cell covers to be removed. Butt cooling in an enclosure. Use of a programmed system for cell operations and maintenance.
- For Søderberg cells: - Complete hood coverage of the anode top, which is connected to a separate gas exhaust and dry alumina scrubber **or: -** Dry anode top in combination with stud hole paste and an increase in the anode height (depending on the effectiveness that is demonstrated). Well-designed and maintained burners for incineration of CO and low molecular weight PAHs and other hydrocarbons in pot exhaust gas where necessary.
- Scrubbing of fluoride and HF from the cell fumes using alumina followed by dust removal in a fabric filter system or a combination of this and a wet scrubber to achieve a minimum of 99.9% removal of total fluoride. The alumina should be reused in the process.
- If sulphur removal is practised using a wet scrubber system, the system should be used with a system to remove fluoride, HF and tars.
- If there is a combined anode plant, the use of an alumina scrubber and fabric filter system or carbon coated filters to remove tar fume from the milling, blending and baking stages. Use of the alumina in the electrolysis process.
- The use of established efficient cleaning methods in the rodding plant to recover fluorides and carbon. The collection of fume containing fluoride from the cleaning process and from the melting of the steel components.
- The use of low sulphur carbon for the anodes or anode paste.
- The use of rotary gas or flux injection for holding furnaces.

EXAMPLE 4.01 CONTROL OF CELL OPERATING CONDITIONS

Description: - The bath temperature, voltage and electrical current are the only parameters for the electrolysis process that can directly be measured. Process control within the electrolysis process is therefore based on the data from this limited number of parameters. The development of microprocessors has made it possible for modern computers to simulate the electrolysis process by calculating complex models for dynamic kinetics and magnetic fields, based on the limited information available. This results in an improved process control and a more smooth operation of the electrolysis. Smooth process operation will in general result in lower emissions of fluorides and dust.

Main environmental benefits:- Improved process control can also be applied to reduce the emissions of PFCs. The anode effects, that cause the PFC emissions, are directly related to low alumina concentrations. The alumina concentration in the electrolyte can not directly be measured due to the very aggressive nature of this medium. Anode effects were therefore used as an additional method to control the alumina concentration. The anode effects occur when the alumina concentration has decreased below 1% and are therefore capable to identify a specific alumina concentration. By simulating the electrolysis, modern computers are capable of calculating and correcting the alumina concentration. The correction of the alumina concentration in the electrolyte reduces the number of anode effects. However, anode effects are still required for periodic adjustment of the simulated alumina concentration. Therefore this improved process control is often provided with an automated anode effect killing system. This system automatically disturbs the gaseous layer beneath the anode occurring during the anode effects using compressed air.

Operational data: - The emissions of PFCs can be reduced by improved process control. For example CWPB cells with central point feeding can in general be operated with an anode effect frequency of 0.2 to 0.5 anode effects per pot per day, resulting in a PFC emission of 0.05 to 0.1 kg per tonne aluminium. When modern computers are applied for process control, the number of anode effects can further be reduced to a frequency less than 0.1 anode effects per pot per day. This reduces the emissions of PFCs to less than 0.03 kg per tonne aluminium.

Cross media effects: - Improved process control within the electrolysis process results in a reduction of the electricity consumption. The conversion to point feeding is associated with higher fluoride emissions in the cell gases and will affect the size of the cell gas dry scrubbing system.

Economics: - Conversion of conventional Søderberg or CWPB plants to point feeder with process controls ~ 100 to 250 € per tonne annual capacity.

Applicability: - All Søderberg and CWPB plants have computer control but there are differences in the control technology and operating philosophy. There are opportunities for optimisation.

Example plants: - Norway, France, Netherlands.

Reference literature: - [tm 100, Nl Al 1998]

EXAMPLE 4.02 USE OF DRY SCRUBBING IN PRIMARY ALUMINIUM

Description: - Dry scrubbing is based on the recovery of fluorides by adsorption on alumina used as scrubbing agent. The fresh alumina is introduced to a reactor stage together with the process air from the electrolysis. Most of the adsorption of the gaseous fluorides (HF) on the alumina takes place in this reactor stage. The mixture of the process air with the alumina then enters a dust removal system where the alumina enriched with fluoride is separated from the process air. In general, bag filters are used for dust removal. An additional adsorption is achieved in these bag filters due to the filter cake that is built up on the filters. The alumina removed from the process air is used as alumina feeding for the electrolysis (so called "secondary alumina feeding").

The main purpose of the dry scrubbing system is to remove the fluorides and dust from the process air. An additional adsorption of SO_2 on the alumina will also occur. This SO_2 is returned to the electrolysis by the secondary alumina feeding. This SO_2 captured by the alumina will therefore be completely released by the electrolysis process when the alumina is heated. Hence, the emission of SO_2 is not reduced by the dry scrubbing system.

Main environmental benefits: - The dry scrubbing system with dust removal ensures very high removal efficiencies, better than 99.9% for total fluorides. The exact cleaning efficiency depends on equipment design, alumina properties and plant flexibility and maintenance. The most efficient dry scrubbing installations, operated with alumina with a high specific surface area as well as recycling the alumina several times to the reactor, reach average efficiency rates of > 99.9% for total fluorides.

Operational data: - A dry scrubbing system is capable of achieving emission levels of:

gaseous fluorides (HF):	0.03 to 0.2 kg per tonne aluminium
total fluorides:	0.05 to 0.3 kg per tonne aluminium;
dust:	0.2 to 0.5 kg per tonne aluminium.

Cross media effects: - Dry scrubbing requires a significant energy consumption of about 350 kWh per tonne aluminium. No other cross-media effects have been identified in the literature available.

Economics: - Investment costs of 5 million € have been identified to improve the cleaning efficiency of an existing dry scrubbing system with dust removal. Based on data from anonymous plants, the investment costs for new dry scrubbing systems with dust removal range from 10 million to 50 million €. Operational costs of 5 to 15 € per tonne aluminium were identified at the anonymous plants.

Applicability: - Most installations.

Example plants: - The vast majority of the primary aluminium plants use dry scrubbing with alumina and supplementary dust removal by bag filters to control their emissions. In some situations, electrostatic precipitators are used for dust removal.

Reference literature: - [tm 100, NL Al 1998]

EXAMPLE 4.03 USE OF WET SCRUBBING IN PRIMARY ALUMINIUM

Description: - The emissions caused by the electrolysis can be abated by wet scrubbing. Wet scrubbing will in general be applied as supplementary abatement to the dry scrubbing. The supplementary wet scrubbing is mainly applied for SO_2 removal but will also reduce the emissions of fluorides and, to a lesser extent, dust. Wet scrubbing can be applied to gases from the electrolysis cells and to the pot-room ventilation gases.

The wet scrubbing process is based on the principle that the pollutants are absorbed and converted by the scrubbing medium. Various cleaning agents can be applied as scrubbing medium. Within the aluminium industry, seawater is often applied as well as individual applications of sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3). The SO_2 is converted into aqueous sulphates by these mediums. Another possibility is to convert the SO_2 to gypsum, using lime containing scrubbing agents such as lime hydrate, limestone or mixtures of calcium- and magnesium hydroxides.

The scrubbing medium has to be refreshed and the medium used has to be discharged to allow continuous absorption and conversion.

Main environmental benefits: - Removal of SO_2 and other acid gases to reduce local, regional and long-range impact of these gases.

Operational data: - Removal efficiency for SO_2 of 80 to over 90% have been identified for wet scrubbers. SO_2 emissions can be reduced to concentrations of 25 to 50 mg/Nm^3 and loads of 0.6 to 4 kg SO_2 per tonne aluminium. In addition the supplementary wet scrubbing results in a reduced emission of fluorides and dust. Emission levels for total fluorides (gaseous and particulate) of 0.02 to 0.2 kg per tonne aluminium have been identified when wet scrubbing is applied as supplementary abatement. In these situations dust emissions were reduced to 0.1 to 0.3 kg per tonne aluminium.

Cross media effects: - All wet scrubbing systems require that the absorbed and converted pollutants are discharged from the system. Discharges can occur as waste water (sea water), fluid waste (NaOH and Na_2CO_3) or as gypsum.
a) Seawater: The effluent from the sea water scrubbers (20 to 300 m^3 per tonne aluminium) at an aluminium plant is slightly acid and contains fluorides, sulphite/sulphate, suspended matter and trace contamination (e.g. nickel) and is deficient in oxygen. The plants using seawater will therefore normally have installations for the removal of particulate matter to comply with national legislation for the discharge of this wastewater to the sea. Wastewater treatment normally includes flocculation and sedimentation. The wastewater treatment results in a sludge that has to be disposed. The sea waster used in the wet scrubbers can also be treated with biocides, which will also be discharged into the sea. Seawater scrubbing requires an additional energy consumption of about 150 kWh per tonne aluminium.
b) NaOH: The scrubbers operated with NaOH require that a concentrated effluent (about 1 m^3 per tonne aluminium) has to be discharged. The pollutants in this effluent can be compared to the pollutants in the discharged seawater but occur in higher concentrations. Nevertheless, the effect on the aquatic environment will remain.

Economics: - Cost estimates have been identified for supplementary wet scrubbing of the process air. The cost estimates are presented for scrubbing systems operated with sea water as well as NaOH.
a) Seawater: the identified investment costs range from 9 to 36 million €. Based on the annual production capacity, investment costs range from 75 to 250 € per tonne capacity.
The identified total annual costs range from 2.6 to 7.5 million €. Based on the annual production capacity, total annual costs range from 40 to 70 € per tonne aluminium.
b) NaOH: the identified investment costs range from 12 to 40 million €. Based on the annual production capacity, investment costs range from 100 to 250 € per tonne capacity.

The identified total annual costs range from 4 to 7 million €. Based on the annual production capacity, total annual costs range from 100 to 200 € per tonne aluminium.

Applicability: - This technique is applicable when sulphur dioxide concentrations in air exceed Long Range, local or regional Air Quality standards. Similar scrubbing techniques may also be applied to remove fluorides, sulphur dioxide and PAHs from pot room ventilation air from some SWPB and Søderberg plants. The investment and operating costs are different in this case.

Example plants: - Wet scrubbing of the process air from the electrolysis is applied in Europe only in Scandinavia. All plants in Norway and Sweden have wet scrubbing. Some of the Soderberg plants also have installed pot ventilation air scrubbing. These wet scrubbers are mainly in operation at seaside aluminium plants, using sea water as scrubbing medium. In addition, one plant in Norway has been identified using NaOH as scrubbing medium, while in the USA one plant has been identified operated with Na_2CO_3.

Reference literature: - [tm 100, NL Al 1998]

4.3.4 Secondary smelting furnaces

Several of the techniques described in section 2.7 and 2.8 are applicable to fume extraction and abatement and the process control systems used by these furnaces. These techniques are not routinely used by all installations at the time of writing. The furnaces that are described as available techniques are the techniques to consider in the determination of BAT. The following features are techniques to consider in the determination of BAT for the furnaces.

- Selection of the feed material to suit the furnace type and abatement and to transfer unsuitable raw materials to other operators using equipment designed for them so that it is possible to:
    a) To prevent the use of salt where practical consistent with achieving the maximum practical yield;
    b) To minimise the use of salt in other cases;
    c) To recover as many by-products as possible e.g. recovery of any salt slag that is produced.

  The aim is to prevent landfill. If landfill is used, a secure, sealed and contained system is needed [tm 206, TGI 1999].

- The use of a sealed charging carriage or similar sealing system if possible.
- The use of oxy-fuel burners where energy and environmental benefits are established.
- The use of enclosures, hoods and targeted fume extraction systems to collect fugitive emissions wherever practical.
- The removal of oil and organic materials using swarf drying, centrifuging or other de-coating method before the smelting or melting stage, unless the furnace and abatement system is specifically designed to accommodate the organic content.
- The use of core-less induction furnaces for relatively small quantities of clean metal.
- The use of afterburners where necessary to remove organic carbon including dioxins.
- Injection of carbon together with lime to reduce acid gases and organic carbon including dioxins.
- The use of heat recovery if practicable.
- The use of suitable filtration technology e.g. fabric or ceramic filters.

The use of metal pumping, sealed charging systems and intelligent fume collection control should be considered for existing processes depending on the furnace type. The following table gives an overview of the advantages and disadvantages of the secondary smelting and melting furnaces.

Furnace type	Variations	Principal application	Advantages	Disadvantages	Gas collection	Comments
Reverberatory	Standard	Melting larger volumes of clean scraps and primary feedstock	▪ Large metal capacity (100t). ▪ Few restrictions on feed stock sizes. ▪ Low salt slag use	▪ Lower thermal efficiency ▪ Restricted feedstock types	Semi sealed	▪ High yields due to quality of feedstock ▪ Molten metal pumps sometimes used
	Side well	As above, but enables efficient recovery of some finer feedstocks.	▪ Large metal capacity. ▪ Wider range of feedstock possible. ▪ Normally no salt slag	▪ Lower thermal efficiency	Semi sealed	▪ High yields possible depending upon quality of feedstock ▪ Molten metal pumps sometimes used
	Sloping Hearth	Separation of aluminium from higher melting point metal contamination (i.e. iron/steel)	▪ Very efficient at removing high melting point contaminants.	▪ Lower thermal efficiency	Semi sealed	▪ Sometimes incorporated into other furnace types. ▪ Yield dependant upon level of contamination.
Rotary	Fixed Axis	Recycling a wide range of feedstocks	▪ No feedstock restrictions ▪ Good thermal efficiency ▪ Efficient de-magging ▪ No skimmings produced ▪ Large charge volumes possible(> 65t)	▪ Relatively high usage of salt flux. ▪ Feedstock size may be restricted	Semi sealed	▪ Resultant salt slags can be reprocessed.
	Tilting	As Above	▪ As above, but lower usage of salt flux and lower capacity.	▪ Feedstock size may be restricted	Semi sealed	▪ Tends to be used for lower scrap grades.
Induction	Coreless	Melting of cleaner scraps or primary feedstock	▪ High yields obtained. ▪ No combustion gases ▪ No salt flux required. ▪ Flexible usage (batch and continuous processing possible)	▪ Relatively small load (< 10t) ▪ Restricted feedstock type ▪ Feedstock size may be restricted	Open, hooded	
	Channel	As above.	▪ High yields obtained. ▪ No combustion gases ▪ No salt flux required	▪ As above, but able to have larger capacities(~20 - 25t)	Semi sealed	
Shaft furnace		Melting clean ingot and process scraps in foundries.	▪ Better thermal efficiency	▪ Restricted feedstock types. ▪ Feedstock size may be restricted	Semi sealed	▪ Used in Meltower process.

Table 4.25: Overview of secondary smelting furnaces

The following examples show how the use of salt flux can be virtually eliminated, reduced in quantity or ultimately recovered. Each option needs to be considered in line with the process technology used. Each of these items has its own inherent advantages and disadvantages, such as restrictions in feedstock material or metal volumes, which must also be considered.

EXAMPLE 4.04 USE OF METAL PUMPING SYSTEM

Description: - Reverberatory furnace with side well, charge well and pumped metal system.

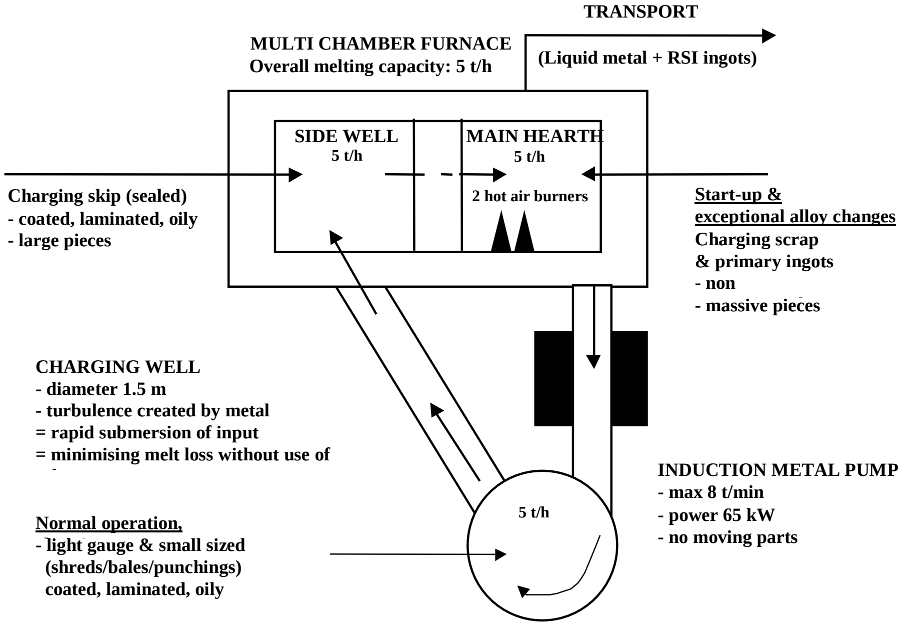


Figure 4.6: An example of a pumped metal system

Main environmental benefits: - Potential elimination of salt flux. Greater range of raw materials than simple reverberatory furnace, improved capture of furnace gases.

Operational data: - Improvement in metal yield from 83 to 88%, reduction in energy costs

Cross media effects: - Reduction of amount of waste produced that requires treatment. Associated reduction in energy usage and emissions from the furnace.

Economics: - Cost (1997) of 30 tonne furnace and Electro Magnetic Pumping system £1800000 (2.73 million €), estimated cost savings (energy, improved yield, flux savings and treatment savings) £832000 (1.26 million €) per year. Pay back 2.2 years.
Cost of pumping system and charge well ~ £300000 (456000 €),.

Applicability: - New and upgraded reverberatory furnaces. Cannot be used for batch processes. Other methods of pumping are also applicable.

Example plants: - Pumping systems are widely used over Europe.

Reference literature: - [tm 123, ETSU 1998]. [tm 122, McLelan 1998]

EXAMPLE 4.05 MINIMISATION OF SALT FLUX

Description: - Minimisation of salt flux by the use of a tilting rotary furnace.

Main environmental benefits: - Reduction in the amount of salt slag produced from 1.8 to < 0.5 kg salt per kg non-metal content.

Operational data: - Reduction of salt usage factor from 1 – 1.8 down to < 0.5

Cross media effects: - Reduction of amount of waste produced that requires treatment. Associated reduction in energy and emissions from treatment process.

Economics: - Not known – cost of furnace less cost savings from purchase and treatment of salt. 4 plants are operating viably.

Applicability: - New and upgraded furnaces. There are size restrictions. Not applicable for all feedstock.

Example plants: - Plants in use in USA, Germany and UK

Reference literature: - [tm 145, Winter 1998].

EXAMPLE 4.06 MINIMISATION OF SALT FLUX

Description: - Minimisation of the quantity of waste generated by the pre-treatment of skimmings. Skimmings are milled and sieved to separate the mainly aluminium fraction from the oxide. The aluminium fraction is recovered in a rotary furnace but the pre-treatment reduces the quantity smelted as well as the amount of salt needed.

Main environmental benefits: - Reduction in the amount of waste produced from 118 kg per 100 kg to 66 kg per 100 kg of skimmings recovered.

Operational data: - 100 kg of untreated skimmings uses ~ 72 kg of salt for smelting and produces 45 kg of aluminium and 118 kg of salt slag residue. Total residue ~ 118 kg.
100 kg of skimmings, after pre-treatment by milling and sieving produces, 70 kg of aluminium grains, 12.5 kg of dust for treatment, 12.5 kg of reusable material and 5 kg of iron. The 70 kg of aluminium grains uses 32.5 kg of salt for smelting and produces 45 kg of aluminium and ~ 54 kg of salt slag residue. Total residue ~ 66 kg.

Cross media effects: - Reduction of amount of salt slag used reduces emissions of chloride, lower reliance on salt slag treatment or disposal. Associated reduction in energy and emissions from treatment process due to a lower furnace burden.

Economics: - Not known – cost of mill and sieve less cost savings from treatment or disposal charges. Many plants are operating viably.

Applicability: - Most skimmings with high oxide content.

Example plants: - Plants in use in Spain, Italy, Germany and UK

Reference literature: - IDALSA 1999.

EXAMPLE 4.07 RECOVERY OF SALT SLAG

Description: - Recovery of salt slag to recover aluminium, salt and oxide portions. Large blocks of salt slag are crushed to manageable size and aluminium granules recovered by sieving (typically up to 10%). The finely crushed material is then dissolved in water so that the chlorides go into solution producing brine, leaving the insoluble aluminium oxide and the finest metallic particles of aluminium, which are not normally economically recoverable as metal. There are some variations in the processes that are used, some use cold water and then concentrate the brine for crystallisation and others use hot water.

Gases are evolved from the dissolution stage of the process and mainly contain ammonia, methane, hydrogen and phosphine. It is possible to use these gases as a fuel for other parts of the process [tm 116, ALFED 1998]. The brine is filtered removing the insoluble oxides and the solution is then sent for crystallisation from which the original sodium and potassium chlorides can be recovered and then re-used as flux in the melting furnaces. The oxides contain Ca, Mg and Al oxides with chloride, fluoride, sulphate and nitrate anions. The washed oxide has been used in the cement industry. Flue dust arising from the treatment of gases from secondary furnaces using sodium bicarbonate are reported to be recovered in the salt recovery process in Austria and Spain

Main environmental benefits: - Reduction of land fill, recovery of salt for reuse, possible production of alumina for use in other industries, recovery of aluminium portion [tm 206, TGI 1999].

Operational data: - Not available.

Cross media effects: - Reduction of amount of waste produced that requires disposal. Potential releases of phosphine to air if after-burning is not used. The crushing operations are potentially very dusty and observations show that they can have a significant environmental impact due to fugitive emissions..

Economics: - Not known – cost of process equipment. Several plants are operating viably and treatment costs are similar to disposal costs but avoid "future liability".

Applicability: - All processes using salt flux.

Example plants: - Germany, Spain, France, Italy and UK

Reference literature: - [tm 116, ALFED 1998]; [tm 145, Winter 1998].

EXAMPLE 4.08 USE OF SEALED CHARGING CARRIAGE

Description: - A charging car or skip is used to transfer scrap into reverberatory furnace. The system is sized so that the skip seals against the open furnace door during the discharge of scrap and so maintains furnace sealing during this period.

Main environmental benefits: - Prevention of fugitive emissions during charging of scrap.

Operational data: - Not available but observations confirm the effectiveness of the system.

Cross media effects: - Positive effect by prevention of fugitive emissions of smoke and fumes.

Economics: - Not available but thought to be low-cost for a suitably sized charging skip.

Applicability: - Potential for some non-rotating furnaces.

Example plants: - The system is operated in Belgium

Reference literature : - [tm 121, Hoogovens 1998].

EXAMPLE 4.09 USE OF TARGETED FUME COLLECTION

Description: - A fume collection system can be designed so that the collection fan capacity can be directed to sources of fume that change over a charging, melting and tapping cycle. Targeting of fume collection capacity can be achieved by using automatically controlled dampers that are linked to the furnace controls e.g. door opening, burner state or furnace inclination. Damper operation can therefore be initiated by charging, melting and tapping operations and the fume collection effort targeted accordingly.

Main environmental benefits: - Prevention and minimisation of fugitive emissions to air.

Operational data: - Non available but observations indicate that such systems are very effective if designed and controlled well.

Cross media effects: - Positive effect. Prevention of fugitive emissions and optimising fan energy consumption.

Economics: - Not available. Relatively low cost of control and damper system.

Applicability: - Most installations.

Example plants: - UK, France

Reference literature: - [tm 106, Farrell 1998]

EXAMPLE 4.10 COLLECTION OF FUME

Description: - Charging and tapping zone fume collection enclosure for a rotary furnace to allow the use of a single extraction point.

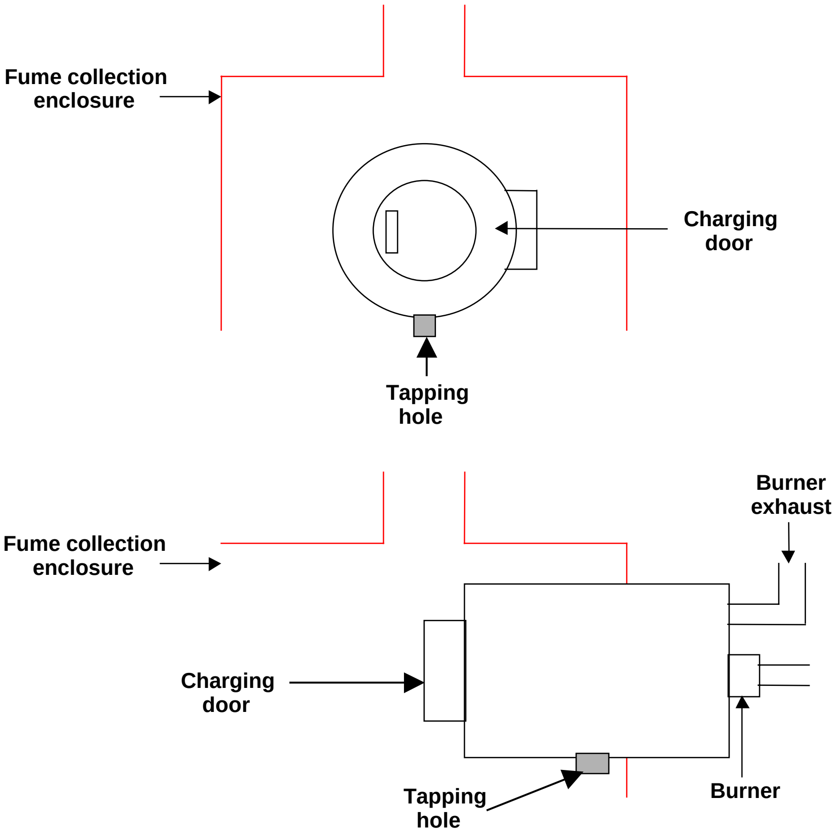


Figure 4.7: A diagram of an integral fume collection system

In applications for the production of other metals, tapping holes on the charging door have been used and allow a more compact enclosure. Furnace lining wear may mean that door end tapping holes may not allow all of the metal to be tapped.

Main environmental benefits: - Easier, effective fume collection from a single point.

Operational data: - Non available but observation shows effective fume capture.

Cross media effects: - Positive effect- good collection efficiency with reduced power consumption.

Economics: - Low cost of modification in use viably in several installations.

Applicability: - All rotary furnaces.

Example plants: - France, UK

Reference literature: - [tm 106, Farrell, 1998]

4.3.5 Refining processes

- The use of chlorine mixed with argon or nitrogen as the de-gassing or de-magging reagent or the use of aluminium fluoride, KF or Na_3AlF_6. The collection and treatment of the resulting gases to remove acid gases if necessary.
- The use of inline flow cells for gas additions to the molten metal if practical.
- The use of in-line ceramic metal filters to remove solid particles from the melt.

The refining processes and techniques for are suitable for use with new and existing installations.

4.3.6 Casting processes

The processes detailed in the section on applied techniques are techniques to be considered in conjunction with effective fume extraction of launders and casters where needed. The potential for dioxin formation during the refining processes for primary and secondary production of aluminium has not been fully investigated. It is recommended that this issue is quantified.

The fume collection processes and techniques for are suitable for use with new and existing installations.

4.3.7 Skimmings

The processes detailed in the section on applied techniques are techniques to be considered in conjunction with the following features to minimise environmental impact: -

- Cooling of skimmings in sealed containers under inert gas.
- The prevention of wetting of the skimmings.
- The treatment and recovery of skimmings if practical.
- Minimisation of material for landfill.

The storage and treatment techniques are suitable for use with new and existing installations.

4.3.8 Integrated anode production

The use of the processes outlined in Chapter 12 are the techniques to consider. The use of the alumina scrubber and fabric filter system from the cell gas treatment could be used for the gases from anode production. A coke filter may be used for the mixing and forming stages.

4.3.9 Fume/gas collection and abatement

4.3.9.1 Primary aluminium

The techniques discussed earlier in this chapter to seal the cells and maintain collection efficiency are techniques to be considered for the collection of fume from the cells involved in the production of primary aluminium. The use of a dry scrubber followed by a fabric filter to remove fluorides is a technique to consider. The collection of the ventilation air from the cell rooms if necessary is also a technique to consider. The use of secondary hoods is also a technique to be considered for the charging of casting furnaces.
The use sea water or caustic scrubbers to remove sulphur dioxide may be considered for the reduction of total SO_2 emissions. The cross-media effect on water needs to be considered on a local basis.

4.3.9.2 Secondary aluminium

The techniques discussed in section 2.7 and 2.8 of this document to seal furnaces, collect fume, remove dust, acid gases and dioxins are techniques to be considered for the various process stages involved in the production of secondary aluminium. The use of secondary hoods is also a technique to be considered for the transfer and casting stages.

There are several site-specific issues that will apply and some of these are discussed earlier in this chapter. Essentially the process technologies discussed in this chapter, combined with suitable abatement will meet the demands of stringent environmental protection.

4.3.10 Process control

The principles of process control discussed in section 2.6 are applicable to the production processes used in this Group. Some of the processes are capable of improvement by the adoption of many of these techniques. The monitoring of cell operating conditions and the use of comparative data bases to anticipate process disturbances such as anode effects and to control point additions of alumina should be considered for all processes.

4.3.11 Wastewater

This is a site-specific issue, existing treatment systems are reported to be to a high standard. All wastewater should be treated to remove solids and oils/tars, absorbed acid gases (e.g. sulphur dioxide, HCl) should be neutralised if necessary. The techniques listed in section 2.9 are the techniques to consider. In a number of installations cooling water and treated wastewater including rainwater is reused or recycled within the processes.

4.3.12 Process residues

The principles of the minimisation and re-used of process residues are techniques to consider.

4.3.12.1 Primary aluminium

Skimmings can be recycled and pot lining can be re-used.

EXAMPLE 4.11 USES OF SPENT POT LINING

Description: - The use of SPL carbon content in thermal processes.

Main environmental benefits: - Use of energy content of the carbon, use of residual AlF_3 as a flux. Destruction of any CN content.

Operational data: - Details not available but there have been successful applications in cement firing, as a carburant in steel production and as a coke substitute in rock wool production.

Cross media effects: - Positive effects. Use of the energy value of SPL. Elimination of waste deposited on land. Avoidance of energy input and associated releases if the SPL is treated thermally.

Economics: - No nett income but avoidance of treatment or disposal charges.

Applicability: - All SPL provided that Waste Transfer regulations allow it.

Example plants: - France, Norway

Reference literature – [tm 106, Farrell 1998]:

4.3.12.2 Secondary aluminium

Furnace linings and filter dusts can be reused in certain processes, the use of sodium bi-carbonate as a dry scrubbing medium can allow the resulting filter dust to be sent to a salt slag recovery system. Salt slag recovery techniques are available to recover salt, aluminium and aluminium oxide. Skimmings can be reused in appropriate processes. Examples are given earlier in this chapter.

4.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector; which for the production of aluminium are fluorides (incl. HF), dust, SO_2, COS, PAH, VOCs, fume, green-house gases (PFCs and CO_2), dioxins (secondary), chlorides and HCl and residues such as bauxite residue, SPL, filter dust and salt slag;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous chapter. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this section are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

The Best Available Techniques are influenced by a number of factors and methodology of examining the techniques is needed. The approach that has been used is given below.

First of all the choice of secondary process depends strongly on the raw materials that are available to a particular site. The most significant factors are their composition, the presence of other included metals, their size distribution (including the potential to form dust) and the degree of contamination by organic material.

Secondly, the process should be suitable for use with the best gas collection and abatement systems that are available. The fume collection and abatement processes used will depend on the characteristics of the main processes, for example some processes are easier to seal. Other processes may be able to treat low-grade materials more easily and therefore reduce the wider environmental impact by preventing disposal.

Finally, the water and waste issues have been taken into account, in particular the minimisation of wastes and the potential to reuse residues and water within the process or by other processes. Energy used by the processes is also a factor that is taken into account in the choice of processes.

The choice of BAT in a general sense is therefore complicated and depends on the above factors. The varying requirements mean that BAT is influenced mainly by the raw materials available to the site and the required throughput of the plant, the issues are therefore site specific.

The following points summarise the recommended methodology that has been used in this work: -

- Is the process industrially proven and reliable?
- Are there limitations in the feed material that can be processed?
- The type of feed and other materials contained in it influences process selection.
- Are there production level constraints? - e.g. a proven upper limit or a minimum throughput required to be economic.
- Can latest and efficient collection and abatement techniques be applied to the process?
- Can the process and abatement combinations achieve the lowest emission levels? The achievable emissions are reported later.
- Are there other aspects such as safety that are related to processes?

At the time of writing several process and abatement combinations are able to operate to the highest environmental standards and meet the requirements of BAT. The processes vary in the throughput that can be achieved and the materials that can be used and so several combinations are included. All of the processes maximise the reuse of residues and minimise emissions to water. The economics of the processes vary. Some need to operate at a high throughput to achieve economic operation, while others are not able to achieve high throughputs.

The collection and abatement techniques used with these processes were discussed under techniques to consider in the determination of BAT and when applied in combination with the metallurgical process will result in a high level of environmental protection.
As indicated in the general preface to this document, this section proposes techniques and emissions that are considered to be compatible with BAT in general. The purpose is to provide general indications of the emission and consumption levels that might be considered as an appropriate benchmark of BAT based performance. This is done by quoting achievable levels in ranges that are generally applicable to both new and upgraded plants. Existing installations may have factors, such as space or height limitations that prevent full adoption of the techniques.

The level will also vary with time depending on the condition of the equipment, its maintenance and the process control of the abatement plant. The operation of the source process will also influence performance as there are likely to be variations in temperature, gas volume and even the characteristics of the material throughout a process or batch. The achievable emissions are therefore only a basis from which actual plant performance can be judged. Process dynamics and other site specific issues need to be taken into account at a local level. The examples given in the section on techniques to consider in the determination of BAT give the concentrations associated with some existing processes.

4.4.1 Materials handling and storage

The conclusions drawn for Best Available Techniques for the materials handling and storage stages are given in section 2.17 of this document and are applicable to the materials in this chapter. These techniques are:

- The use of liquid storage systems that are contained in impervious bunds that have a capacity capable of containing at least the volume of the largest storage tank within the bund. Various guidelines exist within each Member State and they should be followed as appropriate. Storage areas should be designed so that leaks from the upper portions of tanks and from delivery systems are intercepted and contained in the bund. Tank contents should be displayed and associated alarms used. The use of planned deliveries and automatic control systems to prevent over filling of storage tanks.

- Sulphuric acid and other reactive materials should also be stored in double walled tanks or tanks placed in chemically resistant bunds of the same capacity. The use of leak detection systems and alarms is sensible. If there is a risk of ground water contamination the storage area should be impermeable and resistant to the material stored.

- Delivery points should be contained within the bund to collect spilled of material. Back venting of displaced gases to the delivery vehicle should be practised to reduce emissions of VOCs. Use of automatic resealing of delivery connections to prevent spillage should be considered.

- Incompatible materials (e.g. oxidising and organic materials) should be segregated and inert gases used for storage tanks or areas if needed.

- The use of oil and solid interceptors if necessary for the drainage from open storage areas. The storage of material that can release oil on concreted areas that have curbs or other containment devices. The use of effluent treatment methods for chemical species that are stored.

- Transfer conveyors and pipelines placed in safe, open areas above ground so that leaks can be detected quickly and damage from vehicles and other equipment can be prevented. If buried pipelines are used their course can be documented and marked and safe excavation systems adopted.

- The use of well designed, robust pressure vessels for gases (including LPG's) with pressure monitoring of the tanks and delivery pipe-work to prevent rupture and leakage. Gas monitors should be used in confined areas and close to storage tanks.

- Where required, sealed delivery, storage and reclamation systems can be used for dusty materials and silos can be used for day storage. Completely closed buildings can be used for the storage of dusty materials and may not require special filter devices.

- Sealing agents (such as molasses and PVA) can be used where appropriate and compatible to reduce the tendency for material to form dust.

- Where required enclosed conveyors with well designed, robust extraction and filtration equipment can be used on delivery points, silos, pneumatic transfer systems and conveyor transfer points to prevent the emission of dust.

- Non-dusty, non-soluble material can be stored on sealed surfaces with drainage and drain collection.

- Swarf, turnings and other material containing soluble or emulsified oil should be stored under cover to prevent washing away by rainwater.

- Rationalised transport systems can be used to minimise the generation and transport of dust within a site. Rainwater that washes dust away should be collected and treated before discharge.

- The use of wheel and body washes or other cleaning systems to clean vehicles used to deliver or handle dusty material. Local conditions will influence the method e.g. ice formation. Planned campaigns for road sweeping can be used.

- Inventory control and inspection systems can be adopted to prevent spillages and identify leaks.

- Material sampling and assay systems can be incorporated into the materials handling and storage system to identify raw material quality and plan the processing method. These systems should be designed and operated to same high standards as the handling and storage systems.

- Storage areas for reductants such as coal, coke or woodchips need to be surveyed to detect fires, caused by self-ignition.

- The use of good design and construction practices and adequate maintenance.

The summary table for material handling and storage is reproduced below.

Material	Storage	Handling	Pre-treatment	Comment
Fuel and other oils	Tanks or drums in bunded areas.	Secure pipeline or manual system.	Heated storage and pipelines	Back venting of displaced gases
Fluxes and salt.	Enclosed (Silo) if dust forming.	Enclosed conveyors with dust collection.		
Fine dust (Skimmings) etc.	Enclosed if dust forming.	Enclosed with dust collection.	Milling and density separation.	
Swarf	Covered bays if soluble or emulsified oil.	Mechanical loader.	Swarf dryer. Centrifuging	Oil collection if necessary
Coarse dust	Open or covered bays	Mechanical loader.	Swarf dryer if necessary.	Oil collection if necessary
Lump (raw material or slag).	Open	Mechanical loader.		Oil collection if necessary
Whole items, foils and sheets.	Open or covered bays	Mechanical loader.		Oil collection if necessary
Chlorine gas or mixtures containing chlorine	Approved pressure vessels	Approved methods		
Products – Slab, billets, sheets and ingots	Open storage.		Pre-heating	
Process residues for recovery e.g. skimmings, salt slag and linings.	Covered or enclosed depending on dust formation.	Depends on conditions.	Separation by milling and/or dissolution. - Potentially very dusty.	Skimmings and salt slag need to be kept dry. Appropriate drainage system.
Wastes for disposal.	Covered or enclosed bays or covered containers for transport depending on the material.	Depends on conditions.		Appropriate drainage system.

Table 4.26: Summary of handling and storage techniques for aluminium

4.4.2 Process selection

It is only possible to conclude a process based Best Available Technique for the smelting stage of primary aluminium. The other techniques including those for secondary aluminium that are considered to be BAT are listed.

4.4.2.1 Primary aluminium smelting

Taking these factors into consideration the use of centre worked prebaked cells with automatic multiple point feeding of alumina is considered to be BAT for the production of primary aluminium. The process will have the following features: -

- Computer control of the electrolysis process based on active cell databases and monitoring of cell operating parameters to minimise the energy consumption and reduce the number and duration of anode effects.

- Complete hood coverage of the cells, which is connected to a gas exhaust and filter. The use of robust cell covers and adequate extraction rates. Sealed anode butt cooling system.

- Better than 99% fume collection from cells on a long term basis. Minimisation of the time taken for opening covers and changing anodes. Use of a programmed system for cell operations and maintenance.

- The use of established efficient cleaning methods in the rodding plant to recover fluorides and carbon. The use of effective extraction and filtration systems in this area.

- If local, regional or long-range environmental impacts require sulphur dioxide reductions, the use of low sulphur carbon for the anodes or anode paste if practicable or a sulphur dioxide scrubbing system.

- Gases from the primary smelting process should be treated to remove dust, fluorides and HF using an alumina scrubber and fabric filter. The scrubbing efficiency for total fluoride should be > 99.8%, and the alumina used in the electrolytic cells.

- If there is an integrated anode plant the process gases should be treated in an alumina scrubber and fabric filter system and the alumina used in the electrolytic cells. Tars from mixing and forming processes can be treated in a coke filter.

- An established system for environmental management, operational control and maintenance.

4.4.2.2 Secondary aluminium smelting

For the production of aluminium from secondary raw materials, the variation in feed stock also has to be taken into account at a local level. This will influence the combination of furnaces, scrap sorting and pre-treatment and the associated collection and abatement systems that are used. The smelting and melting processes that are considered to be BAT are the Reverberatory furnace, Tilting rotary furnace, Rotary furnace, Meltower Induction furnace depending on the feed materials.

Furnace	Gas Collection	Advantages	Disadvantages	Comments
Reverberatory furnace.	Semi sealed	Large metal capacity	Lower efficiency, restricted feed-stock	Use of sealed charging system (charging car)
Reverberatory furnace with side well/charging well.	Semi sealed	Charging well allows efficient recovery of fine material. Larger range of feed material	Lower thermal efficiency	Use of sealed charging system (charging car)
Rotary Furnace	Semi sealed	No feed stock restrictions. Good thermal efficiency	Relatively high usage of salt slag.	Targeted fume extraction
Tilting rotary furnace	Semi sealed	Efficient for low grade feed including skimmings. Good thermal efficiency	Restricted metal capacity	Minimum use of salt flux compared to fixed rotary furnace.
Induction Furnace	Open, hooded	No combustion gases	Restricted metal capacity and feed stock	Useful for small loads of clean metal
Shaft furnace (Meltower)	Semi sealed	Charge pre-heating		For clean metal

Table 4.27: Furnaces considered being BAT for secondary aluminium production

The process will have the following features: -

- Selection of the feed material to suit the furnace type and abatement and to transfer unsuitable raw materials to other operators using equipment designed for them so that it is possible to:
    a) To prevent the use of salt where practical consistent with achieving the maximum practical yield;
    b) To minimise the use of salt in other cases;
    c) To recover as many by-products as possible e.g. recovery of any salt slag that is produced.

  The aim is to prevent landfill if possible.
- The use of a sealed charging carriage or similar sealed feeding system if possible.
- The use of enclosures or hoods for the feeding and tapping areas and targeted fume extraction systems if practical to minimise energy usage.
- The removal of oil and organic materials using swarf centrifuge, swarf drying or other thermal de-coating method before the smelting or melting stage (to reduce the potential for the emissions of dioxins and organic matter and to maximise energy efficiency), unless the furnace is specifically designed to accommodate the organic content.
- The use of coreless-induction furnaces for relatively small quantities of clean metal.
- The use of afterburners where necessary to remove organic carbon including dioxins.
- The injection of activated carbon and lime if necessary to remove acid gases and organic carbon including dioxins.
- The use of heat recovery if practicable.
- The use of fabric or ceramic filters for dust removal.

4.4.2.3 Other process stages

The techniques to consider in the determination of BAT that are reported for pre-treatment, refining, production of alumina (4.3.2), integrated anode plant (Chapter 12) are considered to be Best Available Techniques and are summarised below.

The particular technique used depends on the raw materials and other facilities available on or near the installation. They form part of the over all process in conjunction with the following processes.

Process Stage	Technique	Comments
Production of alumina	Bayer process	Optimised to reduce energy, remove dust and reuse red mud transport water.
Refining	Use of mixtures of chlorine and argon/nitrogen or salt flux (AlF_3).	Addition via an inline cell for Cl_2,Ar,N_2 injection.
Holding or de-gassing.	Fume collection from furnaces and launders, cooling, fabric filter if necessary.	Casting moulds depend on product.
Anode production.	See Chapter 12	

Table 4.28: Other process stages considered as Best Available Techniques for primary aluminium production

Process Stage	Technique	Comments
Refining	Use of mixtures of chlorine and argon/nitrogen or salt flux (AlF_3).	Inert cover gas or dross press
Skimmings treatment.	Inert cover gas and cooling in a sealed drum or dross press	Ammonia formation if wet.
Holding or De-gassing.	Fume collection from furnaces and launders, cooling, fabric filter if necessary.	

Table 4.29: Other process stages considered as Best Available Techniques for secondary aluminium production

It is recommended that the potential formation of dioxins during the refining and casting stages for secondary aluminium production is investigated further.

4.4.3 Gas collection and abatement

The fume collection systems used for both primary and secondary production should exploit cell or furnace sealing systems and be designed to maintain a suitable depression that avoids leaks and fugitive emissions. Systems that maintain furnace sealing or hood deployment should be used. Examples are through hood additions of material, sealed charging cars and the use of robust rotary valves on feed systems. Secondary fume collection is expensive and consumes a lot of energy. It is often practicable to use an intelligent system capable of targeting the fume extraction to the source and duration of any fume to minimise energy consumption.

Best Available Techniques for gas and fume treatment systems are those that use cooling and heat recovery if practical before a fabric filter. Fabric or ceramic filters that use modern high performance materials in a well-constructed and maintained structure are applicable. They feature bag burst detection systems and on-line cleaning methods.

The acid gas recovery systems, carbon/lime injection for the removal of dioxins and the associated dust and metal recovery stages are those described earlier in this document. The use of alumina as a scrubbing medium for fluoride and HF removal with the use of the reacted alumina in primary aluminium production is considered to be BAT. Fume collection systems will follow the best practice out lined in techniques described in section 2.7.

Processing Stage	**Fume collection**	**Fabric Filter**	**PAH removal**	**VOC removal**
Raw Materials	• (if dusty)	• (if dusty)		
Primary Smelting	•	• (with dry alumina scrubber)	•	
Integrated anode plant	•	•	•	•
Alumina production	•	• (or EP)		
Holding and de-gassing	•	•		

Table 4.30: Abatement applications considered as Best Available Techniques for primary aluminium production

Processing Stage	**Fume collection**	**After burning**	**Filter**	**Acid gas removal**	**VOC removal**
Raw Materials	• (if dusty)		• (if dusty)		
Secondary Smelting	•	• (if needed)	•	•(if needed)	•(if needed)
Swarf drying and de-coating	•(if needed)	•(if needed)	•(if needed)	•(if needed)	•(if needed)
Holding and de-gassing	•(if needed)		•(if needed)		
Salt Slag or Skimmings Treatment	•	• (for hydrogen, phosphine etc)	•		

Table 4.31: Abatement applications considered as Best Available Techniques for secondary aluminium production

The use of or the recycling of skimmings and filter dusts, if it is possible, is considered to be part of the processes. Energy recovery can be applied to most of the stages if there is sufficient heat available and a use for the heat recovered. In its simplest form heat recovery using recuperative burners and charge preheating could be used in secondary aluminium production.

Other abatement systems are considered to be applicable for other parts of the process and an overview is shown in the following table.

Process Stage.	Component in off – gas.	Abatement option.
Raw materials handling	Dust	Prevention and correct storage. Dust collection and fabric filter
Raw materials pre-treatment	Dust Organic material*	Correct pre-treatment Gas collection and fabric filter Process operation, after-burning and correct gas cooling.
Primary smelting (Electrolytic)	Dust, fluoride, PFCs, (Hydrocarbons and PAHs**), Sulphur dioxide	Process operation and gas collection, Alumina scrubber followed by cleaning in a fabric filter. Gas cleaning in wet scrubber if necessary
Secondary smelting	Dust and metals Acid gases/halides Organic material*	Process operation, gas collection and efficient dust removal. Scrubbing if necessary. Process operation, material selection and pre-treatment, after-burning and correct gas cooling, carbon injection, efficient dust removal.
Holding and refining.	Dust, halides and metals Organic material*	Process operation and gas collection/cleaning. Process operation, after-burning and correct gas cooling.
Salt slag and skimmings treatment processes	Dust, ammonia, phosphine and metals	Process operation and gas collection/treatment.
Note. * Organic materials include VOC reported as total carbon (excluding CO) and dioxins. ** If an anode plant is integrated.		

Table 4.32: Summary of potential pollutants and abatement options

4.4.3.1 Emissions to air associated with the use of BAT

Emissions to air comprise the captured/abated emissions from the various sources, plus the fugitive or uncaptured emissions from these sources. Modern, well operated abatement systems result in efficient removal of pollutants and the information at the time of writing indicates that the fugitive emissions can be the largest contributor to the total emissions to air [tm 29, PARCOM 1997].

For primary aluminium the total emissions to air are based on the emissions from:
- The material reception, storage, blending and sampling.
- The smelting, holding and refining furnaces with the associated metal transfer and hot gas handling and cleaning system.
- The skimmings handling system.

For secondary aluminium the total emissions to air are based on the emissions from:
- The material reception, storage, blending sampling and pre-treatment.
- The smelting, holding and refining furnaces with the metal transfer and associated hot gas handling and cleaning system.
- The skimmings and slag cooling and handling systems.

Fugitive emissions may be much higher than collected, abated emissions and should be assessed locally. They can be assessed from the fume capture efficiency and by monitoring (see section

2.7) collection efficiency from primary aluminium electrolytic cells is > 99% on a long-term basis. The untreated cell gas characteristics are shown in table 5.4 and these can be used to indicate the possible impact of fugitive emissions.

Effective and robust hooding systems are used in lead and precious metal production using rotary furnaces and reduce fugitive emissions to air by a significant margin. This technique is applicable to rotary furnaces for the production of aluminium. Sealed charging cars or skips are used with some reverberatory furnaces and also reduces fugitive emissions to air significantly. These techniques are shown earlier in this chapter as examples. The following tables summarise the techniques and the associated collected and abated emissions.

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 - 5 mg/Nm^3	Fabric filter.	Depends on characteristics of dust.
SO_2	Not applicable	Control of sulphur content of the anodes.	Aim to minimise SO_2
Poly fluorinated hydrocarbons	< 0.1 anode effects per cell per day	Process control based on active cell databases.	< 0.1 kg/t Al
HF Total fluoride	< 0.2 mg/Nm^3 < 0.5 mg/Nm^3	Alumina scrubber and fabric filter	For integrated anode production processes, see Chapter 12
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 4.33: Emissions to air associated with the use of BAT for primary aluminium electrolysis

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 - 5 mg/Nm^3	Fabric filter	
Chlorides, fluorides and acid gases	SO_2 < 50 - 200 mg/Nm^3 Chloride < 5 mg/Nm^3 Fluoride < 1 mg/Nm^3	Wet or semi-dry alkaline scrubber.	
NO_x	< 100 mg/Nm^3 < 100 - 300 mg/Nm^3	Low NO_x burner Oxy-fuel burner.	Higher values are associated with oxygen enrichment to reduce energy use. In these cases gas volume and mass emission is reduced.
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 4.34: Emissions to air associated with BAT for holding and de-gassing molten metal from primary and secondary aluminium

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 - 5 mg/Nm^3	Fabric filter	High performance fabric filters can achieve low levels of heavy metals. The concentration of heavy metals is linked to the concentration of dust and contents of the metals in the dust.
Chlorides, fluorides and acid gases	SO_2 < 50 - 200 mg/Nm^3 Chloride < 5 mg/Nm^3 Fluoride < 1 mg/Nm^3	Wet or semi-dry alkaline scrubber.	
NO_x	< 100 mg/Nm^3 < 100 - 300 mg/Nm^3	Low NO_x burner. Oxy-fuel burner.	Higher values are associated with oxygen enrichment to reduce energy use. In these cases gas volume and mass emission is reduced.
Total organic carbon as C	< 5 - 15 mg/Nm^3 < 5 - 50 mg/Nm^3	Afterburner. Optimised combustion.	Pre-treatment of secondary material to remove organic coatings.
Dioxins	< 0.1 - 0.5 ng TEQ/Nm^3	High efficiency dust removal system (i.e. fabric filter), afterburner followed by quenching. Other techniques are available (e.g. adsorption on activated carbon, oxidation catalyst).	

Note. Collected emissions only.
Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period.
For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used. For SO_2 or total carbon removal, the variation in raw gas concentration during batch processes may affect the performance of the abatement system.

Table 4.35: Emissions to air associated with the use of BAT for materials pre-treatment (including swarf drying), melting and smelting of secondary aluminium

4.4.4 Wastewater

This is a site-specific issue, existing treatment systems are reported to be to a high standard. All wastewater will be treated to remove solids and oils/tars, absorbed acid gases (e.g. sulphur dioxide, HF, HCl) should be neutralised if necessary. The techniques listed in section 2.9 are the techniques to consider. In a number of installations cooling water and treated wastewater including rainwater is reused or recycled within the processes.

For primary and secondary aluminium the total emissions to water are based on:

- The alumina production
- The material storage system.

- The electrolytic transformer cooling system.
- The scrubber system if used.
- The wastewater treatment system and run-off water.

Water use is minimal as the processes are essentially dry apart from wet scrubber systems. The following table summarises the concentrations that are achieved using suitable effluent treatment methods. Where suitable, sludges can be returned to the process.

Component	Concentration mg/l	Comment
Suspended solids	14	Includes anode plant
COD	37	Includes anode plant
Fluoride	17	Includes anode plant
Total hydrocarbon	0.8	Includes anode plant
Note: - Associated emissions are from the Aluminium Dunkirk plant and are given as daily averages during process operation.		

Table 4.36: Emissions to water associated with the use of BAT for primary aluminium production with an associated anode plant

4.4.5 Process residues

The principles of the minimisation and re-used of process residues are techniques that form part of BAT.

The production processes in this sector have been developed by the industry to maximise the re-use of the majority of process residues from the production units or to produce residues in form that enables them to be used in other production processes. Sections 4.2.1.4 and 4.2.2.3 give an overview of the potential end uses for residues. Some specimen quantities are also given for specific installations in these sections.

- Particular examples are: -

- The use of SPL in other processes as raw material or as a fuel, if possible.

- Minimisation of salt flux usage where practical.

- The recycling of salt slag to recover aluminium, salt and oxide portions.

- Reuse of furnace linings where possible.

- Reuse of filter dusts from primary aluminium in the process.

- Reuse of filter dusts from secondary aluminium furnaces if possible in the process. Treatment of these filter dusts if necessary to destroy dioxins before disposal.

The quantity of residues produced is strongly dependent on the raw materials in particular the sodium content of primary materials, the content of other non-ferrous metals (e.g. Mg) in secondary materials and the presence of other contaminants such as organic materials. The emissions to land can therefore be very site and material specific and depend on the factors discussed earlier. It is therefore not possible to produce a realistic, typical table of quantities that are associated with the use of BAT without detailing the raw material specification. The principles of BAT include waste prevention and minimisation and the re-use of residues whenever practical. The industry is particularly effective in these practices.

Source	Use/treatment options
Al skimmings	Recovery.
Filter dust	Re-use in process.
SPL	Carburant, flux and furnace linings.
Bricks	From anode furnaces, reuse.
Steel	Recovery.
Carbon dust (anode plant)	Reuse.

Table 4.37: Options for residues from a primary aluminium smelter

Residue	Origin	Treatment	Comments on treatment
Salt slag	Melting in rotary drum furnace	Recovery via grinding, dissolution and crystallisation techniques. Production of reusable substances if possible Al-granulate, mixed salt, Al_2O_3 (and other oxides).	The process should achieve a high environmental standard. Fugitive emissions of dust and gases such as phosphine, hydrogen should be collected and treated. Aim to prevent landfill.
Filter dust	Exhaust gas cleaning	Disposal with pre-treatment or underground site, Partly reconditioned with salt slag or Used in the steel industry	Ban on surface disposal in some countries, thermal treatment possible (neutralisation with $NaHCO_3$ or Na_2CO_3 → use with salt slag)
Furnace lining	Melting furnace	Potential for reconditioning with skimmings, otherwise Leaching + landfill	No surface disposal in some countries. Production of injection moulding compounds reported
Skimmings	All furnaces not using salt, Cleaning of smelter, foundries	Smelting in rotary furnace. Recovery, pellets used in rotary drum furnace, dross dust used in the recovery of salt slag	Aim to prevent landfill

Note. * using Closed Well furnace
** Non metallic products (oxide proportions from Al scrap)

Table 4.38: Options for residues from secondary aluminium production

4.4.6 Costs associated with the techniques

Cost data has been compiled for a variety of process variations and abatement systems. Some costs are included where available with the examples given earlier in this chapter. The cost data is very site specific and depends on a number of factors but the ranges given may enable some comparisons to be made. Other cost data is provided in an appendix to this note so that costs for processes and abatement systems over the whole of the non-ferrous metal industry can be compared.

4.5 Emerging Technologies

- Reuse of filter dust from secondary aluminium production is demonstrated in Spain and Austria. Dust and fume from a rotary furnace is treated with sodium bicarbonate and activated carbon as the scrubbing medium to remove chlorides produced by the salt flux and sodium chloride is formed. The dust is then collected in a fabric filter and can be included with the salt charged to the furnace [tm 145, Winter 1998].

- Several processes exist to recover iron from red mud but have not been commercially exploited [tm 212, Noyes 1993]. Research has also taken place in the use of red mud in construction, bricks and concrete.

- Inert anodes. Development of new carbon free anodes, which would make it possible to construct a completely new electrolytic cell without any directly consumable parts, and producing oxygen at the anode instead of carbon dioxide. This would also eliminate emissions of PAH from the process. The technology for this is at the pilot plant stage, and is not yet satisfactorily documented in a test operation.

- Wettable cathodes. Development of new cathode materials or coatings for existing cathode materials, to achieve better energy efficiency for the electrolysis process. This is at the development stage and has been tested in research cells.

- Alloy separation. Techniques for separation of aluminium scrap into different types of alloy have been tested using laser and eddy current technology. The benefits of this will be easier selection of materials for recycling and the ability to easier produce desired alloys in recycling plants.

- Rotary flux or gas injection for refining. This allows for more controlled addition of fluxes to holding furnaces. The technique is already installed at some plants.

- Catalytic filter bags to control dioxin releases. The catalyst will destroy dioxins rather than simply collecting them.

- The use of an electric arc furnace for salt free melting of drosses.

- Processing of salt slag in a dry state.

- Salt recovery using electro-dialysis rather than concentration.

- Continuous monitoring of HF in stack emissions to allow abatement failure (alumina scrubber/fabric filter) to be detected.

5 PROCESSES TO PRODUCE LEAD, ZINC AND CADMIUM. (+ Sb, Bi, In, Ge, Ga, As, Se, Te)

5.1 Applied Processes and Techniques

These metals are often associated together in ores and concentrates and a number of techniques are used to win and separate the metals. The chemical state (sulphidic or oxidic) and the relative proportion of the metals usually determine the pyrometallurgical or hydrometallurgical technique or combination that are used. Some of the techniques are also used for secondary or mixed primary and secondary raw materials [tm 12, HMIP Zn 1993; tm 102, DFIU Zn 1999]. In some cases secondary materials are separated and portions such as battery paste, are sent to other processors who can deal with that material.

5.1.1 Primary lead

There are two basic pyrometallurgical processes available for the production of lead from lead sulphide or mixed lead and zinc sulphide concentrates: - sintering/smelting or direct smelting. The processes may also be used for concentrates mixed with secondary raw materials.

5.1.1.1 Sintering/smelting using the Blast Furnace or Imperial Smelting Furnace

Lead concentrates are blended with recycled sinter fines, secondary material and other process materials and pelletised in rotating drums. Pellets are fed onto an up draught or down draught sinter machine and ignited. The burning pellets are conveyed over a series of wind-boxes through which air is blown. Sulphur is oxidised to sulphur dioxide and the reaction generates enough heat to fuse and agglomerate the pellets [tm 12, HMIP Zn 1993; tm 102, DFIU Zn 1999].

The sinter product is crushed and screened to the correct size for the furnace. Undersize material is cooled by mixing with de-watered sludge collected from gas cleaning equipment and returned to the blending area.

The sulphur dioxide is recovered from the sinter machine off-gases, which are cooled, cleaned and recovered in the form of sulphuric acid. Cadmium and mercury are also present and are recovered from the off-gases or from the sulphuric acid that is produced.

Sinter is charged to the blast furnace with metallurgical coke. Air and/or oxygen enriched air, is injected through the tuyeres of the furnace and reacts with the coke to produce carbon monoxide. This generates sufficient heat to melt the charge. The gangue content of the furnace charge combines with the added fluxes or reagents to form a slag.

The carbon monoxide reduces the metal oxides in the charge. Slag and lead collect in the furnace bottom and are tapped out periodically or continuously. The slag is quenched and granulated using water, or allowed to cool and is then crushed, depending on its destination or further use.

For smelting bulk lead and zinc concentrates and secondary material, a specially designed blast furnace is used; the Imperial Smelting Furnace. Here, hot sinter and pre-heated coke as well as hot briquettes are charged. Hot air, sometimes oxygen enriched is injected with these raw materials. The reduction of the metal oxides not only produces lead and slag but also zinc, which is volatile at the furnace operating temperature and passes out of the ISF with the furnace off-gases. The gases also contain some cadmium and lead.

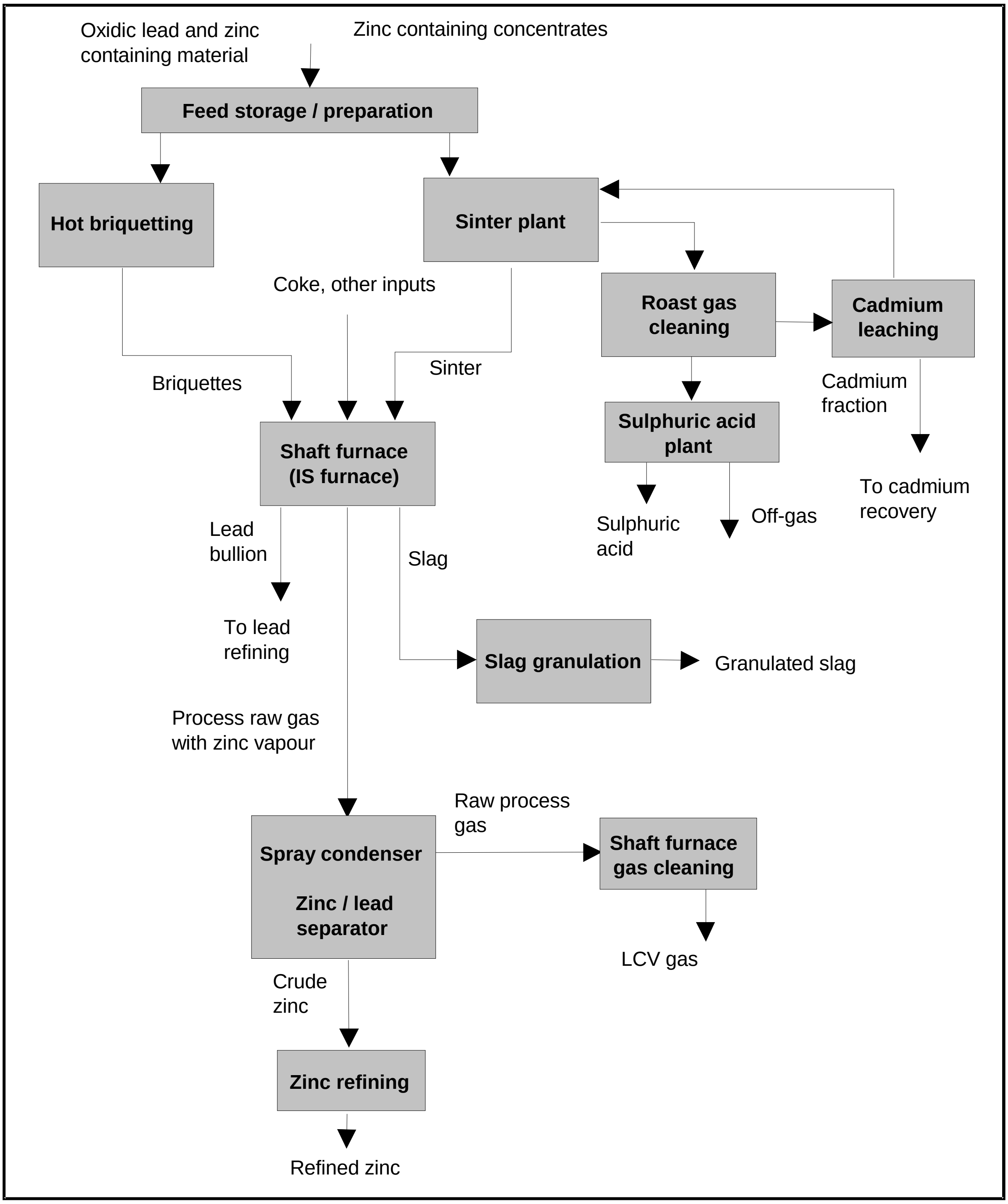


Figure 5.1: Diagram of a typical Imperial Smelting Process for zinc and lead production [tm 102, DFIU Zn 1999]

The furnace gases pass through a splash condenser in which a shower of molten lead quenches them and the metals are absorbed into the liquid lead. The resulting alloy is cooled when zinc floats to the surface and is separated from the lead. The zinc is refined by distillation and this process is covered later in this chapter. Lead is recycled to the splash condenser [tm 12, HMIP Zn 1993; tm 102, DFIU Zn 1999].

After the splash condenser, the low calorific value furnace gases (LCV gas), which contain carbon monoxide and hydrogen, are cleaned and burned to preheat the air and the coke.

5.1.1.2 Direct smelting

Several processes are used for direct smelting of lead concentrates and some secondary material to produce crude lead and slag. Bath smelting processes are used – the ISA Smelt/Ausmelt furnaces (sometimes in combination with blast furnaces), Kaldo (TBRC) and QSL integrated processes are used in EU and Worldwide. The Kivcet integrated process is also used and is a flash smelting process. The furnaces are described in section 2.6 of this document. The ISA Smelt/Ausmelt furnaces and the QSL take moist, pelletised feed and the Kaldo and Kivcet use dried feed.

The sintering stage is not carried out separately in this instance. Lead sulphide concentrates and secondary materials are charged directly to a furnace and are then melted and oxidised. Sulphur dioxide is formed and is collected, cleaned and converted to sulphuric acid. Carbon (coke or gas) and fluxing agents are added to the molten charge and lead oxide is reduced to lead, a slag is formed. Some zinc and cadmium are “fumed” off in the furnace, their oxides are captured in the abatement plant and recovered [tm 120 TU Aachen 1999].

These processes all produce a slag that is rich in lead but the QSL and Kivcet furnaces incorporate an integral reduction zone to reduce the lead content of the slag to an acceptable level, the Kaldo process uses an adjacent slag fuming process. The silica based slag from the QSL process is accepted as construction material at the time of writing. Heat recovery and conversion of sulphur dioxide to sulphuric acid is also featured in these processes. Dust collected in abatement plant is returned to the process and can be washed or leached to reduce halides and Zn / Cd in the recycled dust [tm 120 TU Aachen 1999].

All of these processes have taken some time to commission properly and achieve the anticipated through put and conversion rates. The Kaldo is a two stage process [tm 12, HMIP Zn 1993; tm 35, LRTAP 1995; tm 102, DFIU Zn 1999] and is well established. It is reported that the QSL process has overcome all of the initial problems and is operating effectively. The ISA Smelt/Ausmelt process is operating only on the initial smelting phase at the time of writing and has not been commissioned for the slag reduction phase. The Kivcet furnace has been operating successfully since 1990 [tm 120 TU Aachen 1999].

Process	Lead content of slag %	Comments
QSL	< 3	Efficient operation. Viable process
Kivcet	3 – 5	Successful operation
Ausmelt/ISA Smelt	Not available	Smelting phase only commissioned.
Kaldo furnace	2 – 4	Effective operation – mixed Pb/Cu

Table 5.1: Direct smelting processes

5.1.2 Secondary lead

5.1.2.1 The recovery of lead from scrap batteries

Scrap automotive batteries (automotive, motive power and stand by) are a major source of secondary lead. A typical composition of lead-acid battery scrap is given in the following table [tm 102, DFIU Zn 1999]: -

Component	[wt.-%]
Lead (alloy) components (grid, poles, ...)	25 – 30
Electrode paste (fine particles of lead oxide and lead sulphate)	35 - 45
Sulphuric acid (10 – 20% H_2SO_4)	10 – 15
Polypropylene	4 – 8
Other plastics (PVC, PE, etc.)	2 – 7
Ebonite	1 – 3
Others materials (glass, ...)	< 0.5

Table 5.2: Composition of typical lead-acid automotive battery scrap

There are two main types of process for the recovery of lead from automotive batteries[tm 12, HMIP Zn 1993; tm 35, LRTAP 1995; tm 102, DFIU Zn 1999]: -

a) Batteries are drained of acid and fed whole into a blast or shaft furnace (Varta process) or

Whole batteries and fluxes are fed into a blast furnace via a seal and oxygen enriched air is used in the blast. Antimonial lead bullion is produced, along with a silica based slag and a lead/iron matte that can be recovered in a primary lead smelter [tm 120 TU Aachen 1999].

Organic components in the furnace off-gases are oxidised in an after- burner and the gases are then cooled and filtered in a fabric filter. The filter dust is de-chlorinated and returned to the furnace.

b) Batteries are drained of acid broken and separated into various fractions using automated proprietary equipment (MA and CX processes).

Both the MA and CX (Engitec) processes use hammer type mills to crush the whole batteries. The crushed material then passes through a series of screens, wet classifiers and filters to obtain separate fractions containing metallic components, lead oxide-sulphate paste, polypropylene, non recyclable plastics and rubber and dilute sulphuric acid [tm 106, Farrell 1998]. Some processes use a second milling stage before the plastic fraction is finally treated. Polypropylene is recycled as far as possible. The sulphuric acid drained from the batteries is neutralised unless there is a local use for it and the sodium sulphate produced can be re-crystallised and sold. These are strongly market dependent options.

Several alternatives are used to deal with the sulphur contained in the battery materials.

- Prior to smelting, the lead sulphate paste may be de-sulphurised by reaction with sodium carbonate or sodium hydroxide (in the CX and related processes).
- Lead sulphate can be separated and sent to an installation capable of treating the sulphur content in the gases for example one of the direct smelting primary lead processes.
- The sulphur may be fixed in the slag or as a Fe/Pb matte.

Paste de-sulphurisation prior to smelting can reduce the quantity of slag produced and, depending on the smelting method used, the amount of sulphur dioxide released to the air.

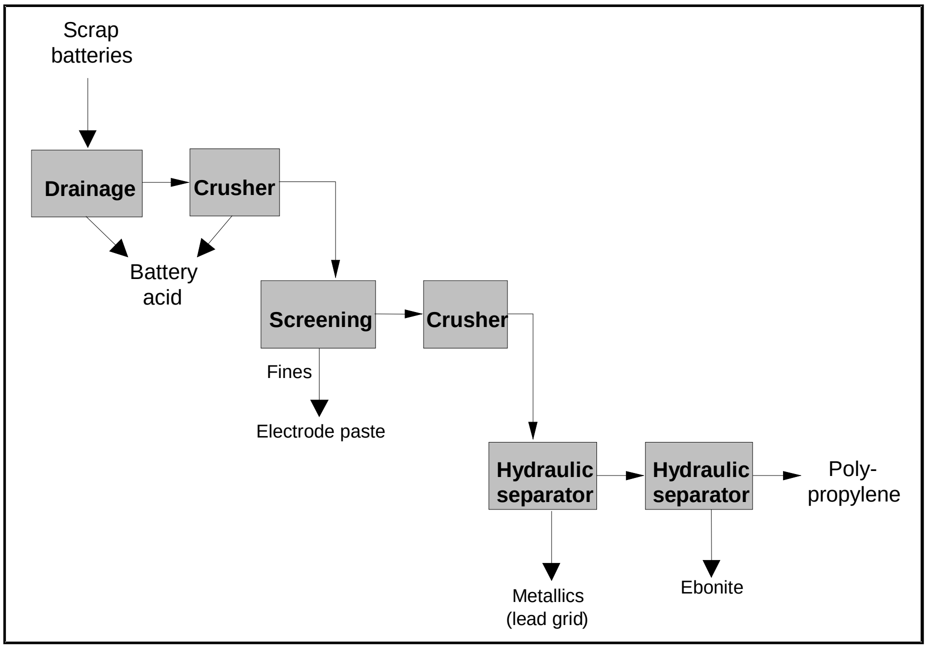


Figure 5.2: Outline of a typical battery recovery process
[tm 102, DFIU Zn 1999]

Smelting can be carried out in the following vessels [tm 102, DFIU Zn 1999]:

- rotary furnace,
- reverberatory furnace and blast or electric furnace,
- rotary kiln,
- ISA Smelt furnace,
- electric furnace.

Rotary and reverberatory furnaces can be either gas or oil fired. Oxygen enrichment is used in several installations. Smelting is usually carried out in batches, slag and metal are tapped out separately and batches of slag are treated to recover more lead and produce a slag that is stable. The bulk of the sulphur in the charge is fixed in the slag, which is a sodium-iron-sulphur compound with small amounts of lead and other metals.

In the ISA Smelt process de-sulphurised paste and reductant are continuously fed into the furnace and lead bullion is tapped periodically. When the process vessel contains the maximum volume of slag, reductant and fluxes are added to produce a high antimony bullion and a discard slag [tm 41, Ausmelt 1997; tm 102, DFIU Zn 1999]. The slag may also be reduced in a separate furnace.

The electric resistance furnace is used for complex secondary materials and uses an open slag bath covered by coke. Raw materials are fed onto the top of the bath where they react to produce metal and slag, which are tapped periodically. The waste gas contains CO and is burnt, flue dust is collected and zinc is recovered from it. It is operated on a campaign basis alternating with secondary copper production in a copper smelter.

Crude bullion produced by either smelting method is refined by the methods described below.

5.1.2.2 Recovery of lead from other scrap and residues

Metallic lead scrap may be in a variety of forms, it may be contaminated by plastic material or bitumen and may be alloyed with other elements, notably tin, antimony and silver. This material is usually recovered in the processes described above as simple melting facilities cannot cope with the partially burnt material in the off-gases. The electric furnace is also used for the recovery of lead from complex lead/copper and lead/precious metals secondary materials. After-burning of the gases is used to destroy CO and hydrocarbons including dioxins.

Clean scrap is melted in specially designed kettles, which are indirectly heated by oil or gas. Scrap is charged from a hopper situated above the kettle. Dross and tramp materials are skimmed from the surface of the molten metal and then pass through a screen that separates fine and coarse fractions. The dross is the fine fraction and is recycled as a non-metallic residue. The tramp material is mostly metal with a higher melting point than lead, and is treated elsewhere.

Residues, largely non-metallic in character, but often mixed with metallic lead scrap, are smelted with fluxes in rotary furnaces. Lead containing residues from the production of tetra-alkyl lead are melted in gas fired reverberatory furnaces.

The lead or lead alloy recovered from scrap or residues is refined, if necessary, using the techniques described below.

5.1.3 Refining of primary and secondary lead

Lead bullion may contain varying amounts of copper, silver, bismuth, antimony, arsenic and tin. Lead recovered from secondary sources may contain similar impurities, but generally antimony and calcium dominate. There are two methods of refining crude lead: electrolytic refining and pyrometallurgical refining. Electrolytic refining uses anodes of de-copperised lead bullion and starter cathodes of pure lead. This is a high cost process and is used infrequently.

A pyrometallurgical refinery consists of a series of kettles, which are indirectly heated by oil or gas [tm 4, HMIP Pb 1993, tm 102, DFIU Zn 1999]. Copper is the first element to be removed and separates as sulphide dross. If the crude metal is deficient in sulphur more must be added in the form of sulphur powder or pyrite. The sulphide dross is removed from the metal surface by mechanical skimmers that discharge into containers.

Arsenic, antimony and tin are removed by oxidation. The usual method, often referred to as "lead softening", involves a reaction with a mixture of sodium nitrate and caustic soda, followed by mechanical skimming to remove the oxide dross. Air/oxygen can also be used as the oxidising agent. Depending on the crude lead composition, i.e. the amount of impurities, the molten salt mixture may be granulated in water and the impurities separated hydro-metallurgically.

De-silvering is carried out by the Parkes process, which makes use of the preferential solubility of silver in zinc. Zinc is added to the lead at about 470 °C and the mix is then allowed to cool to 325 °C. A silver-lead-zinc alloy separates and forms a crust on the surface. The crust is removed and zinc separated from the silver by vacuum distillation. The silver bullion is further refined using oxygen to produce crude silver. Excess zinc is removed from the de-silvered lead by vacuum distillation and then by treatment with caustic soda.

Bismuth is removed by treatment with a mixture of calcium and magnesium (the Kroll-Betterton process). A calcium-magnesium-bismuth alloy is formed as dross on the surface of the lead and is removed by skimming. The dross is then oxidised using lead chloride, chlorine gas or a caustic soda / sodium nitrate mixture and the calcium magnesium oxide is removed by skimming. A bismuth-lead alloy is recovered and undergoes further refining to produce bismuth.

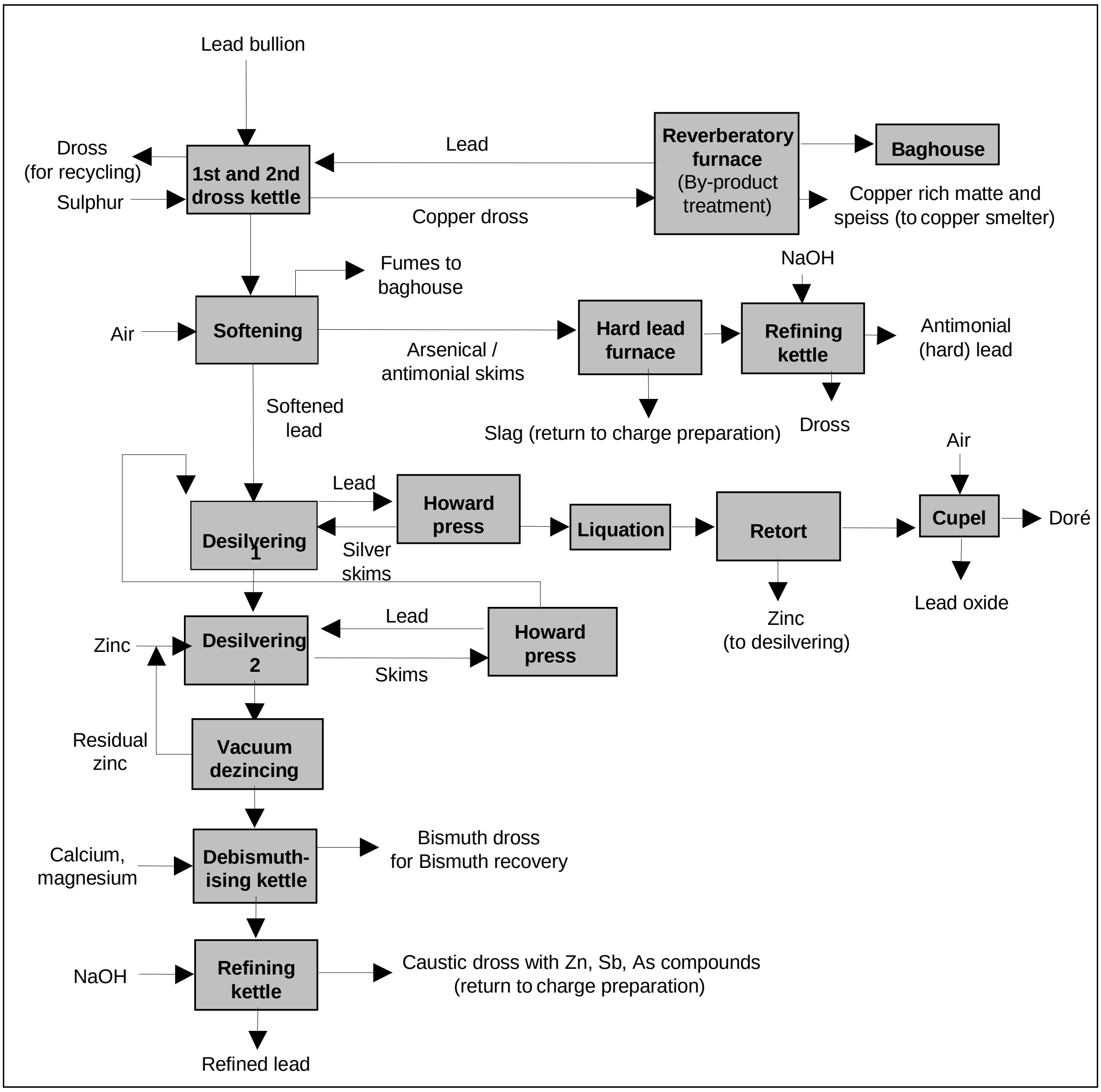


Figure 5.3: Diagram of lead refining processes
[tm 102, DFIU Zn 1999]

The pure lead is cast into blocks or ingots. Fume, drosses, litharges and other residues are usually smelted in a small blast furnace or a rotary furnace to produce lead bullion which is recycled to the refining circuit.

5.1.4 Melting and alloying processes for lead

Melting and alloying are usually carried out in indirectly heated crucible furnaces or kettles using electricity or oil or gas. Refined lead is melted in a kettle and alloying elements are added. Temperature control of the melt can be important. Lead and lead alloys are usually cast into permanent cast iron moulds [tm 4, HMIP Pb 1993].

Static moulds and conveyor casting machines are used to produce blocks, slabs and ingots. Continuous casting machines are used to produce rod for reduction to wire. Fume extraction is used at the launders and tapping points.

5.1.5 Primary zinc

Zinc can be produced from primary raw materials by pyrometallurgical or hydrometallurgical methods. Pyrometallurgical methods are used in other parts of the World but have gradually lost their importance and are not used in EU for simple zinc concentrates. Determining factors are the need for an extra distillation stage to obtain high-grade zinc and the relatively low zinc extraction efficiency. The pyrometallurgical Imperial Smelting Furnace process (ISF) is however still of importance in EU because it enables complex lead-zinc concentrates and secondary material to be treated simultaneously, yielding saleable lead and zinc. It can also consume residues from other processes [tm 12, HMIP Zn 1993; tm 101, NL Zn 1998; tm 102, DFIU Zn 1999].

5.1.5.1 The pyrometallurgical route

The pyrometallurgical route is used for mixed zinc/lead concentrates and secondary material and uses the Imperial Smelting Furnace, which is outlined above in lead production and is illustrated in section 2.6. The electro-thermic furnace is used in other parts of the world. Zinc produced in the Imperial Smelting Furnace may contain varying amounts of cadmium, lead, copper, arsenic, antimony and iron and the process uses a refining stage.

Zinc from the ISF is refined by reflux distillation in columns containing a large number of refractory trays (New Jersey Distillation). The lower ends of the columns are heated externally by natural gas. The upper ends are not heated and run cool enough to reflux the higher boiling point metals before vapours pass to a condenser [tm 12, HMIP Zn 1993; tm 102, DFIU Zn 1999]. The New Jersey distillation column is also used for secondary zinc materials [tm 120 TU Aachen 1999].

Distillation proceeds in two stages; first the separation of zinc and cadmium from lead and then separation of cadmium from zinc. In the first stage, molten zinc is fed into a column where all the cadmium and a high proportion of the zinc is distilled. The mixture is condensed and fed directly to a second column. This column is operated at a slightly lower temperature to distil mainly cadmium, which is condensed as a zinc-cadmium alloy. The alloy is transferred to a cadmium refinery. The metal run-off from the bottom of the second column is high-grade zinc (SHG) of 99.995% purity [tm 120 TU Aachen 1999].

The run-off metal from the first stage is zinc with lead, tin, arsenic, iron, antimony and copper impurities. This alloy is cooled to separate lead, which is recycled to the ISF splash condenser, and an inter-metallic compound of iron, zinc and arsenic, which is recycled to the ISF itself.

The zinc is then treated with sodium to remove residual arsenic and antimony as sodium arsenides and antimonides, which are also recycled to the ISF. The zinc produced in this way is of a lower grade (GOB), but free of cadmium, and is used mainly for galvanising.

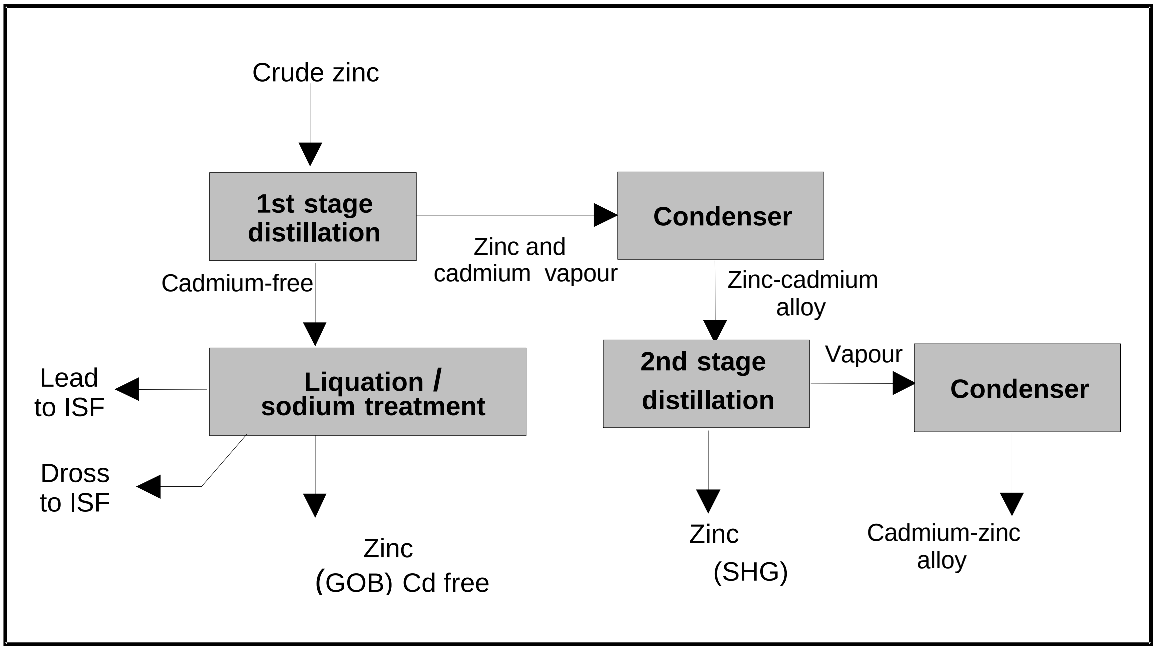


Figure 5.4: Diagram of zinc/cadmium distillation [tm 102, DFIU Zn 1999]

5.1.5.2 The hydrometallurgical route

The hydrometallurgical route is used for zinc sulphide (blendes), oxide, carbonate or silicate concentrates and is responsible for about 80% of the total world output [tm 101, NL Zn 1998; tm 102, DFIU Zn 1999]. The majority of the EU production facilities use the electrolytic process, with a total production capacity of 1665000 t/a in 1997.

Sulphide concentrates are roasted first in fluidised bed roasters to produce zinc oxide and sulphur dioxide. Roasting is an exothermic process and no additional fuel is used, the heat generated is recovered. The zinc oxide (calcine) passes from the furnace and is collected and cooled. Roaster gases are treated in hot EPs to remove dust (which is passed to the calcine). Other dust and volatile metals such as Hg and Se are removed in a gas cleaning train that incorporates scrubbing systems and wet EPs. The sulphur dioxide is then converted to sulphuric acid in a conventional recovery system [tm 101, NL Zn 1998; tm 102, DFIU Zn 1999; tm 12, HMIP Zn 1993; tm 101, NL Zn 1998; tm 120, TU Aachen 1999].

Leaching of the calcine is carried out in a number of successive stages using a gradually increasing strength of hot sulphuric acid. The initial stages do not dissolve significant amounts of iron but the later ones do. The leaching process is carried out in a variety reactors using open tanks, sealed vessels and pressure vessels or a combination of them [tm 101, NL Zn 1998; tm 102, DFIU Zn 1999].

Leaching may be stopped after the Neutral Leach. The leach residue is sent to an ISF and added to the sinter feed. Zinc, lead and silver are recovered as metals, sulphur as H_2SO_4. Instead of an ISF, a Waelz Kiln may be used but SO_2 absorption is necessary in such a case.

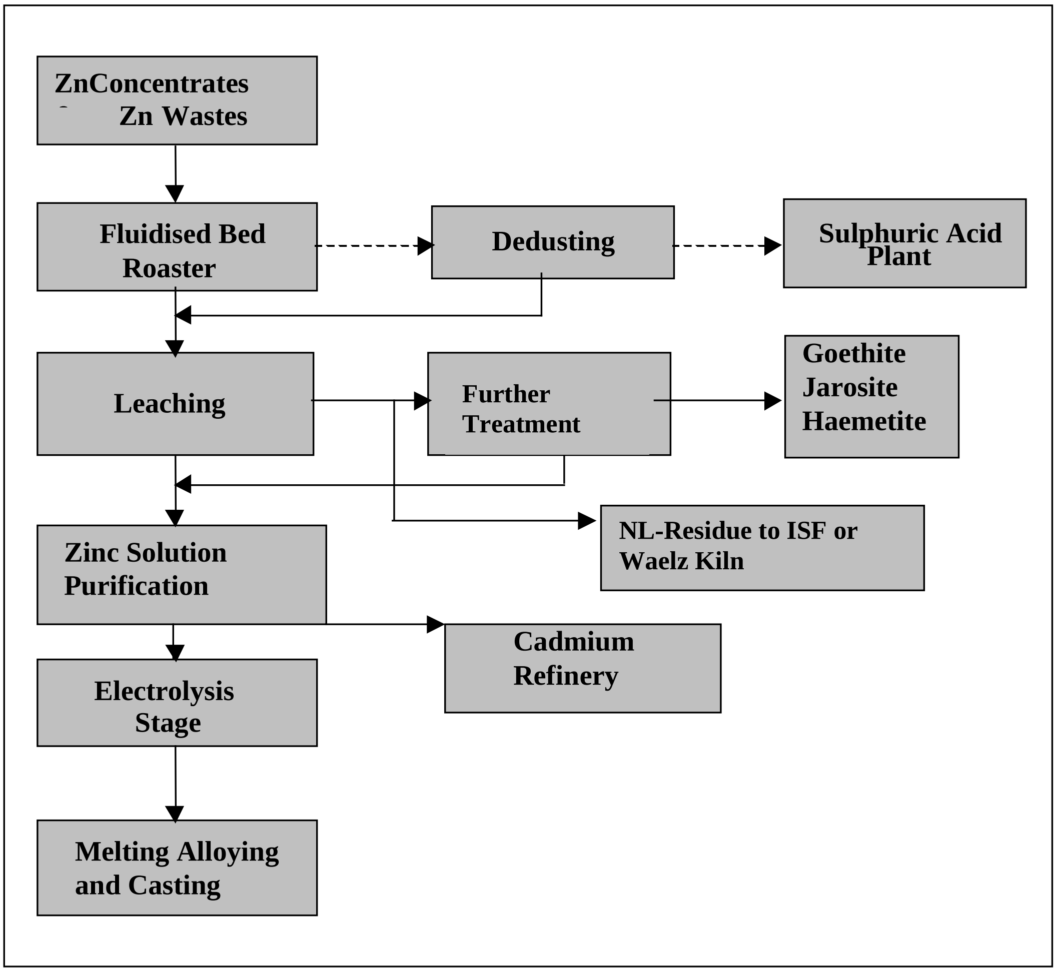


Figure 5.5: Diagram of the zinc hydrometallurgical process

Other metals are also dissolved during the process and are removed after leaching. Iron is the major impurity and the iron is precipitated in 3 basic forms; Jarosite, Goethite or Haemetite. The form of these precipitates is used to give the process names [tm 101, NL Zn 1998; tm 102, DFIU Zn 1999]. The precipitation stages are: -

- As Jarosite using ammonia and zinc calcine for neutralisation. Up to 3 stages are used depending on whether Ag/Pb recovery is undertaken. A single stage process known as the "Conversion Process" is also used.
- As Goethite using zinc sulphide for pre-reduction, oxygen for re-oxidation and zinc calcine for neutralisation.
- As Haemetite using sulphur dioxide or zinc sulphide for pre-reduction and an autoclave with oxygen for precipitation. In this case a sulphur residue is produced as well as an iron residue.

The main differences in the iron precipitates are their volume and ease of filterability. There are also significant differences in process capital and operating costs [tm 120 TU Aachen 1999]. The balance of these with the disposal costs of the residue may be influenced by non-process related costs. The Haemetite process was thought to be very attractive as the residue volume was lower and haemetite was a potential raw material for iron. The process has not proved to be viable and the haemetite was not acceptable to the iron and steel industry.

It has been reported [tm 139, Finland Zn 1999] that the Jarosite process is capable of high zinc recoveries even with concentrates containing 10% Fe. Similar recoveries with the Goethite process rely on a low iron content in the calcine (or ZnO) that is used for the precipitation stage.

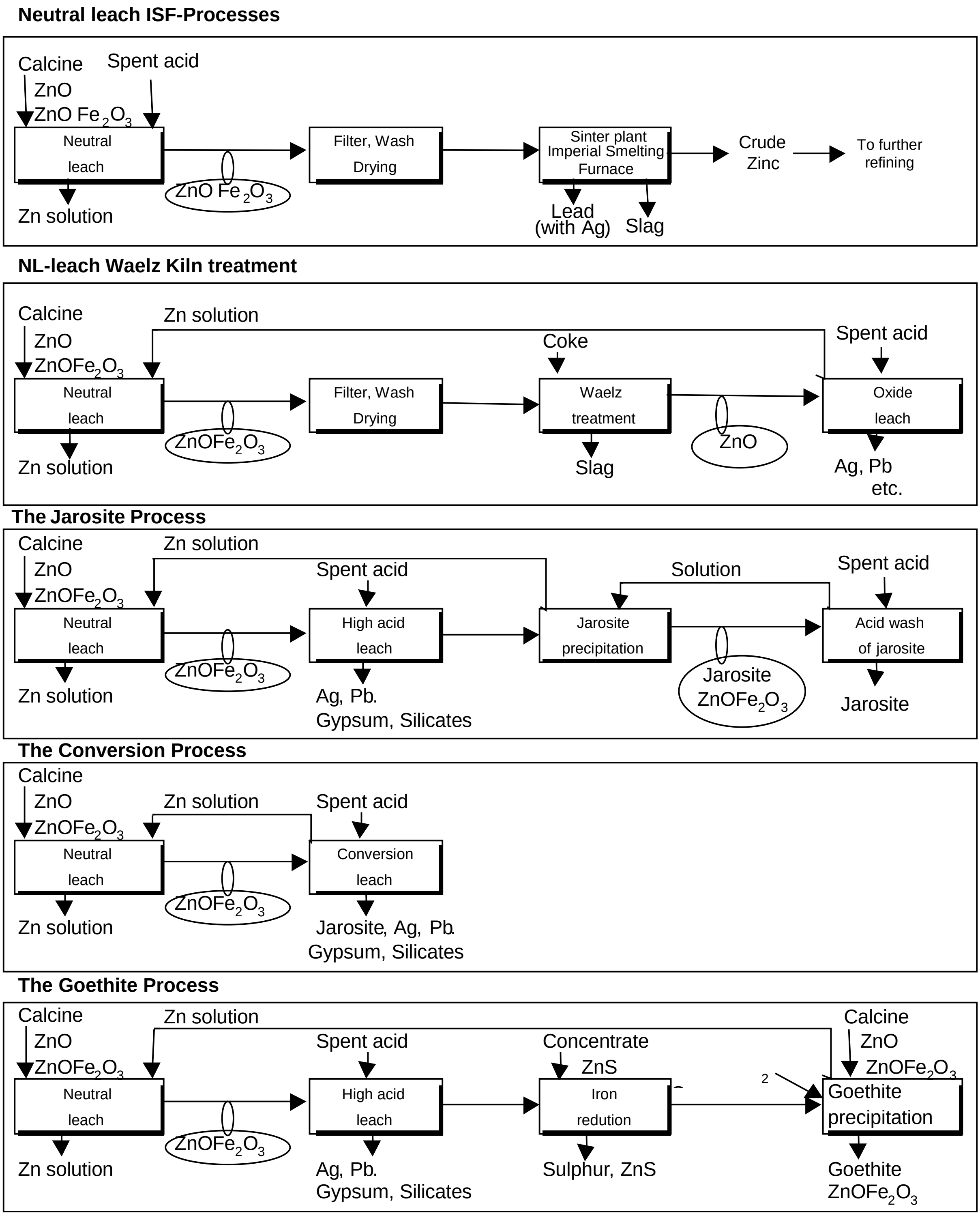


Figure 5.6: Simplified flow sheets of some iron removal processes

Two applications are known where concentrate is leached directly without calcination i.e. at Korea Zinc and Outokumpu Zinc. At Korea Zinc the iron is left in solution during the leaching and is then precipitated in a separate step as goethite, whereas at Outokumpu the iron is precipitated as jarosite simultaneously with the leaching of the sulphides.

The concentrate together with the slurry from the Conversion process and acid from the electrolyses are fed to the reactors where the leaching takes place by sparging oxygen into the slurry. The rest of the dissolved iron in the solution from the conversion and the iron dissolved from the concentrate is precipitated as jarosite:

$$3ZnS+3Fe_2(SO_4)_3+(NH_4)_2SO_4+9H_2O+1.5O_2=2NH_4[Fe_3(SO_4)_2(OH)_6]+3ZnSO_4+3H_2SO_4+3S$$

A sulphur concentrate is separated from the slurry by flotation and stored separately from the jarosite residue. This sulphur concentrate is not used for H_2SO_4 production and is a hazardous waste like Goethite and Jarosite. The equipment used in the process is much the same as conventionally used in zinc hydro-metallurgy. A flow sheet of the process operated by Outokumpu Zinc is shown below [tm 139, Finland Zn 1999].

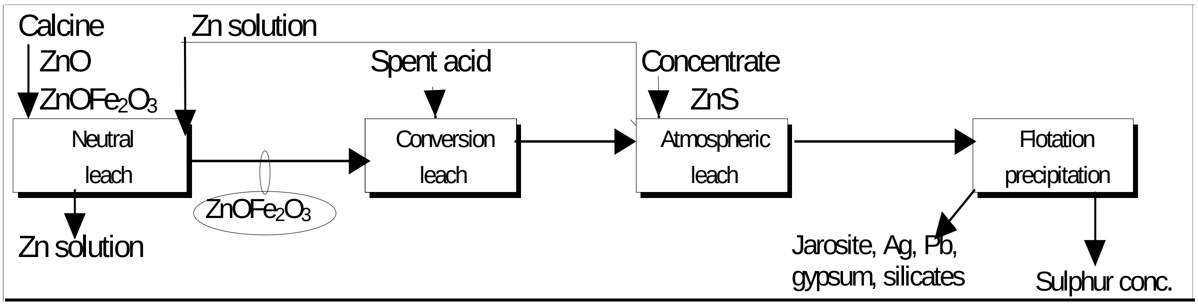


Figure 5.7: Concentrate leaching process

Whatever residue is produced by the various process options zinc removal is maximised by washing the residue. Other soluble metals may be treated by precipitation as hydroxides or sulphides. The residues are stored in landfill areas, usually on or near the site in a manner that isolates them from ground or surface water. Water from the storage area is normally recycled back to the process. Developments are taking place to avoid the residues or at least to render them more inert by fixation and this is reported in Emerging Techniques.

Slurry from the final leaching stage is settled and the overflow solution is treated to remove impurities. The solid in the underflow is filtered and washed on a filter. The filter cake is disposed of and the filtrate is recycled to the process. Different flow sheets are used depending on factors such as the choice of the iron removal process and the available integrated impurity recovery processes.

For example more or less extensive treatment of the leach residue is carried out by further leaching or physical separation techniques before it is disposed of [tm 120 TU Aachen 1999]. This is reflected in the recovery rates and composition of possible lead or lead/Ag by products.

Purification of the zinc bearing solution takes place in a number of consecutive stages. The processes used are dependent on the concentrations of the various metals contained in the concentrate and vary accordingly. The basic processes involve the use of zinc dust or powder to precipitate impurities such as Cu, Cd, Ni, Co and Tl. Precipitation of Co and Ni also involve the use of a second reagent such as As or Sb oxides. Variations in temperature occur from plant to plant. Other reagents such as barium hydroxide and dimethyl glyoxime may also be used to remove lead and nickel. The recovery route for the copper by-product can affect the choice of process.

Hydrogen may be evolved and arsine or stibine occurrence is monitored. Collection and treatment of the released gases depends on the presence of these gases, local overall engineering, open air or enclosed building operations can be used but scrubbing the gases from the reactors using an oxidising solution for arsine removal is reported to be most effective.

The purified solution passes to a cell house where zinc is electro-won using lead anodes and aluminium cathodes. Zinc is deposited at the cathodes and oxygen is formed at the anodes, where sulphuric acid is also generated and is recycled to the leaching stage. Acid mist is formed during this process and various coverings are used on the cells to minimise this. Cell room ventilation air can be de-misted and the acid mist recovered. Heat is produced during electrolysis and this is removed in a cooling circuit, this can be designed to optimise the water balance of the process but may be a further source of mists.

The cathodes that are produced are stripped automatically or manually and are then melted in electric furnaces and alloys made [tm 120 TU Aachen 1999]. A small part of the zinc produced is made into zinc powder or dust for the purification stages. These can be produced by air, water or centrifugal atomisation of a stream of molten zinc or by condensing zinc vapour in an inert atmosphere.

One of the main issues in the hydrometallurgical process route is the disposal or use of the precipitated iron. Special containment sites are used for disposal at the moment but pressure on landfill options is increasing, this factor is discussed later and the options are assessed. Several approaches are being developed to allow these residues to be used and these are covered in emerging techniques.

Restricting the process to neutral leaching only is one alternative method that can be used to avoid the production of these intractable wastes. In this case iron remains in the leach residue along with a significant portion of the zinc. This residue is used as the feed for a pyrometallurgical process to recover the zinc, lead, silver, sulphur and to bring the iron into a slag.

5.1.6 Secondary zinc

Approximately 30% of the yearly zinc consumption in Europe is secondary or recycled zinc. Approximately 50% of this secondary zinc is recycled within the consumers or users industry. This is particularly true in the galvanising and brass sector; scrap arising from the production or processing of products can be recycled almost immediately.

Residues and scrap, which are relevant and significant to the secondary zinc industry, include: -

- dust from copper alloy making,
- residues from the die casting industry,
- ashes, bottom and top drosses from the galvanising industry,
- old roofing and other sheet materials,
- non-ferrous fraction from the shredding of old cars and of other mainly steel containing products,
- dust from electric arc steel making and cast iron making,
- residues from chemical uses of zinc and burnt tyres.

The process route used to recover zinc depends on the form and concentration of zinc, and the degree of contamination [tm 120 TU Aachen 1999].

5.1.6.1 General processes

Physical separation, melting and other high temperature treatment techniques are used. Chlorides are removed and the residues are used to produce zinc metal or alloys for re-use, impure metal or oxide, which will be refined further in the primary zinc processes. Alternatively they can be further treated to produce commercial grades zinc oxide, powders or dust [tm 120 TU Aachen 1999; tm 206 TGI 1999].
Process details are very often confidential but examples of these specific treatments are: -

- Galvanisers ashes which arise during galvanisation of pieces, wire and tubes are essentially a mixture of zinc metal and zinc oxide, contaminated with ammonium and zinc chloride. They are ball-milled to liberate the phases. Separation is accomplished by sweeping the mill with a stream of air to entrain the non-metallic components, which are then collected by a fabric filter. Alternatively, a screen is incorporated into the mill, which passes the fine non-metallic fraction, but retains the coarse metallic fraction. In either case, the metallic fraction is discharged from the mill, melted and cast into ingots for sale, re-use or further treatment.

- Bottom dross (also called hard zinc or spelter) is a zinc iron alloy, also containing some lead, which forms and accumulates in holding furnaces and tanks used for batch galvanising. Blockages may result and automatic removal systems are used. Top dross is a zinc-iron-aluminium alloy generated from continuous hot dip galvanising. Drosses or skimmings and other residues from the die-cast industry contain a mixture of zinc metal and zinc oxide, with little or no chlorides. The treatment schemes summarised above are all applied to these materials. The same applies to old roofing and other sheet materials as well as to residues from the chemical uses of zinc or zinc products.

- Processing scrap vehicles in a series of mills produces shredder residue. After the removal of the non-metallic fraction, the non-ferrous fraction is separated from other steel-based products by magnetic separation. Heavy media separation and other techniques are then used to treat it followed by selective melting to recover zinc.

  The residue is melted in two stages in a gas-fired reverberatory furnace. in the first stage lead is melted at 340 °C and is tapped and cast into ingots. In the second stage, the temperature is raised to 440 °C and zinc is melted, tapped and cast into ingots. An alternative process uses an indirectly fired rotary kiln with a perforated inner lining. Zinc melts and flows out through the liner into a holding furnace from where it is cast into ingots. Further refining is always necessary.

Zinc oxide is also produced from residues, in particular the dust from electric arc steel making furnaces. Waelz kilns and slag fuming furnaces can be used.

5.1.6.2 Waelz kilns

The process is designed to separate zinc (and lead) from other materials by reducing, volatilising and oxidising zinc (and lead) again [tm 102, DFIU Zn 1999; tm 120 TU Aachen 1999].

The dust, other secondary raw materials and coke fines are loaded into silos. The materials are mixed and can also be pelletised. It is then sent directly to the kiln feeding system or for intermediate storage. Weighing equipment can be used to control the quantity of reduction materials (coke) according to the zinc content of the raw materials and of fluxes for the desired slag quality.

The normal operating temperature inside a Waelz kiln is about 1200 °C. Inside the kiln solid materials are first dried and then heated up by the counter current flow of hot gas and contact with the refractory lined walls. Depending on the inclination, length and rotation speed, the material has an average residence time between 4 and 6 hours in the kiln. In the strongly reducing atmosphere of the solid bed, zinc, lead and other heavy metals are reduced. Zinc and lead are evaporated into the gas atmosphere; chlorides and alkalis (depending on the slag basicity) are vaporised together with the heavy metals. As there is a surplus of air in the kiln, the metal vapours are oxidised. The mixed oxides are drawn from the kiln with the process gases and separated in the gas treatment system.

The gas treatment system typically comprises a settling chamber for removal of coarse dust that is carried over mechanically, a cooling step for gas cooling with water and an electrostatic precipitator to remove the Waelz Oxide. Air-cooling followed by a fabric filter is also used. Techniques to minimise and remove dioxins are used where needed, these are covered in section 2.8.

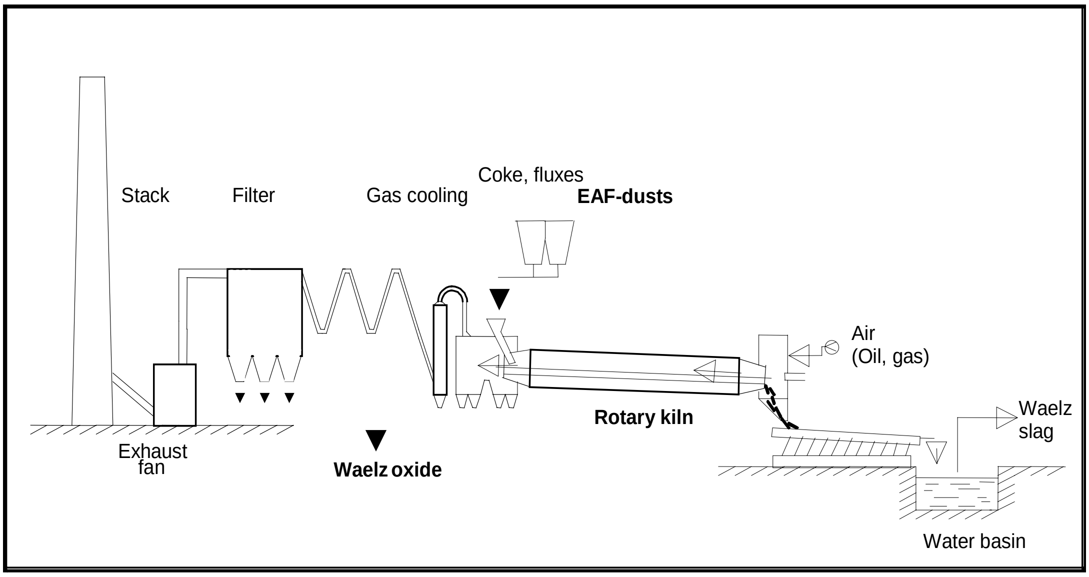


Figure 5.8: Waelz Kiln

The slag produced in the kiln is discharged continuously from the end of the furnace into a quench system. After cooling, screening and crushing, the slag can be used as a material in civil engineering e.g. for road construction. In addition, the slag can be suitable as a flux for cement clinker production or as an iron source in the iron and steel industry.

The Waelz oxide that is produced can be processed in a number of ways. The most basic process is hot briquetting or sintering for sale to pyrometallurgical zinc plants e.g. Imperial Smelting Process. If the lead oxide content is high, a calcination step can also be used to volatilise the lead.

Waelz oxide can also be leached in a two-stage process using sodium carbonate in the first stage and water in the second stage to remove chloride, fluoride, sodium, potassium and sulphur. The purified final product is dried and can be used as a feed material for the zinc electrolysis process.

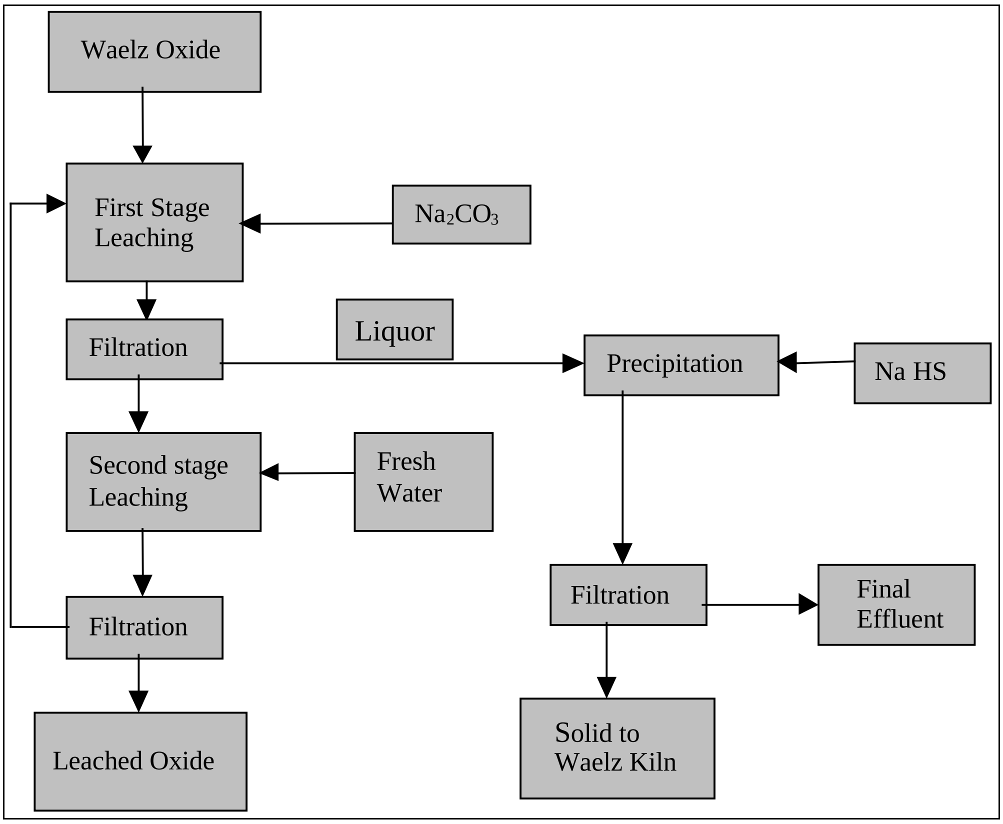


Figure 5.9: Waelz Oxide leaching process

5.1.6.3 Slag fuming processes

These processes are also used to recover zinc from residues. Electric arc furnace dust, most of the slags from lead smelting operations and other residues from zinc reduction contain lead and zinc that will be lost if they are not treated further. These materials may be fumed with a source of carbon such as coal, to recover lead and zinc and to raise heat from the process [tm 120 TU Aachen 1999].

Cyclone or converter type furnaces are used to raise the temperature above 1200 °C to volatilise the metals and then form the oxides that are then recovered from the gases in a filtration stage. The cyclone furnace is operated with oxygen enriched air but the converter is operated with sub-stoichiometric air. Excess heat is produced and this is recovered in a waste heat boiler and electricity is generated. The slag produced is used for construction purposes.

5.1.7 Melting and alloying processes for zinc

Melting and alloying are usually carried out in indirectly fired crucible furnaces or induction furnaces, temperature control is practised to ensure that zinc is not volatilised forming fume. The fuel is usually either gas or oil. The gas or oil burner can be located outside the crucible, which is encased in a combustion box, or inside the crucible as an immersion tube heater [tm 13, HMIP Zn 1993; tm 101, NL Zn 1998].

In both cases, temperature control is critical, as the casting temperature must not exceed 450 °C for most alloy compositions to avoid metal loss by fuming.
Alloy additions are usually made as solids, but in certain operations molten aluminium is added from an adjacent melting furnace.

When alloys are made from impure raw materials, fluxes are needed to absorb the impurities. The standard flux used contains zinc chloride, magnesium chloride and sodium silico-fluoride. The use of this flux results in the emission of gaseous silicon tetrafluoride, which is removed by wet scrubbing. The tetrafluoride is decomposed to form hydrogen fluoride that is absorbed by the scrubbing medium.

5.1.8 Casting processes for zinc

Zinc is melted in electric furnaces and temperature control is practised to prevent fuming. The zinc bath is periodically skimmed to remove solids ('dross': zinc oxide and zinc chloride). A flux is often added to reduce the loss of zinc in the 'dross'. The dross can be recycled within the ISF or to the roaster in the electrolytic zinc process.

Metal is usually cast into permanent moulds that are commonly made of cast iron. Stationary or continuous conveyor casting machines are used.

Static moulds and conveyor casting machines are used to produce blocks and ingots. Continuous casting machines are used to produce rod for reduction to wire.

5.1.9 Production of zinc dust

Zinc dust is produced as a product for other industrial processes and as reagent for use during the leach liquor purification route. Molten zinc produced by the same techniques outlined above is sprayed under pressure through an atomising nozzle and is then rapidly cooled in an inert atmosphere to produce dust [tm 120 TU Aachen 1999]. Air, water or centrifugal atomisation of a stream of molten zinc can also be used to produce dust. The dust is removed in bag filter system and conveyed to the process or packaged.

5.1.10 Cadmium

5.1.10.1 Production of cadmium from lead and zinc processes

Cadmium is produced as a by-product from many of the metal recovery processes. The production of zinc and lead are the main sources [tm 120, TU Aachen 1999].

In the Imperial Smelting Furnace (ISF), cadmium is recovered via two separate routes. Some cadmium follows zinc and is eventually recovered as condensate from the second stage distillation. The balance is recovered from the flue dust from the gas cleaning section that precedes the sulphuric acid plant. It is leached with sulphuric acid and is then stripped from this liquor.

Cadmium cementate, recovered from the purification of zinc solutions are also refined hydro-metallurgically. In this process the cementate is leached in a sulphuric acid medium, the solution purified, and cadmium metal electro-won. The purified $ZnSO_4$ solution is returned to the main zinc circuit.

Cadmium is also recovered as cadmium chloride liquor by an ion exchange process. The liquor is directed to an immersed trommel with high-grade zinc strip that starts an exchange reaction and results in the production of cadmium sponge and zinc chloride liquor. The sponge, which can also be produced from sulphate solutions is melted with caustic soda (sodium hydroxide) flakes to remove remaining zinc and the product is cast and sold or if impure, sent to further cadmium refining. Cadmium can also be recovered as the carbonate and electro-winning techniques can be used to recover it.

In the cadmium refinery, cadmium from both routes is combined and distilled at high temperature. The condensate is cadmium containing approximately 1% zinc and the run-off is high grade zinc. The distilled cadmium is melted with caustic soda and sodium nitrate to remove residual zinc. Cadmium recovered from hydro-metallurgical routes is treated in a similar way but a vacuum distillation stage is also used.

5.1.10.2 Production of cadmium from batteries

The other main source of cadmium is from the recycling of Ni-Cd batteries. Several recycling initiatives exist and they supply batteries to the industry for automatic sorting and recovery. Ni-Cd batteries are first of all pre-treated thermally to remove plastic coatings and open the battery cases. The opened batteries are then heated in a closed retort to volatilise and then condense the cadmium, which is then cast into moulds. Nickel and iron residues are then recycled. Each of the process stages uses high quality extraction and abatement systems to remove dust, metals and VOCs such as dioxins. The process is dry and is isolated from the drainage system.

5.1.11 Production of other metals (In, Ge, Ga, As, Te, Sb, Bi)

Other metals are sometimes present in the concentrates that are used for zinc and lead production. They tend to be concentrated in the slags, drosses, flue dusts and residues produced during processing and these residues comprise the feed material for these metals.

Recovery processes can be complex and many are commercially confidential. The processes combine several techniques such as leaching, cementation, solvent extraction, chlorination, electro-winning and vacuum distillation. These techniques can be followed by zone refining and crystal growth techniques to produce ultra pure metals.

5.2 Present Emission and Consumption Levels

The main environmental issues of the zinc and lead industry are air and water pollution and the generation of hazardous wastes. The facilities generally have their own wastewater treatment facilities and wastewater recycling is usually practised. Many wastes are reused but the major item is leach residue that has a high environmental impact [tm 101, NL Zn 1998; tm 102, DFIU Zn 1999]. Some local aspects, like noise, are relevant to the industry. Due to the hazardous nature of some solid and liquid waste streams, there is also a significant risk for soil contamination.

The following tables give input and output balances for some lead and zinc plants in Europe.

Input	[t/a]	**Output**	[t/a]
Primary raw materials	125000	Zinc	100000
Secondary raw materials	125000	Lead bullion	35000
Coke	100000	Sulphuric acid	125000 - 200000
		IS furnace slag	70000
		Cadmium carbonate	n. a.

Table 5.3: Input and output data for an ISP plant (1998)
[tm 102, DFIU Zn 1999]

Inputs	**[t/a]**	**Outputs**	**[t/a]**
Battery lead paste others	82000	Lead	90000
Lead concentrates	40000	Sulphuric acid	25000
Recycled flue dusts	34000	Slag	10000
Fluxes	3500	Mercury residue	20
Coal or coke	7100	Flue dust (recycled to the furnace)	34000
Oxygen	13300		

Table 5.4: Input and output data for the ISA Smelt furnace (lay out and preliminary data)
[tm 102, DFIU Zn 1999]

Input	**[t/a]**	**Output**	**[t/a]**
Lead-containing materials	130000	Lead bullion	90000
Fluxes (limestone, ...)	20000	Slag	50000
Nitrogen	12500	Sulphuric acid	60000
Oxygen	46000	Doré silver	250
Coal (dust)	12000	Calomel	2 – 5
Natural gas	1300	Zinc-cadmium carbonate	100 – 150

Table 5.5: Input and output data for the QSL plant (1997)
[tm 102, DFIU Zn 1999]

Input			**Output**		
Melting materials	*[t/t Pb]*	2.12	*Products*		
Battery scrap	[%]	63	Lead and lead alloys	[t/t Pb]	1
Other melting materials	[%]	21	Battery paste	[t/t Pb]	0.5
Bullion, scrap lead	[%]	16	Polypropylene compounds	[t/t Pb]	0.07
Reagents	[t/t Pb]	0.14	*Residues*		
Steel borings	[%]	46	Residual plastics	[t/t Pb]	0.10
Petrol coke	[%]	32	Slag	[t/t Pb]	0.23
Soda	[%]	22	*Others* Exhaust gases	[Nm^3/t Pb]	70000
Others: Electric energy	[MWh/t Pb]	0.26			
Natural gas	[MWh/t Pb]	1.19			
PP chips (external)	[t/t Pb]	0.04			

Table 5.6: Input and output data for a battery recovery plant without de-sulphurisation (1998) [tm 102, DFIU Zn 1999]

Input			**Output**		
Melting materials	*[t/t Pb]*	1.41	*Products*		
Battery scrap	[%]	79.0	Lead and lead alloys	[t/t Pb]	1
Other melting materials	[%]	3.8	Sodium sulphate	[t/t Pb]	0.096
Bullion, scrap lead	[%]	16.6	Polypropylene chips	[t/t Pb]	0.051
Flue dust incinerator	[%]	0.6	*Residues*		
Reagents	[t/t Pb]	0.307	Residual plastics	[t/t Pb]	0.108
:- NaOH	[%]	49.8	Metallurgical slag	[t/t Pb]	0.18
Steel borings	[%]	9.4	*Others* Exhaust gases	[Nm^3/t Pb]	37000
Petrol coke	[%]	17.6			
Soda	[%]	23.1			
Others Electric energy	[MWh/t Pb]	0.20			
Natural gas	[MWh/t Pb]	0.73			
Steam	[MWh/t Pb]	0.84			

Table 5.7. Input and output data for a battery recovery plant with de-sulphurisation (1998) [tm 102, DFIU Zn 1999]

Input	[t/a]	Output	[t/a]
Battery scrap	65000	Refined lead and alloys	28000
Battery plates	4000	Battery paste	32500
Scrap lead	6000	PP fine grains	2750
		Ebonite and separators	3500
		Slag	3300

Table 5.8: Input and output data for a battery recovery plant with paste removal (1998) [tm 102, DFIU Zn 1999]

Input	[per tonne lead bullion]	Output	[per tonne lead bullion]
Used batteries, dry	1100 kg	Lead bullion	1000 kg
Other lead scrap, waste	320 kg	Flue dusts	32 kg
Fluxes (limestone)	14 kg	Excess slag	50 kg
Coke (foundry coke)	109 kg	Return slag	500 kg
Other inputs (iron)	67 kg	Off-gas	18200 Nm^3
Lead carbonate (from flue dust treatment)	40 kg	Iron/lead matte	140 kg
Slag (return)	500 kg		
Oxygen	43 Nm^3		
Natural gas	15 Nm^3		
Electrical energy	107 kWh		

Table 5.9: Input and output data for a battery recovery plant with whole battery smelting (1998) [tm 102, DFIU Zn 1999]

Material	Description
Feed	Concentrates (50 - 55% Zn)
Products	Zinc (99.99%) Cadmium Sulphuric Acid
Waste	Goethite or Jarosite 30 - 40000 t/a Neutralised acid sludge (special waste or recirculated)
Intermediate Products	Pb/Ag residue 12000 t/a Cementates Neutral Leach Residue
Typical Production	Zn 100000t/a Sulphuric acid 175000 t/a Cd 300 t/a

Table 5.10: Typical data for a zinc electrolysis plant. Roast - Leach – Purification - Electrolysis [tm 102, DFIU Zn 1999]

Metal%	Zn Concentrate	Neutral Leach Residue *	Copper Cementate *	Pb/Ag Residue *	Jarosite **	Goethite **
Zn	53	16 - 27	5.9	5.8	2 - 6	4 - 9
Fe	7.3	15 - 35		9	20 - 32	31 - 43
Pb	1.6	3.6		10 - 25	< 2	< 2
S	32	3 - 11		4	10 - 13	2 - 5
Cu	0.6	0.3 - 2.4	55	0.1	< 0.2	< 0.3
Cd	0.24	0.1 - 0.3	0.3	0.2	< 0.1	< 0.1
Ag	0.016	0.036		0.115	< 0.01	< 0.01
SiO_2	1.7	4.0		12		
Note. *Composition, may vary depending on feed concentration and treatment. **Amounts depend on Fe content of the feed.						

Table 5.11: Typical composition of feed and products for a zinc electrolysis plant

Inputs	t/a	Outputs	t/a
Zn Residues (EAF dust etc)	90000	Waelz Oxide	33000
Coke Breeze	25000	Slag	70000
Silica Sand	13000	Kiln Gas (m^3/a)	30000
Sodium Carbonate	3300	Treated Water (m^3/a)	150000
NaHS (m^3/a)	11		
Industrial Water (m^3/a)	300000	Treated Oxide	30000
Natural Gas (Th 000/a)	7900	Zinc Content	19500
Electrical Energy MWh/a	5700		
Diesel Oil (m^3/a)	440		

Table 5.12: Input and output data for a Waelz kiln using a two stage oxide leaching process

Inputs	[t/a]	Outputs	[t/a]
Retort residue, dry	27700	Waelz oxide	17000
Zinc carrier, dry (EAF dust, ...)	33700	Slag	48200
Coke breeze	10800	*Clean gas [Nm³/h]*	*70000 – 90000*
Silica	7500		
Sweepings, rubble	2100		
Air [Nm³/h]	*5000 – 10000*		
Lime	1000		
Electrical energy [MWh/a]	*4620*		
Natural gas [Nm³/a]	*92000*		

Table 5.13: Input and output data for a Waelz plant (1996/97)
[tm 102, DFIU Zn 1999]

5.2.1 Energy

The energy requirement for the different lead and zinc processes varies to a large extent. It depends on the quality of the feed and the products, the use of latent or waste heat and the production of by-products. The following two tables show the average energy requirements of the different processes.

Process	**Electric kWh/t Pb**	**Coke kg/t Pb**	**Coal kg/t Pb**	**Nat Gas Nm^3/t Pb**	**Fuel Oil l/t Pb**	**O_2 Nm^3/t Pb**	**Iron kg/t Pb**
Pb shaft furnace. Primary	180 - 300	150 - 225		50 - 70			120 - 170
Pb shaft furnace. Secondary	50	100 - 140		35	1		65 - 110
Rotary furnace Secondary with CX system and Na_2SO_4 production	160		60	65		90	30
QSL	*		100	20		330	
Kivcet	250*	105			25	450	
TBRC	450 - 550	40			30	140	
* Totally or partially covered by waste heat conversion							

Table 5.14: Energy requirement of various lead processes

Process	**Energy related to: -**	**Electrical kW/h per t**	**Coke kg/t**	**Natural gas Nm^3/t**
Zinc electrolysis	t zinc	4100		
ISF & NJ distillation	t zinc t Metal	1050 750	1100 785	220 160
Waelz kiln	t WO leached	200	850	20
Slag fuming	t slag	150	250	

Table 5.15: Energy requirement of various zinc processes

5.2.2 Emissions to air

The emissions can escape the process either as stack emissions or as fugitive emissions depending on the age of the plant and the technology used. Stack emissions are normally monitored continuously or periodically and reported.

The main emissions to air from zinc and lead production are: -

- sulphur dioxide (SO_2), other sulphur compounds and acid mists;
- oxides of nitrogen (NO_x) and other nitrogen compounds;
- metals and their compounds;
- dust.
- VOCs and dioxins.

Other pollutants are considered to be of negligible importance for the industry, partly because they are not present in the production process and partly because they are immediately neutralised (e.g. chlorine) or occur in very low concentrations. Emissions are to a large extent bound to dust (except cadmium, arsenic and mercury that can be present in the vapour phase) [tm 101, NL Zn 1998].

The sources of emissions from the process are: -

- roasting (Most emissions occur during unscheduled shutdown);
- other pre-treatment (battery breaking);
- transport and handling of material
- smelting and refining;
- leaching and purification;
- electrolysis;
- casting;
- sulphuric acid plant.

Component	**Roasting sintering smelting**	**Leaching and purification**	**Electrolysis**	**Battery Breaking**	**Casting etc.**	**Sulphuric acid plant**
Sulphur oxides	••*	•	•• (acid mist)	•	•	•••
Nitrogen oxides	•*				•	•
Dust and metals	•••*	•	•	•••	•••	
VOC and dioxins	•(••)**				•*	

Note. ••• more significant …………………..• less significant.
*The direct emissions from the roasting or smelting stages are treated and/or converted in the gas cleaning steps and sulphuric acid plant; the remaining emissions of sulphur dioxide and nitrogen oxides of the sulphuric acid plant are still relevant. Fugitive or non-captured emissions are also relevant from these sources. Secondary smelting of battery paste is a source of SO_2.
** Dioxins and VOC may be present if secondary materials are used that contain dioxins or are contaminated with organic materials. VOCs may also be present during solvent extraction processes used for the production of Ga, Ge etc.

Table 5.16: Significance of potential emissions to air from lead, zinc and cadmium production

Besides process emissions, fugitive emissions occur. The major fugitive emission sources are [tm 101, NL Zn 1998]:

- dust from storage and handling of concentrates (10 t/y);
- leakage from roasters and smelters;
- dust from the exhaust gases of leaching and purification vessels (1 t/y);
- exhaust gases of cooling towers of the leaching and purification units (0.7 t/y);
- exhaust gases of cooling towers of the electrolysis process (08 t/y);
- dust from the exhaust gases of casting furnaces (1.8 t/y);
- miscellaneous (0.7 t/y).

Although fugitive emissions are difficult to measure and estimate there are some methods that have been used successfully (section 2.7). The following table gives some emission data based on the upgrading of a lead process from blast furnace to ISA Smelt [tm 102, DFIU Zn 1999] and illustrates the potentially high level of fugitive emission.

	Conventional plant (1990) [kg/a]			**ISA Smelt plant (1997) [kg/a]**			**Reduction rate [%]**		
Emissions	**Controlled**	**Fugitive**	**Total**	**Controlled**	**Fugitive**	**Total**	**Controlled**	**Fugitive**	**Total**
Lead	5236	19555	24791	911	540	1451	83	97	94.1
Cadmium	330	242	572	3.81	0.24	4.05	99	> 99	99.3
Antimony	151	309	460	25.8	1.77	27.52	83	> 99	94
Arsenic	77.6	141.5	219.1	4.03	1.55	5.58	95	99	97.5
Thallium	21.9	16.1	38	1.27	< 0.01	1.27	94	> 99	96.7
Mercury	16.7	0.4	17.1	0.87	< 0.01	0.87	95	> 97	95
Sulphur dioxide [t/a]	*7085*	-	*7085*	*140.4*	-	*140.4*	98	-	98
Note – Preliminary data for the ISA Smelt plant. Lead production 1990 - 96724t; 1997 - 86941t.									

Table 5.17: Significance of plant improvements on fugitive emissions

5.2.2.1 Sulphur dioxide and other sulphur compounds

The major sources of sulphur dioxide emission are fugitive emissions from the oxidation stages, direct emissions from the sulphuric acid plant and the emission of residual sulphur in the furnace charge. Good extraction and sealing of the furnaces prevents fugitive emissions and the collected gases from oxidation stages are passed to a gas cleaning plant and then to the sulphuric acid plant.

After cleaning, the sulphur dioxide in the gas from the sintering, roasting or direct smelting stages is converted to sulphur trioxide (SO_3). The efficiency generally lies between 95 to 99.8% depending on the sulphuric acid plant used (single or double absorption) and the concentration of sulphur dioxide in the input gas and its variation or stability. SO_2 concentrations in the off gas from 200 - 2300 mg/Nm^3 can be emitted. A very small amount of SO_3 is not absorbed and is emitted together with the SO_2. During start up and shut down there may be occasions when weak gases are emitted without conversion. These events need to be identified for individual installations, many companies have made significant improvements to process control prevent or reduce these emissions [tm 101, NL Zn 1998; tm 102, DFIU Zn 1999].

Lead sinter and some secondary raw materials contain residual sulphur and sulphates. It has been reported [tm 129, Madelin 1991] that 10% of the sulphur content of lead concentrate remains in the sintered material that is fed into the furnaces. Similarly, the sulphate content of battery scrap may be significant depending on the way it is pre treated and whether the paste is included. In most cases the sulphur is fixed in the slag or in other by-products. The extent of fixation depends on the fluxes used and the other metals associated with process, for example copper matte may be produced when Pb/Cu concentrates are treated together. Pb/Fe matte is produced under reducing conditions when iron turnings are added. In other cases SO_2 may be emitted and may need further treatment.

During electrolysis, emissions of aerosols (diluted sulphuric acid and zinc sulphate) takes place to the hall. These emissions leave the cell room via the (natural) ventilation or from the cooling towers. The emission is small compared with the emissions from the sulphuric acid plant but as they are in the form of an aerosol form, they can be dealt with in mist eliminators or dust abatement [tm 101, NL Zn 1998]. Some processes use coverings for the cells such as foam or plastic beads to reduce mist formation [tm 139, Finland Zn 1999]. One plant has been recently modified to improve roasting and to collect fugitive emissions from the whole of the process. Sulphur dioxide emissions were reduced from 3000 to 1200 g per tonne of metal produced. Emissions from other processes are shown below.

Process	Product	Total Metal Production Tonnes per year	Sulphur Dioxide produced g/t of Metal
Roasting & Electrolysis	Zinc	105000 to 235000	2500 to 5500
ISF and sinter plant.	Zinc + Lead	100000 Zn 45000 Pb	5000 - 9000
QSL	Lead	90000	1000
ISA	Lead	90000	7500
Battery – Whole	Lead	35000	7800
Battery – De Sulphurised Paste	Lead	35000 to 40000	1070 to 2000
Battery – paste excluded	Lead	35000	3200
Batteries + Extra Paste	Lead	10000	210 (FGD system)
Lead shaft furnace and sinter plant	Lead	110000 Pb	10000 – 45000
Batteries – MA process	Lead	33000	6600

Table 5.18: Sulphur dioxide production from several zinc and lead processes

Mists from battery breakers can also be responsible for similar emissions. Emissions from the smelters using battery-derived material contain SO_2, the concentration depends on whether the paste is smelted or is de-sulphurised first or is fixed with the slag. Typical figures are 50-500mg/Nm^3 [tm 102, DFIU Zn 1999].

5.2.2.2 Nitrogen oxides

The roasting and smelting stages are potential sources of nitrogen oxides (NO_x). NO_x may be formed out of nitrogen components that are present in the concentrates or as thermal NO_x. The sulphuric acid produced can absorb a large part of the NOx and this can therefore affect sulphuric acid quality. If high levels of NO_x are present after the roasting stages, treatment of the roasting gases may be necessary for reasons of product quality and environmental reasons. Other furnaces that use oxy-fuel burners can also show a reduction in NO_x. The range for all of the processes is 20 to 400mg/Nm^3.

5.2.2.3 Dust and metals

Dust carry over from the roasting and smelting processes are potential sources direct and fugitive emissions of dust and metals. The gases are collected and treated in the gas cleaning processes of the sulphuric acid plant. Dust is removed and returned to the process.

The gases leaving splash condensers in the ISF, from distillation columns and from the tapping points are also potential sources. Good extraction and abatement is needed at these points to prevent fugitive emissions. Slag treatment and quenching also gives rise to dust. The range of dust emissions from these captured sources is < 1 to 20 mg/Nm^3. The slags and drosses produced during the recovery of lead from batteries can contain Sb, when these residues become wet, there are potential emissions of stibine which is a poisonous gas.

Process	Product	Production (tonnes)	Zinc grams per tonne of metal	Pb grams per tonne of metal
Roasting	Zinc	130000 Zn	10	
Roasting	Zinc	215000 Zn	45	
Roasting	Zinc	235000 Zn	45	
Roasting	Zinc	105000Zn	11	
ISF and sinter plant	Zinc + Lead	100000 Zn 45000 Pb	30 - 90	5 – 40
QSL	Lead	90000 Pb	7.2	10 – 20
ISA Smelt	Lead	90000Pb	-	10 - 30
Battery – Whole	Lead	35000 Pb		< 15
Battery – De Sulphurised Paste	Lead	40000 Pb		10
Battery – De Sulphurised Paste	Lead	35000 Pb		5 - 25
Battery – Oxide paste sold	Lead	35000 Pb		5 - 25
Batteries + Extra Paste	Lead	10000 Pb		5 – 25
Battery – MA	Lead	33000	-	20
Lead shaft furnace and sinter plant	Lead	110000 Pb	< 20	60 - 130
Roasting	Zinc	21000 Zn	70	2

Table 5.19: Mass release of metals from some European processes (controlled emissions only)

De-aeration of vessels in the leaching and purification stages can emit dust and metals. Arsine can be emitted from the purification stages of zinc. Cadmium can be emitted from the distillation stages and the cadmium plants.

Emissions of aerosols takes place in the cell room and battery breakers and can contain metals. The range of mist and dust emissions from these sources is 0.1 to 4mg/Nm^3.

The melting, alloying, casting and zinc dust processes are potential emission sources of dust and metals. The range of dust emissions is reported to be 200 to 900mg/Nm^3 in the crude gas [tm 101, NL Zn 1998; tm 102, DFIU Zn 1999]. Fume collection and abatement systems are used and cleaned gas values are below 10mg dust/Nm^3 [tm 102, DFIU Zn 1999].

Metals are associated with the dusts emitted, approximately 50% is zinc. Cadmium and lead are not present when pure zinc is melted, alloyed and cast.

5.2.2.4 VOCs and dioxins

The formation of dioxins in the combustion zone and in the cooling part of the off-gas treatment system (de-novo synthesis) may be possible in some processes particularly if plastic components are included in the secondary materials that are fed into a process. Dioxins have also shown to present in some dusts from Waelz kilns treating EAF dust.

5.2.3 Emissions to water

Metals and their compounds and materials in suspension are the main pollutants emitted to water. The metals concerned are Zn, Cd, Pb, Hg, Se, Cu, Ni, As, Co and Cr [tm 26, PARCOM 1996; 28, WRC 1993 tm 101, NL Zn 1998; tm 102, DFIU Zn 1999].

Other significant substances are fluorides, chlorides and sulphates.

- metals;
- materials in suspension;
- chlorides, fluorides, sulphates.

Possible wastewater streams are:

- Waste water from wet scrubbers;
- Waste water from wet electrostatic precipitators;
- Waste water from the mercury-removal step;
- Wastewater from battery breaking and classification stages;
- Wastewater from slag granulation;
- Wastewater from various hydro-metallurgical processes;
- Anode and cathode washing liquid effluent;
- Sealing water from pumps;
- General operations, including cleaning of equipment, floors, etc.;
- Discharge from cooling water circuits;
- Rainwater run-off from surfaces (in particular storage areas) and roofs.

Wastewater from the gas cleaning of the smelter and fluid-bed roasting stages are the most important sources. Other sources are the process effluent from electrolysis, battery breaking and cleaning plus miscellaneous sources.

5.2.3.1 Waste waters from abatement plant

Generally wet gas cleaning systems operate with liquid recycling. A monitored bleed keeps suspended solids and dissolved salts within certain defined limits. The bleed is either treated separately or in an integrated water treatment plant to remove solids and dissolved species before discharge. The destination of the separated material depends on the origin of the wastewater.

Wet scrubbers after the roasting process are operated with a SO_2-saturated acidic solution. The scrubber removes fluorides, chlorides, most mercury and selenium and the some particles that pass the mechanical gas treatment. To avoid the build up of contaminants, some liquid needs to be bled continuously from the scrubber. Dissolved SO_2 is removed during treatment prior to the discharge.

Wet electrostatic filters will also produce an acidic scrubber liquid. This is recycled after filtering. Some liquid needs to be bled from this circuit to remove build up of contaminants. This bleed liquor is treated and analysed before discharge [tm 101, Personal Discussions 1998].

The mercury-removal step involves a gas-liquid contact tank in which the liquid contains a reagent that combines with mercury and removes it. Mercury chloride ($HgCl_2$) is frequently used and reacts with metallic mercury from the gas to form a solid Hg_2Cl_2-precipitate (so-called "calomel"). The relatively clean liquid is discharged as wastewater for further treatment. The solid Hg_2Cl_2 is sold for mercury recovery or treated to produce mercury chloride again. The following table provides an indication of the composition of the gas cleaning liquids before treatment.

Component	**Concentration** (dissolved)	**Composition of** Suspended solids
Solids		250 – 1500 mg/l
Sulphate	13 – 25 g/l	
Chloride	1.3 - 1.8 g/l	
Fluoride	0.3 - 0.5 g/l	
Mercury	0.1 - 9 mg/l	5 – 30% of suspended solids
Selenium	0.1 - 50 mg/l	10 – 60% of suspended solids
Arsenic	5 – 95 mg/l	< 0.05% of suspended solids
Zinc	0.1 - 2.5g/l	2 – 6% of suspended solids
Cadmium	1 – 95 mg/l	
Lead	1 – 13 mg/l	5 – 50% of suspended solids

Table 5.20: Typical gas cleaning effluents

5.2.3.2 Battery recovery

The battery breaking and washing stages produces an effluent which is acidic and contains lead and other metals in suspension and solution. This effluent is neutralised and the water is recycled in the process. If possible the acid is used elsewhere. A portion is usually bled from the system to control dissolved salts.

These processes also produce contaminated surface water and consequently this water is also treated and reused. It is common practice to discharge a bleed of this sealed water circuit after further treatment and analysis. Road and surface contamination is minimised by frequent wet cleaning of roads, hard standing areas and lorries and by good practice in cleaning up spillages.

The quality and quantity of wastewater depends on the process used, the composition of the raw materials that are used in the process and the practices used by the operators. The reuse of process and rainwater is common.

5.2.3.3 Electrolyte bleed effluent

Electrolyte may be bled from the cells to control the build up of impurities e.g. magnesium, that may have a detrimental impact on the operation of the electrolytic cells. For zinc production, the flows in the electrolytic cells belong to the same (closed) water circuit as the leaching and purification stages. The sulphuric acid formed during electrolysis is fed to the leaching process and the remaining liquid is purified and fed to the electrolysis [tm 101, NL Zn 1998; tm 102, DFIU Zn 1999].

The effluent bleed of the electrolytic-leaching-purification circuit is strongly acidic and contains high concentrations of zinc and suspended solids. The volume of the bleed depends strongly on the composition of the zinc concentrates that are used in the roasting. Components that tend to build up in the circuit, especially magnesium, will determine the bleed flow and the treatment required.

5.2.3.4 Miscellaneous sources

The electrodes used during the electrolysis need to be rinsed periodically to remove deposited material upon the surface. Manganese dioxide is formed on the surface of the anodes by the reaction of oxygen with dissolved manganese. After rinsing of the anodes, the manganese is separated from the rinse water for external re-use.

	Effluent	Flow	Main components [mg/l]					
Process	**[m³/a]**	**[m³/h]**	**Pb**	**Cd**	**As**	**Zn**	**Ni**	**COD**
Electrolysis		40 - 200	0.01 - 0.5	0.001 - 0.3		0.01 - 6.0		
ISP		380 - 420	0.05 - 0.5	0.005 - 0.035	0.005 - 0.1	0.05 - 1.0		
Waelz Kiln with Oxide Leaching Plant	150000	25	< 0.2	< 0.15	< 0.5	< 3.0	< 2.0	
Waelz Kiln	60000	9 - 10	0.3 - 0.5	0.05 - 0.2		0.8 - 1.0		
CX + Rotary Furnace	190000	12.7	0.12 - 1.4	0.06 - 0.09	0.05 - 0.5	0.14 - 1.6	0.1 - 0.7	13 - 225
MA + Rotary Furnace	124000		0.02	0.07	< 0.0005	0.27	0.09	
Whole battery	150000	40	0.4	0.01	< 0.001	0.01	< 0.05	96
Shaft Furnace	17000		< 0.2	< 0.1		< 0.3		
QSL	90000	10	0.1	< 0.05	< 0.05	0.3	< 0.05	20
CX + Rotary Furnace + Pb refinery	46800		0.3	0.03	0.037			83
Ausmelt	110000	13	0.01 - 0.09	0.001 - 0.01	0.001 – 0.1	0.01 - 0.2		50 – 200

Table 5.21: Typical wastewater analyses

Cathodes are cleaned after removal of the zinc or lead sheets. The anode and cathode washing liquid effluents are acidic and likely to contain copper, zinc, lead and suspended solids [tm 101, NL Zn 1998; tm 102, DFIU Zn 1999].

Process unit	Operation/source	Use/treatment options
General	Rain water from roads, yards, roofs Wet cleaning of roads Cleaning of lorries, ...	Waste water treatment plant/reuse Waste water treatment plant Recirculation, waste water treatment plant
Battery separation	Spills	Used for the desulphurisation/waste water treatment plant
Paste desulphurisation	Spills	Used in the desulphurisation process/waste water treatment plant
Smelting and melting operation	Cooling water from furnace, machinery and equipment	Recirculation
Slag granulation	Wet ESP effluent Granulation water	Recirculation, waste water treatment plant Recirculation
Gas cleaning system	Condensate from gas cooling, wet ESP Condensate from mercury removal Leakage	Removal of suspended dusts and reuse as feed, waste water treatment plant After mercury removal to waste water treatment plant Recirculation
Sulphuric acid plant	Cooling water equipment Leakage	Recirculation Waste water treatment plant
Cadmium plant	Solution after cadmium removal Leakage	Waste water treatment plant Either to cadmium removal or waste water treatment plant
Feed storage	Surface water (rain/wetting)	Waste water treatment plant
Sinter plant	Scrubber (sinter fine cooling)	Waste water treatment plant
Roast gas cleaning	Wet gas cleaning	Waste water treatment plant
Cadmium leaching	Cadmium leaching	Waste water treatment plant
IS furnace	Gas cleaning Gas cleaning coke heating chamber	Waste water treatment plant; recirculation Recirculation
Slag granulation	Granulation waste water	Recirculation, waste water treatment plant
Roasting/roast gas cleaning	Wet cleaning of roast gases	Waste water treatment plant
Leaching	General operations including wet gas cleaning	Return to leaching
Purification	General operations	Return to leaching
Electrolysis	Cleaning of cells, anodes and cathodes	Return to leaching
All process units	Maintenance	Waste water treatment plant
Waste water treatment plant	Effluent treatment	Reuse for certain applications/discharge

Table 5.22: Summary Table of Potential Wastewater Sources and Options

Cooling water from the granulation of slag is usually re-circulated in a closed circuit system.

5.2.4 Process residues and wastes

The production of metals is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). The most important process specific residues are listed below.

Solid residues derived from various process and abatement stages may have one of three possible destinations.

- Recycling in or upstream of the process;
- Downstream treatment to recover other metals;
- Final disposal, if necessary after treatment to ensure safe disposal.

The following solid waste arisings are significant: -

The electrolytic production of zinc is one of the main sources of solid waste in the non-ferrous industry. Relatively large quantities of iron based solids are generated by the leaching process. Jarosite and goethite are classified as hazardous waste because of the content of leachable of elements such as Cd, Pb and As. The leaching and purification processes and electrolysis of zinc and the refining stages of lead also generate other metal rich solids. These are usually rich in a specific metal and are recycled to the appropriate production process.

The ISF or direct smelting furnaces are also significant sources of solid slags. These slags have been subjected to high temperatures and generally contain low levels of leachable metals, consequently may then be used in construction.

Solid residues also arise as the result of the treatment of liquid effluents. The main waste stream is gypsum waste ($CaSO_4$) and metal hydroxides that are produced at the wastewater neutralisation plant. These wastes are considered to be a cross-media effect of these treatment techniques but many are recycled to pyrometallurgical process to recover the metals.

Dust or sludge from the treatment of gases are used as raw materials for the production of other metals such as Ge, Ga, In and As etc or can be returned to the smelter or into the leach circuit for the recovery of lead and zinc.

Hg/Se residues arise at the pre-treatment of mercury or selenium streams from the gas cleaning stage. This solid waste stream amounts to approximately 40 - 120 t/y in a typical plant. Hg and Se can be recovered from these residues depending on the market for these metals.

5.2.4.1 Leaching residues

The production of iron based solids (goethite, jarosite or hematite) accounts for the greatest volume of waste depending on the process used. The composition is shown in the following table [tm 101, NL Zn 1998].

Process	Fe%	Zn%	Pb%	Cu%	Cd%
Hematite (with integrated direct leaching)	65 - 67	< 0.2	< 0.01	< 0.02	< 0.01
Hematite (without direct leaching)	59	1	0.01	0.02	0.02
Goethite	40 - 42	5 - 9	< 2	< 0.3	< 0.1
Para-goethite	40	n.a.	n.a.	n.a.	n.a.
Conventional jarosite	20 - 30	2 - 6	0.2 - 6	< 0.2	0.05 - 0.2
Low contaminant jarosite	32	0.3	0.1	0.2	0.001
Dor jarosite	26	1	4	0.08	0.05

n.a. = not available

Table 5.23: Example compositions of different types of residues
[tm 101, NL Zn 1998; tm 120, TU Aachen 1999]

Typically, these residues account for: -

- Jarosite - 0.35 to 0.80 tonnes per tonne of zinc produced.
- Goethite - 0.3 to 0.35 tonnes per tonne of zinc produced.
- Haemetite – 0.2 tonnes per tonne of zinc produced.

Haemetite processes have been unable to compete in economic terms as the process is significantly more complex and expensive to operate. In addition, haemetite has not proved to be acceptable as a raw material in other industries.

There are still some leachable metals in slurry after filtering and washing. The residue can be treated to a less leachable form with neutralisation and sulphide treatment. The disposal of these residues can be considerable cost as specially constructed, lined ponds or isolated areas are used to contain the material. Particular care is taken about leakage and these ponds have a major need to monitor groundwater [tm 101, NL Zn 1998; tm 102, DFIU Zn 1999]. There is a significant cross media effect compared to processes that are capable of producing an inert residue.

As reported earlier in 5.1.5.2, leaching residues can be treated in ISF or Waelz Kiln.

Pyrometallurgical treatment of these residues is also practised in Korea to produce a non-leachable slag and recoverable metal oxides [tm 41 & 43, Ausmelt 1997], problems with contaminant build up have been reported [Zn Expert response to 1st Draft, 1998]. Other developments are reported in Emerging Techniques.

5.2.4.2 Pyrometallurgical slags and residues

Slags from the Blast Furnace, ISF, Direct Smelting and Waelz kiln processes usually contain very low concentrations of leachable metals. They are therefore generally suitable for use in construction [tm 102, DFIU Zn 1999]. The slag output is between 10 and 70% of the weight of the metal produced dependant on the raw materials used.

Slags from the battery processing plants account for 13 to 25% of the weight of lead produced. They may be suitable for construction uses depending on the leachability of the metals they contain. The leachability is influenced by the fluxes used and the operating conditions [tm 102, DFIU Zn 1999]. The use of sodium based fluxes (Na_2CO_3) to fix sulphur in the slag causes an increase in the quantity of leachable metals. These slags and drosses from battery recovery processes can contain Sb. This is normally recovered but storage in damp conditions can cause the emission of stibine.

A number of standard leachability tests are used by Member States and these are specific to the Country in question.

Component	Eluate (according to DEVS4) [mg/l]
Zn	0.02 - 0.1
Pb	0.005 – 0.1
As	0.001 - 0.02
Fe	0.05 - 0.2
Cu	< 0.001 – 0.05
pH	7 – 11

Table 5.24: Eluate values of granulated IS furnace slag
[tm 102, DFIU Zn 1999]

	Eluate (according to DEVS4)
Component	Waelz slag (mg/l)
Zn	0.05
Pb	0.02
As	0.008
Cr_{tot}	0.002
Ni	0.005
Fe	0.5
Cu	0.05
F	1
Cl	5
pH	9.9

Table 5.25: Eluate values for acidic Waelz slag
[tm 102, DFIU Zn 1999]

Component	Eluate (according to DEVS4) (mg/l)
As	0.05
Cd	0.001
Cu	0.005
Pb	0.02 – 0.2
FeO	< 0.05

Table 5.26: Eluate values for slag from QSL process
[tm 102, DFIU Zn 1999]

Refining step	Solid output	Use/treatment options
Drossing/de-copperising	Copper dross	Further processing to recover copper and lead
Softening (Harris process/oxygen softening)	Harris slags Antimony slag	Hydrometallurgical treatment for metal recovery Pyrometallurgical treatment for metal recovery
De-silvering	Zinc-silver crust	Recovery of noble metals
De-zincing	Zinc metal	Reuse for de-silvering
De-bismuthising	Bismuth crust	Recovery of bismuth
Removal of alkali metals and alkaline-earth metals	Mg-Ca oxide dross	Internal recycling as flux
Finishing	Caustic dross	Internal recycling

Table 5.27: Solid Material from the refining of lead bullion

The drosses and solids, removed during the zinc and lead melting and refining stages, contain metals that are suitable for recovery.

5.2.4.3 Other materials

The battery processing plants also produce polypropylene from the crushed battery cases. The total plastic content accounts for 11 to 20% of the weight of lead produced [tm 102, DFIU Zn 1999]. There are a number of plastics fabricating plants designed specifically for this material and they produce granular polypropylene for the automobile industry. Effective washing of the polypropylene fraction and separation of other plastic components such as ebonite or PVC is essential to produce products within specification.

The following tables show the use or treatment options for the residues produced by several processes.

Production step	**Product or residue**	**Quantity kg/t Zn**	**Use or treatment option**
Leach/electrolysis.			
Roaster/sulphuric acid plant	Sulphuric acid Steam Hg-product Acid sludge	1750 2000 0.3 - 0.8 < 0.5	Sale Energy conversion Sale Controlled disposal or back to roast
Leaching plant	Neutral leach residue	500 - 600	To ISF, Waelz kiln or hot acidic leach
	Goethite or Jarosite PbAg-concentrate Final residue if Pb/Ag conc. removed	300 - 650 40 - 120 150	Controlled disposal Ag recovery Controlled disposal
Purification	Cadmium Cu-cementate	2 - 4 up to 10	Sale Sale
Wastewater treatment	Precipitated. Sludge	10*	Disposal or to Pb-/Zn-smelter
ISF			
Sinter plant/sulphuric acid plant	Acid sludge Hg-product	0.25 0.15	Controlled disposal Depending on composition, sale or to controlled disposal
	Flue dust Sulphuric acid	200 1300	To Cd-plant Sale
Cadmium plant	Cadmium carbonate	18	Sale
	Thallium sulphide Leach residue	0.25 180	Controlled disposal To sinter plant
Imperial Smelting Furnace	ISF slag	600 - 900	Sale or controlled disposal**
Waste water treatment	Precipitated sludge	30	Recycled to sinter plant
New Jersey Distillation			
Liquation	Lead Hard zinc	15*** 25 - 50***	To Pb refining or ISF Return to ISF
As-removal	Dross	< 1 - 5*	Return to ISF
Waste gas treatment	Flue dust	10	Return to sinter plant

Note. *estimated value ** depending on quality and regulations. *** amount may vary with the feed.

Table 5.28: Residues from zinc processes
[tm 120, TU Aachen 1999]

Production step	Product or residue	Quantity kg/t Pb	Use or treatment option
Slag fuming plant			
Slag fuming	Slag	700	Water resistant construction material
	Matte	2.5 - 25	To Cu-smelter
	Steam	2500	Energy conversion
Battery process – short rotary			
Physical treatment of batteries	Na_2SO_4 (CX)	140	Sale
	Battery paste (MA)	500	To primary smelter
	Polypropylene	70 - 80	Sale
	Residual plastics	100 - 130	Disposal or incineration
Smelting	Slag	150 - 200	Disposal
	Flue dust	25 - 60	After treatment back to Pb - smelter
Refining	Dross	60 - 90	To primary smelter
Waste water	Precipitated sludge		Return to smelter
Battery process – blast furnace			
Feed preparation	Spent acid	100	External use or neutralisation
Shaft furnace	FePb Matte	< 150	Sale to primary PbCu-smelter
	Slag	50	Road construction
		500	Return slag
	Flue dust	< 50	External/internal recycling
Refining	Dross	80	Sale to metal recovery
Primary lead shaft furnace			
Sinter machine	Flue dust	up to 100	After Cd-leach return to sinter-machine
	Return sinter	up to 3000	Return to sinter-machine
H_2SO_4-plant	H_2SO_4	600	Sale
	Calomel		Sale or to controlled disposal
	Acid sludge		
Cd-plant	CdZn precipitate		Sale
Shaft furnace	Slag	500 + 600 return	
	Flue dust	up to 80	Return to sinter-machine
Waste water treatment	Sludge	3	Partly return to sinter-machine

Table 5.29: Residues from lead processes
[tm 120, TU Aachen 1999]

Production step	Product or residue	Quantity kg/t Pb	Use or treatment option
Kivcet process			
Smelter	Slag	700	Controlled disposal
	Flue dust I	110	Return to smelter
	Flue dust II	100	To zinc-Leach
	Steam	1300	Energy conversion
H_2SO_4-plant	H_2SO_4	1100	Sale
	Calomel	< 0.10	Sale
	Acid sludge	0.5	Controlled disposal
Water treatment	Sludge		
Kaldo process			
TBRC (Kaldo)	Slag	350	To fuming
	Flue dust	160	Return to smelter
	Steam	700	Energy conversion
H_2SO_4plant	H_2SO_4	500	Sale
	Calomel		
	Acid sludge		
Water treatment	Sludge		
QSL process			
Smelter	Slag	440	Road construction
	Flue dust	60	Return to smelter
			After Cd-leach
	Steam	1300	Energy conversion
H_2SO_4 plant	H_2SO_4	720	Sale
	Calomel	0.02 - 0.05	Sale
	Acid sludge	0.5	Return to smelter
Cd-plant	CdZn-precipitate	1.1	Sale
Water treatment	Sludge		Return to smelter
ISA Smelt/Ausmelt furnace			
Smelter	Prim. Slag	600	Return to smelter*
	Final slag	275	
	Flue dust	250	Return to smelter or to leaching plant
	Drosses	125	Return to smelter*
	ZnO-dust	50	To zinc-smelter
	Steam		Energy conversion
H_2SO_4-plant	H_2SO_4	350	Sale
	Acid sludge	< 1	Return to smelter
	Hg-precipitate	0.2	Calomel-production
Dust leaching	CdZn-precipitate	1.1	To zinc-smelter
	Lead residue	40	Return to smelter
Water treatment	Sludge	< 5	Return to smelter

Note. * Special campaigns for slag reduction.

Table 5.30: Residues from direct smelting lead processes
[tm 120, TU Aachen 1999]

5.3 Techniques to Consider in the Determination of BAT

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2 “common processes” apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

The control of furnace operating parameters and the prevention of fugitive emissions from furnaces and the tapping and pouring processes is also important. Techniques used by other sectors are also applicable particularly those relating to the use of sulphur recovery systems.

The techniques to consider on a site by site basis are strongly influenced by the raw materials that are available to a site, in particular the type and variability of the concentrate or secondary raw materials, the metals they contain can be crucial to the choice of process. Some processes have a dedicated single source of raw material but the majority of installations in Europe buy concentrate on the open market and need to maintain flexibility in processing a range of raw materials. In a similar manner the standard of collection and abatement systems used worldwide in the industry reflects local, regional and long-range environmental quality standards and direct comparison of the environmental performance of process combinations is therefore difficult. It is possible however, to judge how a particular process can perform with the appropriate, modern abatement equipment.

The processes described above are applied to a wide range of raw materials of varying quantity and composition and are also representative of those used worldwide. The techniques have been developed by the Companies in this sector to take account of this variation. The choice of pyro-metallurgical or hydrometallurgical technique is driven by the raw materials used, their quantity, the impurities present, the product made and the cost of the recycling and purification operation [tm 120 TU Aachen 1999]. These factors are therefore site specific. The basic recovery processes outlined above therefore constitute techniques to consider for the recovery processes when used with appropriate abatement stages. The techniques to consider for collection and abatement stages and other aspects of process operation and control are covered in section 2.6, 2.7 and 2.8.

5.3.1 Materials storage, handling and pre-treatment processes

The raw materials are concentrates, secondary raw materials, fluxes and fuel, other important materials are products, sulphuric acid, slags, sludges and process residues. Important aspects are the prevention of leakage of dust and wet material, the collection and treatment of dust and liquids and the control of the input and operating parameters of the handling and feeding processes. The issues specific to this group are: -

The potentially dusty nature of concentrates and fluxes means that enclosed storage, handling and treatment systems may be needed in these instances. The dust generated by some crushing operations means that collection and abatement may be applicable for this process. Similarly granulation water may require settlement or other treatment prior to discharge

Concentrates are mixed with fluxes to produce a fairly constant feed therefore the general practice is sampling and analysis to characterise the concentrates and store individual concentrates separately so that an optimum blend can be prepared for smelting.

Feed blends can be prepared from dosing bin systems using belt weighers or loss in weight systems. Final mixing and homogenisation can take place in mixers, pelletisers or in the conveying and metering systems. Enclosed conveyors or pneumatic transfer systems are used for dusty material. Hot gas rotary dryers or steam coil dryers can be used if the process requires a dry feed, steam coil dryers use waste heat from other parts of the process provided that the heat balance allows it. The drier and associated dust abatement stage therefore depends on site-specific conditions such as the reliability of the steam supply. Fabric or ceramic filters achieve better dust removal efficiencies than EPs when used at this stage of the process.

Acid produced during the process can be stored in double walled tanks or tanks placed in chemically resistant bunds. The treatment of acid slimes from the sulphuric acid plant and weak acid from scrubbing systems depends on local processing or disposal requirements unless there is a local use for the material.

Sludges and other metallic residues that are destined for recovery off site can be stored drums or other suitable ways depending on the material. Sludges produced during the process that are destined for on site disposal should be washed free of zinc or other metals and de-watered as far as possible. Disposal facilities should be totally contained and leak proof, they are subject to local control and regulation. Water from the sludge containment areas can be returned to the process.

There are a variety of secondary raw materials used and they range from fine dusts to large single items. The metal content varies for each type of material and so does the content of other metals and contaminants. Batteries are a common source of lead and can contain acid, the storage and handling therefore needs to take account of the acid content and any acid mists that can be formed. Nickel cadmium batteries are usually dry but other batteries may be present and leakage of electrolyte is possible, this should be taken into account in the storage and separation method used. The techniques used for storage, handling and pre-treatment will therefore vary according to the material size and the extent of any contamination. These factors vary from site to site and the techniques discussed in section 2.4 will be applied on a site and material specific basis. The following issues apply to this group of metals.

- The storage of raw materials depends on the nature of the material described above. The storage of fine dusts in enclosed buildings or in sealed packaging is used. Secondary raw materials that contain water-soluble components are stored under cover. The storage of non-dusty, non soluble material (except batteries) in open stockpiles and large items individually in the open can be used.

- Pre-treatment stages are often used to produce sinter or to remove casings or coatings and to separate other metals. Milling and grinding techniques are used with good dust extraction and abatement. The fine dust that is produced may be treated to recover other metals, pneumatic or other density separation techniques are used.

- Fine dusts can be stored and handled in a manner that prevents the emission of dust. They are often blended and agglomerated to provide a consistent feed to the furnace.

Material	Storage	Handling	Pre-treatment	Comment
Primary Raw Materials.				
Coal or Coke.	Covered Bays, Silos.	Covered conveyors if non-dusty. Pneumatic.		
Fuel and other oils.	Tanks or drums in bunded areas.	Secure pipeline or manual system.		
Fluxes.	Enclosed (Silo)	Enclosed conveyors with dust collection. Pneumatic.	Blending with concentrates or other material.	
Concentrates.	Enclosed	Enclosed with dust collection. Closed conveyor or pneumatic.	Blending using conveyors. Drying or sintering	
Secondary Materials.				
Fine Dust	Enclosed or drummed.	Closed conveyor or pneumatic.		EAF dust
Coarse dust (raw material or granulated slag)	Covered Bays	Mechanical loader.		Oil collection if necessary
Lump (raw material or slag).	Open	Mechanical loader.		Oil collection if necessary
Whole Items	Open or Covered Bays	Mechanical loader.		Oil collection if necessary
Batteries - Lead Acid - Ni/Cd	 Covered storage Sealed drums or containers	 Mechanical loader and conveyor. Mechanical loader and conveyor.	 Crushing or whole feed. Plastic removal and pyrolysis	 Acid collection. Reuse if possible. Separation of Fe and Ni
Products and Residues.				
Acids: - Waste acid Product Acid	 Acid resistant tanks. Acid resistant tanks.		 Use in process or neutralisation. Sale	
Products -Cathodes, ingots and sows. - Dust	 Covered concrete area. Drums or bags.	 Mechanical loader		
Process residues for recovery.	Covered or enclosed depending on dust formation.	Depends on conditions.		Appropriate drainage system. Potential of Sb and As to hydrolyse.
Wastes for Disposal.	Covered or enclosed bays or sealed (drums) depending on the material.	Depends on conditions.		Appropriate drainage system.

Table 5.31: Storage, handling and pre-treatment methods for lead, zinc and cadmium

- Sintering is used to prepare concentrates for some of the smelting processes up draft and down draft sintering machines can be used and recent developments of a steel belt sintering process may be appropriate. Collection of fume and gases is important and the up draft sintering process is inherently easier for fume capture. Gases contain sulphur dioxide and will have abatement and sulphur dioxide recovery processes down stream. The sulphur dioxide content is usually low and variable and this influences the design of the sulphuric acid plant.

- Zinc concentrates are roasted prior to hydro metallurgical processing. Fluidised bed roasters are almost universally used and need good extraction and calcine removal systems. Gases are treated in an integrated abatement and sulphur dioxide recovery processes.

5.3.2 Primary lead smelting processes

The lead smelting processes to consider are [tm 120 TU Aachen 1999]: -

- For mixed lead and zinc concentrates after sintering - the Imperial smelting furnace incorporating a splash condenser and New Jersey distillation column for zinc and cadmium purification and separation. Sintering stages should have good gas collection.
- For lead concentrates and some secondary raw materials - the blast furnace and the electric furnace after sintering or roasting or smelting of the concentrates. The direct smelting processes that use the Kaldo, ISA Smelt/Ausmelt, QSL or Kivcet processes.
- For mixed copper and lead concentrates - the electric furnace after roasting the concentrate in a fluidised bed roaster.

Furnace	Gas Collection	Advantages	Disadvantages	Comments
Blast Furnace 110000 t/a Pb	Semi-sealed	Robust metallurgical performance	Older technology – needs modern process control	Double bell seal in feed hopper or cold top operation
Imperial Smelting Furnace 100000 t/a Zn 40000 t/a Pb	Sealed	Robust metallurgical performance. Use of LCV gas.	Older technology – needs modern process control	Double bell seal in feed hopper
ISA Smelt/Ausmelt 90000 t/a Pb	Sealed or Semi-sealed	Primary and secondary raw materials	Slag reduction stage not commissioned	High SO_2 in off gas. Mixed Cu/Pb.
QSL 90000 t/a Pb	Sealed	Primary and secondary raw materials. Process is now reliable.	Frequent tuyere replacement	Integrated process with energy recovery. High SO_2 in off gas.
Kivcet 90000 t/a Pb	Sealed	Primary and secondary raw materials. Process reliability not reported.	High lead content of slag	Integrated process with energy recovery. High SO_2 in off gas.
Kaldo Furnace 65000 t/a Pb	Enclosed	Primary and secondary raw materials	Expensive	Mixed Cu/Pb materials.

Table 5.32: Overview of primary lead smelters

The abatement system to consider for primary smelting processes is dust removal and the removal of other metals followed by the recovery of sulphur dioxide. This is usually achieved by conversion to sulphuric acid in a double contact process with four or more passes, sometimes a caesium-doped catalyst is used. Conversion of part of the SO_2 into liquid SO_2 can be practised, with the balance being converted into sulphuric acid. The use of a single contact plant or WSA process is a technique to consider for weak sulphur dioxide gas streams.

The gases are cooled (with heat/energy recovery) and cleaned before conversion. A combination of coolers and hot electrostatic precipitators or a combination of scrubbers (radial or jet) and wet EPs are used. Mercury recovery systems are employed using the techniques discussed in section 2.8.

Steel belt, up-draught or fully enclosed down-draft sintering processes are techniques to be considered. Steel belt sintering has several advantages for certain metal groups and can minimise gas volumes, reduce fugitive emissions and recover heat.

5.3.3 Secondary lead smelters

The range of secondary materials and the variation in metal content and degree of contamination has lead to the development of a range of smelters for secondary materials. The blast furnace, the ISA Smelt furnace, the TBRC, the electric furnace and the rotary furnace are used for a wide range of materials [tm 120 TU Aachen 1999]. The furnaces mentioned above are techniques to consider in the determination of BAT.

Several of the techniques described in section 2.6, 2.7 and 2.8 are applicable to fume extraction and abatement and the process control systems used by these furnaces. These techniques are not routinely used by all installations at the time of writing. The process control system for some blast furnaces is considered to be suitable for development.

Gases from secondary smelters contain some sulphur dioxide dependent on the source of the material. In particular the desulphurisation of battery paste may be needed unless paste is treated separately in a primary smelter or the sulphur can be fixed in a lead/iron matte or in the slag using a sodium based flux or other fluxes that can perform the same function. If the sulphur is not fixed a scrubber system may be needed. The gases can contain significant quantities of the more volatile metals such as antimony and cadmium etc. The abatement stages for secondary smelting involves gas cooling (with heat/energy recovery), coarse particle separation if necessary and fabric filtration. Sulphur dioxide removal and after-burning may be needed depending on the composition of the furnace gases (e.g. VOCs and dioxins). The collected dusts are recycled to recover metals.

In several instances there may be significant concentrations of organic material (including dioxins) depending on the raw material used. For example EAF dust will have a high dioxin content and whole battery feed (or incomplete separation) will provide a significant load of organic carbon and chlorinated plastic material. After burning or carbon adsorption and high efficiency dust removal may be needed in these cases.

EXAMPLE 5.01 USE OF AN AFTERBURNER

Description: - Use of afterburner, cooling system and fabric filter to remove VOC, metals and dust from a furnace off gas. The example used is part of a lead acid battery recovery system that uses the pyrolysis products of the plastic content as fuel in the afterburner. The abatement system incorporates an afterburner to destroy VOCs.

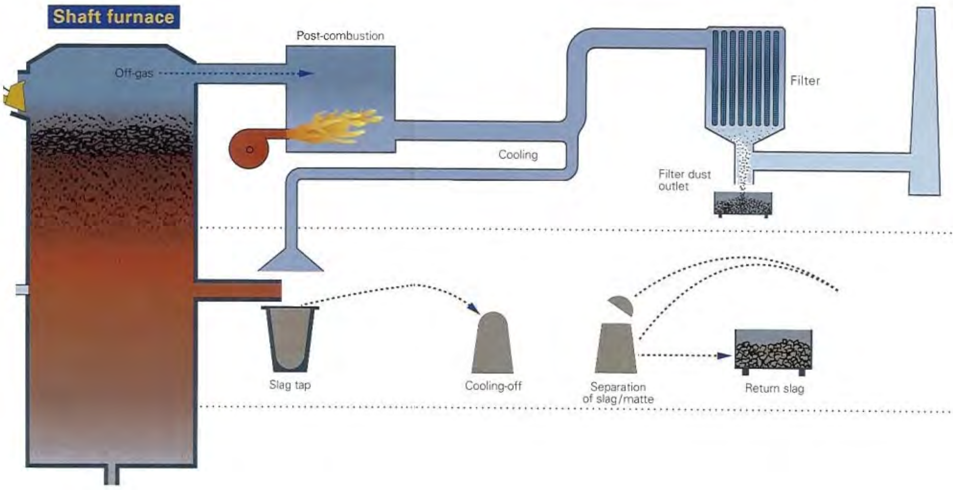


Figure 5.10: Afterburner system used with a whole battery smelter

Main environmental benefits: - Destruction VOCs and recovery of energy from the off gases. Removal of dust and metals from the off gas allows the filter dust to be returned to the furnace.

Operational data: -

Substance in the off-gas (65000 m^3/h)	**Content**
Dust [mg/Nm^3]	< 1.0
Lead [mg/Nm^3]	< 0.5
Cadmium [mg/Nm^3]	< 0.05
Carbon$_{total}$ [mg/Nm^3]	< 10
Sulphur dioxide [mg/Nm^3]	< 500
Nitric oxide (NO_x as NO_2) [mg/Nm^3]	< 50
Carbon monoxide [mg/Nm^3]	< 50
Hydrogen chloride (HCl) [mg/Nm^3]	< 5
Hydrogen fluoride (HF) [mg/Nm^3]	< 0.5
PCDD/PCDF (Σ TE, NATO) [ng-TE/Nm^3]	< 0.1

Table 5.33: Performance data for after-burning

The off-gas amounts to 65000 Nm^3/h. Emissions as dust, carbon monoxide and sulphur dioxide are monitored continuously. Calcium hydroxide additive can be injected into the off-gas channel, to prevent sulphur dioxide emissions peaks. The fabric filter dust has a lead content of up to 65 wt-% and can be recycled back to the smelting furnace as input material after chlorine removal. In order to achieve this, the filter dust is treated externally in a hydrometallurgical process to produce lead carbonate. The lead carbonate is returned and fed as raw material to the shaft furnace.

Cross media effects: - Positive effect reducing emissions, use of organic content as fuel. Potentially negative by loss of plastic and energy cost of replacement.

Economics: - Not available but data for a similar system is in the annex on costs. Several plants are operating viably.

Applicability: - Most furnaces with high organic loading.

Example plants: - Germany, Belgium, and Sweden.

Reference literature: - [tm 102, DFIU Zn 1999, tm 120, TU Aachen 1999]

The following table gives an overview of the advantages and disadvantages of the secondary smelting furnaces for various materials.

Furnace	Gas Collection	Advantages	Disadvantages	Comments
Rotary furnace	Sealed during operation. Charging area hooded	Robust, well established.	Range of raw materials. Potential fugitive emissions.	Integral feeding and tapping zone. Oxygen enrichment
Ausmelt / ISA Smelt	Integral hooding, sealed charging system	High smelting rate. Wide range of raw materials	Still developing	Oxygen enrichment
Blast furnace	Sealed via double bell or door.	Robust process. Wide range of raw materials.	Process control systems need development	Afterburner for organic material and CO
Electric furnace	Sealed	Low gas volume.	Some feed restrictions.	Afterburner for organic material and CO
TBRC	Enclosed system	Compact, high smelting rate. Rotation gives high reaction rate.	Expensive	Oxygen enrichment
Note. In all cases abatement systems need to take account of the raw materials and their pre-treatment. After-burning, sulphur dioxide removal, gas cooling and dust removal (fabric filter) will be used in various combinations depending on the pre-treatment applied.				

Table 5.34: Overview of secondary smelting furnaces

The comparison of battery processing techniques has been made to assess the main process types. There is a balance between the recovery of polypropylene from the cases and the use of the plastic content as a fuel in the process. The most obvious comment is that the energy content of the battery case needs to be compared to the energy cost of making the plastic and moulding it. There are however local effects such as the existence of a local outlet for PE and other plastics and potential local uses of acid and heat and long range factors such as the potential effects of sulphur dioxide. These factors must be assessed on a site-specific basis.

The other factor that needs to be determined at a local level is the desulphurisation of battery paste, the potential for sulphur fixing in Pb/Fe matte or in the slag and the possible facilities for smelting battery paste in another installation. White slag produced by the use of soda based fluxes may not be suitable for disposal locally. Other fluxes are available to fix the sulphur in the slag and avoid soluble components but the details are not available at the time of writing.

5.3.4 Slag treatment

Slag fuming and slag reduction stages that were discussed earlier as available techniques are the techniques to consider in the determination of BAT. The specific feed materials will influence the final process choice. The techniques discussed in section 2..8 that are appropriate to the process are also techniques to consider.

5.3.5 Refining of lead

The processes that were discussed earlier as available techniques are all techniques to consider in the determination of BAT. The specific content of other metals will influence the final process choice. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes in particular temperature control of the kettles and fume collection and abatement systems. Refining kettles are not considered suitable for melting scrap lead that is contaminated with organic materials.

5.3.6 Primary zinc

The New Jersey Distillation column is a technique to consider for the pyro-metallurgical production of primary zinc used in conjunction with the ISF for mixed lead and zinc concentrates.

Furnace	Gas Collection	Advantages	Disadvantages	Comments
Zinc electro-winning. 105000 – 235000 t/a Zn	Sealed roaster	Proven performance	Iron precipitate	
Imperial Smelting Furnace 100000 t/a Zn 40000 t/a Pb	Sealed	Robust metallurgical performance		LCV gas usage
New Jersey Distillation Column 20000 to 100000 t/a Zn	Sealed	Integrated with ISF for zinc production Proven performance	Blockage problems	Process control and vibration detection needed

Table 5.35: Overview of primary zinc smelters

The hydrometallurgical processes are very important in the production of zinc. The processes that were discussed earlier as available techniques are all techniques to consider in the determination of BAT [tm 120 TU Aachen 1999]. The specific feed materials will influence the final process choice. As reported earlier the Goethite process relies on a low iron content of the calcine (or ZnO) used for precipitation while the Jarosite process is able to give good zinc recoveries even with a high iron content (up to 10%) [tm 139, Finland Zn 1999). In both cases effective washing of the precipitated iron is needed. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes.

Because the hydrometallurgical processes involve leaching and electrolytic stages adequate disposal of leached material and electrolyte bleed needs to be considered. The connection of reactors and filters to suitable scrubbers or de-misters should be considered to prevent the emission of aerosols. The techniques discussed in section 2.9 to prevent emissions to water for example by containing drainage systems are relevant. Techniques to render the Jarosite or Goethite residues inert should be used if possible.

5.3.6.1 Chemical refining

The processes that were discussed earlier as available techniques are all techniques to consider in the determination of BAT. The specific feed materials will influence the final process choice. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes for example the removal of arsine and stibine by scrubbing gases from the chemical treatment stages with an oxidising agent such as potassium permanganate.

5.3.6.2 Electro-winning

Electro-winning processes that feature optimised cell dimensions (spacing, number of cells etc), and use aluminium cathode blanks are techniques to be considered. Mechanised (and automatic) harvesting and stripping as well as more elaborate short circuit detection is also worth considering depending on the scale of the operation.

Electro-winning produces gases that are evolved at the anode and will produce an acid mist. This needs to be collected and removed, extraction and mist elimination are used and collected mist returned to the process. Scrubbing the collected gases does not allow reuse of the mist and contributes to wastewater. Cell coverings can be used to reduce the amount of mist formed. Organic or plastic bead layers can be used.

EXAMPLE 5.02 COLLECTION AND TREATMENT OF ELECTROLYTE MIST

Description: - Collection of cell gases or cell-room ventilation air so that they can be de-misted.

Main environmental benefits: **-** Removal of acid mist that would be other wise emitted to the local environment. Improvement in the workplace conditions.

Operational data: - Non available, subjective comparison with un-modified plant shows a significant improvement inside and outside of the plant.

Cross media effects: - Positive effect, by recovering acid that can be returned to the process. Energy cost of fans.

Economics: - Not assessed but is economically viable in a number of installations.

Applicability:- All electro-winning processes.

Example plants: - Spain.

Reference literature:**-** [tm 106, Farrell 1998]

Electrolyte cooling should be practised and the heat recovered if possible. De misting of the cooling air should be carried out.

The processes and the techniques for control, mist collection and acid gas removal are suitable for use with new and existing installations.

Sealed tank house drainage systems, the recovery of electrolyte bleed are also techniques to be considered.

5.3.7 Secondary zinc

The processes that were discussed earlier as available techniques are all techniques to consider in the determination of BAT. The specific feed materials will influence the final process choice. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes.

5.3.7.1 Waelz Kilns and slag fuming furnaces

The processes that were discussed earlier as available techniques are all techniques to consider in the determination of BAT.

EXAMPLE 5.03 WASHING OF WAELZ OXIDE

Description: - Waelz oxide can also be leached in a two-stage process using sodium carbonate in the first stage and water in the second stage to remove chloride, fluoride, sodium, potassium and sulphur. The purified final product is dried and can be used as the feed material for the zinc electrolysis process.

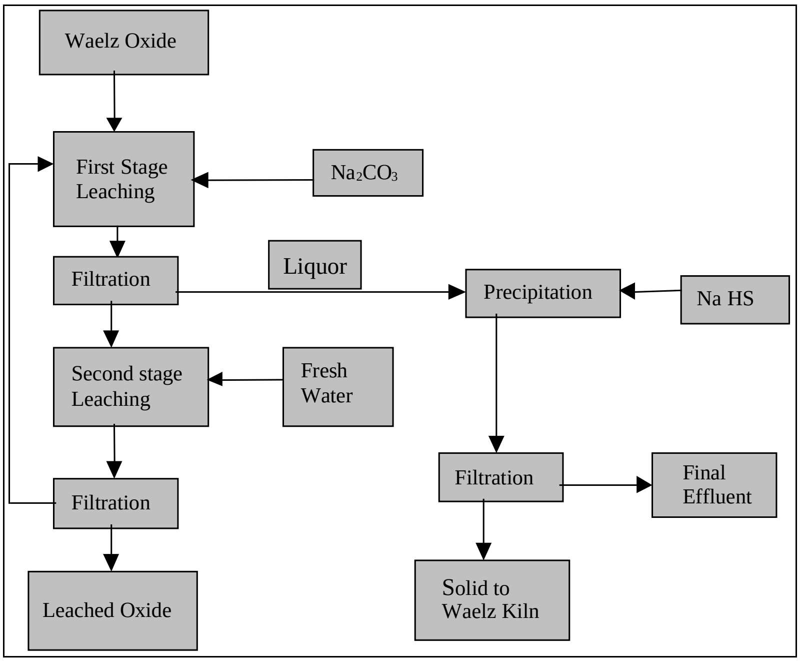


Figure 5.11: Diagram of a Waelz oxide washing circuit

Main environmental benefits: - Positive overall - Fixation of impurities in the furnace slag or in the effluent treatment sludge. Energy cost of process.

Operational data:

Component	Unwashed Waelz oxide	Washed Waelz oxide
Zn%	55 - 60	60 - 68
Pb%	7 - 10	8 - 11
S%	0.5 - 1	< 0.15
F%	0.2 - 0.5	< 0.15
Cl%	4 - 8	< 0.15
K_2O%	1 - 3	< 0.15

Table 5.36: Effect of washing

Component	Waste water after treatment with NaHS
Zn mg/l	0.1 - 0.2
Pb mg/l	0.05 - 0.15
Cd mg/l	0.01 - 0.15

Table 5.37: Wastewater from the washing process

Cross media effects: - Positive by simplifying the use of Waelz oxide in a leach/electrolysis stage.

Economics: - Not assessed but process is in use and is economically viable.

Applicability: - Most Waelz kilns.

Example plants: - Spain, Germany.

Reference literature: - [tm 95, Borja Garcia-Egocheaga 1998]

The techniques discussed in Chapter 2 should also be considered in conjunction with these processes in particular the techniques to prevent the formation of and destroy dioxins.

The processes and the techniques for Waelz oxide leaching are suitable for use with new and existing installations.

5.3.8 Cadmium and other metals

The processes that were discussed earlier as available techniques are all techniques to consider in the determination of BAT. The specific feed materials will influence the final process choice and thallium separation practised if necessary. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes. VOCs and odours may also be present during solvent extraction processes used for the production of Ga, Ge etc.

5.3.9 Fume/gas collection and abatement

The techniques discussed in section 2.7 and 2.8 of this document for the removal of SO_2, VOCs, dioxins and dust are techniques to consider for the various process stages involved in the production of the metals in this group. The use of secondary hoods is also a technique to consider. The design of the hooding system needs to take account of access for charging and other furnace operations and the way the source of process gases change during the process cycle. This can be achieved by the use of a system of intelligent control to target fume emissions automatically as they occur during the cycle without the high-energy penalty of continuous operation.

The use of hoods for tapping and casting is also a technique to consider. Tapping fumes will consist mainly of oxides of the metals that are involved in the smelting process. The design of the hooding system needs to take account of access for charging and other furnace operations and the way the source of process gases change during the process cycle. An example of a co-incident hood for charging and tapping is shown below.

EXAMPLE 5.04 COLLECTION OF FUME

Description: - Co-incident charging and tapping zone for a rotary furnace.

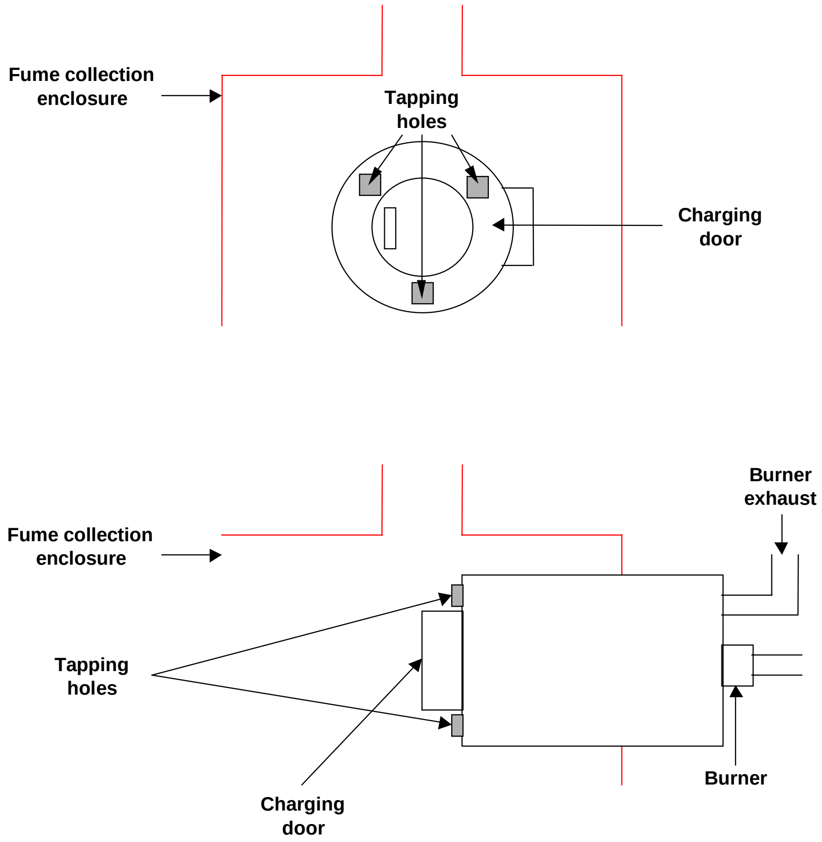


Figure 5.12: Co-incident fume collection system

Furnace lining wear may mean that door end tapping holes may not allow all of the metal to be tapped.

Main environmental benefits: **-** Easier fume collection from a single point.

Operational data: - Non available.

Cross media effects: - Positive effect - good collection efficiency with reduced power consumption.

Economics: - Low cost of modification. Several examples are operating viably.

Applicability: - All rotary furnaces.

Example plants: - France, UK, Germany

Reference literature: **-** [tm 106, Farrell, 1998; tm 120, TU Aachen 1999]

There are several site-specific issues that will apply and some of these are discussed earlier in this chapter. The process technologies discussed in this chapter, combined with suitable abatement are capable of meeting the demands of stringent environmental protection.

Reagent Used.	Component in off - gas.	Treatment Method.
Solvents, VOCs, (for In, Ga etc)	VOC	Condensation. Activated carbon, Bio-filter
Chlorine, HCl (for In, Ga etc)	Cl_2	Collection. Caustic scrubber system
Nitric Acid (for In, Ga etc)	NO_x	Oxidise and absorb, recycle, scrubber system
Ammonia (for In, Ga etc)	NH_3	Recovery, scrubber system
Antimony or arsenic oxides	Stibine or arsine	Oxidise and absorb in a scrubber system

Table 5.38: Chemical treatment methods for gaseous components

5.3.10 Sulphuric acid plants

The sulphur dioxide produced during the smelting, sintering and roasting stages can have a severe environmental impact and is removed from the gases in either a sulphuric acid plant or by recovery as sulphur dioxide. The various processes used for sulphur dioxide removal are described in section 2.8 of this document and need to be assessed in relation to the sulphur dioxide concentration produced by the sintering, roasting or smelting stage. The process used also depends on local markets for liquid sulphur dioxide, generally conversion to sulphuric acid is used. There are several factors that affect the production of sulphuric acid and some are specific to this metal section. These are all techniques to consider in the determination of BAT.

The use of oxygen enrichment in some direct smelters results in a high sulphur dioxide content and although this is subsequently diluted to below 14% SO_2 for conversion, the gas volume reduction allows significant savings to be made in the size of ducts, blowers and abatement plant. The other factor that is present with high gas strength is the potential to use the excess heat present in the gas particularly after the catalysis stages, which are strongly exothermic. The subsequent dilution of the gas also ensures the presence of sufficient oxygen for the catalytic process.

The other factor affecting the sulphur dioxide content is the low and variable content of gases from some sinter plants. This variation of SO_2 content means that the design of the acid plant needs to take this into account in the scrubber and heat transfer stages and in the choice of catalyst. As reported earlier the choice of catalysts is now greater and caesium oxide doped catalysts may be capable of improving performance. With a low gas strength heat may need to be added to the gases to maintain the correct temperature in the catalyst passes.

The performance of a metallurgical acid plant is dependent on the performance of the gas cleaning section. If the cleaning system is not effective in removing impurities from the incoming gas, the performance of the contact section will deteriorate. Although the design of wet gas cleaning systems may differ widely, they have the following requirements and features in common:

- Solid contaminants must be removed, giving a final gas quality of < 1 mg dust/Nm^3 (optically clear).
- Sulphur trioxide content of the gas must be reduced to the level of 15 - 25 mg/Nm^3.
- Fluorides and chlorides must be removed to prevent damage to downstream tower brickwork and converter catalyst.
- The gas must be cooled to a temperature satisfying the acid plant water balance. The temperature is dependent on the SO_2 concentration of the gas and the concentration of the acid produced. A gas with 4 - 6% SO_2 requires cooling to temperatures below 30 °C while

a gas with an SO_2 content well above 10% can tolerate gas temperatures of approximately 35 - 40 °C, when producing 98.5% grade acid

The rate of conversion of sulphur dioxide to sulphur trioxide is generally reported for these processes and can be in the range 98.5 to 99.8% for the gases produced from various processes. There are however, several factors that affect the conversion rate and these must be taken into account at a local level. The factors are: -

- Input gas cleanliness to reduce poisoning of the catalyst.
- Input gas strength and consistency. Higher strength gases and more consistent SO_2 concentrations tend to enable higher conversion efficiencies to be achieved. This is due in part to the consistent inter-pass gas cooling that can be achieved when there are few variations in concentration.
- Choice of catalyst. Caesium oxide doped catalysts tend to increase conversion rates provided that the other factors are controlled to prevent poisoning. Routine catalyst changes may allow improvements to be made to the catalyst during maintenance but to be fully effective must be accompanied by improvements in other areas.
- Correct input gas temperature, oxygen content and water balance (see above).
- Effective adjustment of gas conditions, in particular the temperature, between the catalyst passes.

Conversion rates therefore vary with time and steady state values can be misleading however the following examples illustrate the performance that can be achieved by well designed plants operating with different input gas characteristics.

EXAMPLE 5.05 WET GAS SULPHURIC ACID (WSA) PROCESS FOR AN OFF-GAS WITH A LOW SO_2 CONTENT

Description: - The process is well suited for treating off-gases where the SO_2 content is low. Up to 99.3% of the SO_2 is converted catalytically into SO_3, which reacts with water in the gas forming gaseous sulphuric acid. The acid is condensed in a WSA condenser. The heat economy and low sensitivity to the water balance means that no extra sulphur burning is required. The catalyst used in the WSA technology is a potassium and sodium promoted vanadium catalyst in 10 and 20 mm extruded rings.

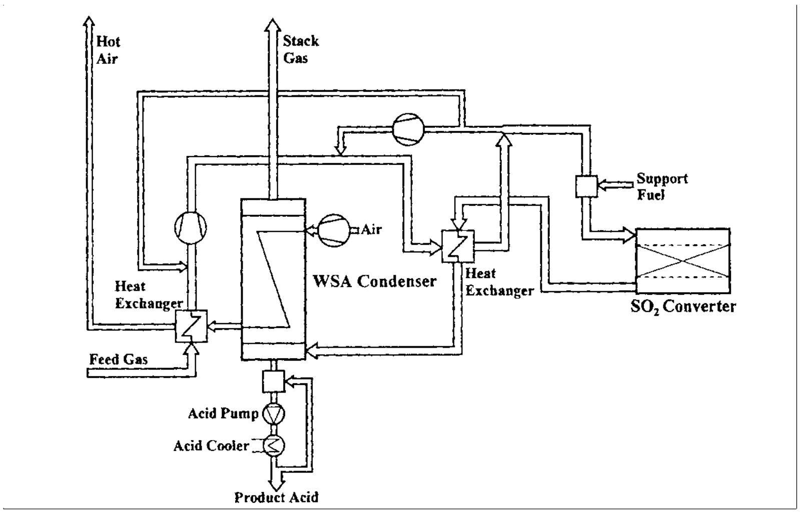


Figure 5.13: Diagram of WSA process

Main environmental benefits: - The conversion of SO_2 into sulphuric acid reduces the SO_2 emission and subsequently the effect of acid rain.

Operational data: - Typical performance data of a WSA plant is presented in the next table.

	Lead roasting
Flow Nm^3/h	100000
T_{inlet} °C	30 - 35
T_{outlet} °C	105
H_2O inlet, vol.%	5.5
O_2 inlet, vol.%	14.2
SO_2 content, vol.%	2.0 - 3.5
Conversion%	99
SO_3 in clean gas mg/Nm^3	< 28
H_2SO_4 product, wt%	> 97.5
Temp. of product °C	21
Acid production, MTPD	~290
Energy consumption (electricity & fuel) kWh/t	200 - 300 (at 2.7% SO_2)
Cooling water consumption Gcal/h/tonne acid	0.25 (ΔT = 5 °C)

Table 5.39: Performance of WSA system

Cross media effects: - The WSA process does not generate any waste products or wastewater and does not use any absorbents or other chemicals.

Economics: - Not available but several plants operate viably

Applicability: - The WSA process is applicable to all new and existing plants especially for molybdenite and lead rosters where the SO_2 content is lower than 5 - 6%.

Example plants: - France

Reference literature: - [tm/165, Bendixen, Haldor Topsøe, 1996],[tm/166, Bendixen, Haldor Topsøe, 1996], [tm/167, Bendixen, Haldor Topsøe, 1997], [tm/ SADACI 1999]

EXAMPLE 5.06 SULPHURIC ACID PLANT OPERATING UNDER VARYING GAS CONDITIONS.

Description: - Gas cleaning and washing section. Double contact sulphuric acid plant, 4 passes. Weak acid to neutralisation ~ 12 – 15 m^3/h with 5% H_2SO_4.

Main environmental benefits: - High conversion rate for sulphur dioxide More than 99.6% achieved with a recent installation.

Operational data:

Outlet conditions (measured values):		
Off-gas volume:	34200	Nm^3/h
SO_x	685	mg/Nm^3
SO_3	28	mg/Nm^3
NO_x (as NO_2)	114	mg/Nm^3
Cl^- (as HCl)	1.1	mg/Nm^3
F^- (as HF)	Not detectable	
Average concentration: -		
Cd	0.02	mg/Nm^3
Hg	not detectable	
Tl	not detectable	
As	< 0.05	mg/Nm^3
Se	not detectable	
Sb	not detectable	
Pb	0.17	mg/Nm^3
Cu	0.25	mg/Nm^3
PCDD/PCDF	not detectable	

Table 5.40: Performance of the sulphuric acid process

Cross media effects: - Positive effect – Reduction of main emissions of sulphur dioxide by conversion to sulphuric acid, recovery of the heat from the gases and evolved during conversion.

Economics: **-** Several plants are operating viably. See also appendix on cost

Applicability: - Off gases from roaster or smelter. These features can also be applied to most existing installations.

Example plants: - Germany

Reference literature: **-** [tm 102, DFIU Zn 1999]

The other factor that is important when high strength gases are used in a sulphuric acid plant is the residual SO_2 content in the exhaust gases. Most European plants operate with a conversion efficiency in the range 99.5 to 99.8%. The% conversion excludes the period during start up and shutdown operations and emergency events.

5.3.11 Process control

The principles of process control discussed in section 2.6 are applicable to the production processes used in this Group. Some of the furnaces and processes are capable of improvement by the adoption of many of these techniques. Particular attention is needed for the temperature measurement and control for furnaces and kettles used for melting the metals in this group so that fume formation is prevented or minimised.

The processes and the techniques for furnace control and melting temperature control are suitable for use with new and existing installations.

5.3.12 Wastewater

This is a site-specific issue, existing treatment systems are reported to be to a high standard. All wastewater should be treated to remove dissolved metals and solids in some cases a two stage precipitation process is used with a hydroxide stage followed by a sulphide stage to ensure the removal of lead and cadmium [tm 171, Steil & Hahre 1999]. The techniques listed in section 2.9 are the techniques to consider. In a number of installations cooling water and treated wastewater including rainwater is reused or recycled within the processes.

5.3.13 Process residues

The processes that were discussed earlier as available techniques are all techniques to consider in the determination of BAT. The specific feed materials will influence the final process choice. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes.

5.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector; which are for the production of lead and zinc are dust, metal fume, VOCs (including dioxins), odours, SO_2, other acid gases, VOCs, wastewater, residues such as sludge, filter dust and slag;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this chapter that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous section. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this section are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

Best Available Techniques are influenced by a number of factors and a methodology of examining the techniques is needed. The approach that has been used is given below.

First of all the choice of process depends strongly on the raw materials that are available to a particular site. The most significant factors are their composition, the presence of other included metals, their size distribution (including the potential to form dust) and the degree of contamination by organic material. There may be primary materials available from single or multiple sources, secondary raw materials of varying quality or a combination of primary and secondary raw materials.

Secondly the process should be suitable for use with the best gas collection and abatement systems that are available. The fume collection and abatement processes used will depend on the characteristics of the main processes, for example some processes avoid ladle transfers and are therefore easier to seal. Other processes may be able to treat recycled materials more easily and therefore reduce the wider environmental impact by preventing disposal.

Finally, the water and waste issues have been taken into account, in particular the minimisation of wastes and the potential to reuse residues and water within the process or by other processes. Energy used by the processes is also a factor that is taken into account in the choice of processes.

The choice of BAT in a general sense is therefore complicated and depends on the above factors. The varying requirements mean that BAT is influenced mainly by the raw materials available to the site and the required throughput of the plant, the issues are therefore site specific. There are advantages for some primary process that are capable of accepting some secondary materials.

The following points summarise the recommended methodology that has been used in this work: -

- Is the process industrially proven and reliable?
- Are there limitations in the feed material that can be processed? -e.g. In primary smelting some processes are suited for “simple” concentrate and others for complex feed smelting.
- The type of feed and other metals contained in it (e.g. Cu, Sb, Bi) influences process selection.
- Are there production level constraints? - e.g. a proven upper limit or a minimum throughput required to be economic.
- Can latest and efficient collection and abatement techniques be applied to the process?
- Can the process and abatement combinations achieve the lowest emission levels? The achievable emissions are reported later.
- Are there other aspects for example those related to safety?

At the time of writing several process and abatement combinations are able to operate to the highest environmental standards and meet the requirements of BAT. The processes vary in the throughput that can be achieved and the materials that can be used and so several combinations are included. All of the processes maximise the reuse of residues and minimise emissions to water. The economics of the processes vary. Some need to operate at a high throughput to achieve economic operation, while others are not able to achieve high throughputs.

The collection and abatement techniques used with these processes were discussed under techniques to consider in the determination of BAT and when applied in combination with the metallurgical process will result in a high level of environmental protection.

As indicated in the general preface to this document, this section proposes techniques and emissions that are considered to be compatible with BAT in general. The purpose is to provide general indications of the emission and consumption levels that might be considered as an appropriate benchmark of BAT based performance. This is done by quoting achievable levels in ranges that are generally applicable to both new and upgraded plants. Existing installations may have factors, such as space or height limitations that prevent full adoption of the techniques.

The level will also vary with time depending on the condition of the equipment, its maintenance and the process control of the abatement plant. The operation of the source process will also influence performance as there are likely to be variations in temperature, gas volume and even the characteristics of the material throughout a process or batch. The achievable emissions are therefore only a basis from which actual plant performance can be judged. Process dynamics and other site specific issues need to be taken into account at a local level.

5.4.1 Materials handling and storage

The conclusions drawn for Best Available Techniques for the materials handling and storage stages are shown in section 2.17 of this document and are applicable to the materials in this chapter.

5.4.2 Process selection

It is not possible to conclude that a single production process can be applied to this group of metals. The techniques for the following process stages are considered to be BAT for the raw materials that are available.

5.4.2.1 Primary lead smelting

Taking the methodology into consideration the following techniques, when used with appropriated collection and abatement techniques, are considered to be BAT for the production of lead.

Good gas collection and abatement systems and energy recovery applied to these processes offer advantages in energy efficiency, cost, throughput and ease of retrofitting.

Gases from the sintering, roasting and direct smelting processes should be treated to remove dust and volatile metals, to recover heat or energy and the sulphur dioxide recovered or converted to sulphuric acid depending on local markets for sulphur dioxide.

Applied Technique	Raw Materials	Comments
Kaldo process TBRC (Totally enclosed).	Pb concentrate and secondary (most grades).	Dry feed, variable sulphur dioxide. Operated in a complex installation with other Cu smelters.
ISF and New Jersey Distillation	Zn/Pb Concentrates.	Sintered feed. Enclosed sintering stage needed.
QSL	Pb concentrate and secondary material.	Moist, pelletised feed
Kivcet furnace	Cu/Pb concentrate and secondary material.	Dry feed
Kaldo Furnace	Pb concentrate and secondary material.	Moist, pelletised feed
ISA Smelt Furnace	Pb concentrate and secondary material.	Moist, pelletised feed
Blast Furnace	Complex lead bearing primary and secondary materials	High performance process control, gas collection and abatement systems are needed. Enclosed sintering stage needed or combined with another furnace.

Table 5.41: Primary lead smelters considered as BAT

5.4.2.2 Secondary lead smelting

For the production of lead from secondary raw materials the variation in feed stock also has to be taken into account at a local level and this will influence the combination of furnaces and the associated collection and abatement systems that are used. The processes that are considered to be BAT are: - The blast furnace (with good process control), ISA Smelt/Ausmelt, the electric furnace and the rotary furnace.

The submerged arc electric furnace is used for mixed copper and lead materials. It is a sealed unit and is therefore inherently cleaner than the others, provided that the gas extraction system is adequately designed and sized. At the time of writing the electric furnace is used for secondary material containing sulphur and is connected to a sulphuric acid plant. The gas volume produced is reported to be lower than the other furnaces and the size of the abatement plant could therefore be smaller.

Applied Technique	Raw Materials	Comments
Sealed submerged arc electric furnace.	Cu / Pb materials	Sealed furnace, lower gas volumes.
ISA Smelt.	Secondary (most grades).	Slag treatment stage needs to be demonstrated.
Rotary furnace	Most secondary materials.	Batch process, can offer flexibility for various materials.
Blast furnace.	Whole batteries	High energy efficiency. Requires high performance control, afterburner abatement and monitoring of emissions.
Melting crucibles and kettles	Clean lead and clean scrap only	Temperature control of kettles is needed.

Table 5.42: Secondary lead smelters considered as BAT

5.4.2.3 Lead refining processes

The refining stages that are considered to be BAT are any of the techniques that are listed as applied techniques, the combination of refining processes will depend on the metals contained in the lead bullion.

Copper removal and separation as a sulphide dross. Arsenic, antimony and tin are removal by oxidation with a mixture of sodium nitrate and caustic soda, followed by mechanical skimming to remove the oxide dross. Air/oxygen can also be used. De-silvering by the Parkes process and zinc removal by vacuum distillation. Bismuth removal by treatment with a mixture of calcium and magnesium in the Kroll-Betterton process.

The processes would be used with efficient primary and if necessary, secondary fume collection systems. Temperature control of the refining kettles is particularly important to prevent lead fume and indirect heating is more effective in achieving this.

5.4.2.4 Primary zinc

The roasting and sulphur recovery systems and the hydro-metallurgical processes that were discussed earlier as techniques to consider are all considered being BAT. The specific feed materials that are available to the operator will influence the final process choice, particularly the way in which iron is precipitated. The appropriate techniques to monitor and remove arsine and stibine should also be considered in conjunction with these processes.

5.4.2.4.1 Electrolyte purification

The processes that were discussed earlier as techniques to consider are all considered being BAT. The specific feed materials will influence the final process choice. Particular attention should be paid to assessing the potential of arsine and stibine emissions during the electrolyte purification stages with the removal of arsine and stibine by scrubbing gases from the chemical treatment stages with an oxidising agent such as potassium permanganate.

5.4.2.5 Secondary zinc

The processes that were discussed earlier as techniques are all considered being BAT provided good process control, gas collection and abatement systems are used. The processes include

- Physical separation, melting and other high temperature treatment techniques followed by the removal of chlorides.

- The use of Waelz kilns, cyclone or converter type furnaces to raise the temperature to volatilise the metals and then form the oxides that are then recovered from the gases in a filtration stage.

The specific feed materials will influence the final process choice. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes in particular the control of furnace temperature and the fume collection and abatement systems.

5.4.2.6 Cadmium and other metals

The processes that were discussed earlier as techniques are all considered being BAT. The specific feed materials will influence the final process choice. The appropriate techniques discussed in Chapter 2 should also be considered in conjunction with these processes in particular the handling, storage, pre-treatment and fume collection and abatement systems. Because these metals and their compounds are particularly toxic, extra care should be taken with choice of process, control and abatement systems.

5.4.2.7 Other process stages

5.4.2.7.1 Electro winning

The processes that were discussed earlier as techniques to consider are all considered being BAT. The specific feed materials will influence the final process choice. The appropriate techniques discussed in Chapter 2 should also be considered in conjunction with these processes in particular the prevention and the collection and recovery of cell room mists.

Process Stage	Technique	Comments
Electro-winning	Permanent cathode, reduction of mist formation at the cell	Mist collection returns the acid to the process.
Slag fuming and waelz kiln.	Methods reported above capable of producing a product for direct use.	Energy recovery. Destruction of dioxins
Battery crushing	2 stage process to allow stage separation and minimise contamination of plastic fraction	Collection and re-use of battery acid. Collection of mists.

Table 5.43: Summary of other process stages considered as Best Available Techniques

5.4.2.8 Gas collection and abatement

The fume collection systems used can exploit furnace-sealing systems and be designed to maintain a suitable furnace depression that avoids leaks and fugitive emissions. Systems that maintain furnace sealing or hood deployment can be used. Examples are through hood additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems. An intelligent fume collection system capable of targeting the fume extraction to the source and duration of any fume will consume less energy.

Best Available Techniques for gas and fume treatment systems are those that use cooling and heat recovery if practical before a fabric filter except when carried out as part of the production of sulphuric acid and this is covered below. Fabric filters that use modern high performance materials in a well-constructed and maintained structure are applicable. They feature bag burst detection systems and on-line cleaning methods.

The sulphur recovery systems and the associated dust and metal recovery stages are those described in section 2.8 of this document, the production of sulphuric acid is most applicable technique unless a local market exists for sulphur dioxide. The gas cleaning stage that is used prior to the sulphuric acid plant will contain a combination of dry EPs, wet scrubbers, mercury removal and wet EPs. The factors that affect the processes in this section are described above under the section techniques to consider in the determination of BAT.

Slag granulation systems need a venturi scrubber or wet EP because of the high steam loading. The ISF process gases also need to use wet scrubbing so that the gases are cooled prior to use as a fuel.

Process Stage	Component In Off -gas	Abatement option
Raw Materials Handling	Dust and metals	Correct storage Dust collection and fabric filter
Raw Materials Pre-treatment (mechanical de-coating/stripping)	Dust and metals	Correct pre-treatment Gas collection and fabric filter
(thermal de-coating)	Organic material*	Process operation, after-burning, carbon injection and correct gas cooling.
Primary Roasting and Smelting. Sintering	Dust, metals and sulphur dioxide. Hg	Process operation, gas collection, gas cleaning (dry and wet EP etc), cooling and sulphuric acid plant.
ISF	CO, metal vapour	Wet scrubbing (to cool gas) prior to use as LCV gas.
Slag granulation	Steam, dust, H_2S, SO_2,	Wet ESP, scrubber
Secondary Smelting	Dust and metals	Process operation and gas collection, cooling and fabric filter.
	Organic material*	Process operation, after-burning, carbon injection and correct gas cooling.
	Sulphur dioxide**	Scrubbing if necessary.
Chemical refining	Mist and metals (As, Sb)	Process operation and gas collection with oxidising scrubber.
Solvent extraction	VOC and Odour	Containment, Condenser. Carbon or bio filter if necessary.
Electro-winning	Acid mists	Gas collection and scrubbing/ de-misting.
Thermal refining	Dust and metals	Process operation. Gas collection, cooling and fabric filter.
	Sulphur dioxide**	Scrubbing if necessary.
Melting, alloying, casting and dust production.	Dust and metals	Process operation. Gas collection cooling and fabric filter.
	Organic material*	Process operation, after-burning, carbon injection and correct gas cooling.
Slag fuming and Waelz kiln processes	Dust and metals	Process operation. Gas collection, cooling and fabric filter or wet EP if wet quenching is used.
	Organic material*	Process operation, after-burning, carbon injection or carbon injection and correct gas cooling.

Note. * Organic materials include VOC reported as total carbon (excluding CO), dioxins and CO, the exact content depends on the organic content of the raw materials used.** Sulphur dioxide may be present if sulphur containing raw materials (e.g. battery paste) or fuels are used and sulphur is not fixed in a slag or matte.

Table 5.44: Summary of abatement options for components in the off-gas

Fume collection systems follow the best practice outlined in techniques described in section 2.7. The abatement systems that are considered to be BAT for the components likely to found in the off gases are summarised in the following table. There may be variations in the raw materials that influences the range of components or the physical state of some components such as the size and physical properties of the dust produced, these should be assessed locally.

5.4.2.9 Emissions to air associated with the use of BAT

Emissions to air comprise the captured/abated emissions from the various sources, plus the fugitive or uncaptured emissions from these sources. Modern, well operated systems result in efficient removal of pollutants and the information at the time of writing indicates that that the fugitive emissions can be the largest contributor to the total emissions.

For all processes the total emissions to air are based on the emissions from:

- The materials handling and storage, drying, pelletising, sintering, roasting and smelting stages.
- Slag fuming and Waelz kiln processes.
- Chemical refining, thermal refining and electro-winning stages.
- Melting, alloying, distillation, casting etc stages.

Fugitive emissions can be highly significant and can be predicted from the process gas capture efficiency and by environmental monitoring (see section 2.7).

The following tables summarise the techniques and the associated emissions.

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Low SO_2 off-gas streams (~ 1 – 4%)	> 99.1	Single contact sulphuric acid plant or WSA, (tail gas SO_2 content depends on feed gas strength)	For low-grade SO_2 gases. Combined with dry or semi-dry scrubber to reduce SO_2 emission and produce gypsum if a market is available.
SO_2 – rich off-gas streams (> 5%)	> 99.7% conversion factor	Double contact sulphuric acid plant (Tail gas SO_2 content depends on feed gas strength). A de-mister may be appropriate for the final removal of SO_3	Very low levels for other air-borne pollutants will be reached due to intensive gas treatment prior to the contact plant (wet scrubbing, wet EP and, if necessary, mercury removal to ensure H_2SO_4 product quality

Note. Collected emissions only.
Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period.
For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.

Table 5.45: Emissions to air from primary smelting, roasting and sintering associated with the use of BAT in the lead and zinc sector

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Acid mists	< 50 mg/Nm³	De-mister Wet alkaline scrubber.	A de-mister will allow the collected acid to be reused.
Arsine, stibine	< 0.5 mg/Nm³	Oxidising scrubber	
VOC or solvents as C	< 5 mg/Nm^3	Containment, condenser, carbon or bio filter	
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 5.46: Emissions to air from chemical refining, electro-winning and solvent extraction

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 - 5 mg/Nm^3	Fabric filter (Temperature control of melting kettles or vessels is needed to prevent volatilisation of metals.)	High performance fabric filters can achieve low levels of heavy metals. The concentration of heavy metals is linked to the concentration of dust and content of the metals in the dust.
NO_x	< 100 mg/Nm^3 < 100 - 300 mg/Nm^3	Low NO_x burner. Oxy-fuel burner.	Higher values are associated with oxygen enrichment to reduce energy use. In these cases gas volume and mass emission is reduced.
Total organic carbon as C (if present)	< 5 - 15 mg/Nm^3 < 5 - 50 mg/Nm^3	Afterburner. Optimised combustion.	
Dioxins (if present)	< 0.1 - 0.5 ng TEQ/Nm^3	High efficiency dust removal system (i.e. fabric filter), afterburner followed by quenching. Other techniques are available (e.g. adsorption on activated carbon, oxidation catalyst).	Treatment of a clean de-dusted gas may be required to achieve low levels
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 5.47: Emissions to air from the melting of clean material, alloying and zinc dust production

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 - 5 mg/Nm^3	Fabric filter, wet EP. (A wet EP may be applicable to gases from slag granulation or wet gas quenching.)	High performance fabric filters can achieve low levels of heavy metals. The concentration of heavy metals is linked to the concentration of dust and content of the metals in the dust.
SO_2	< 50 - 200 mg/Nm³	Wet alkaline scrubber. Alkali semi-dry scrubber and fabric filter	
NO_x	< 100 mg/Nm^3 < 100 - 300 mg/Nm^3	Low NO_x burner. Oxy-fuel burner.	Higher values are associated with oxygen enrichment to reduce energy use. In these cases gas volume and mass emission is reduced.
CO and metal vapour	Not emitted	Wet scrubber	To cool and clean the gases of an ISF prior to use as a fuel.
Total organic carbon as C	< 5 - 15 mg/Nm^3 < 5 - 50 mg/Nm^3	Afterburner. Optimised combustion.	Pre-treatment of secondary material to remove organic coatings if necessary.
Dioxins	< 0.1 - 0.5 ng TEQ/Nm^3	High efficiency dust removal system (i.e. fabric filter), afterburner followed by quenching. Other techniques are available (e.g. adsorption on activated carbon, carbon/lime injection).	
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used. For SO_2 or total carbon removal, the variation in raw gas concentration during batch processes may affect the performance of the abatement system.			

Table 5.48: Emissions to air from materials pre-treatment, secondary smelting, thermal refining, melting, slag fuming and Waelz kiln operation

The metal content of the dust varies widely between processes. In addition for similar furnaces there are significant variations due to the use of varying raw materials. It is therefore not accurate to detail specific achievable concentrations for all metals emitted to air in this document.

Some metals have toxic compounds that may be emitted from the processes and so need to be reduced to meet specific local, regional or long-range air quality standards. It is considered that low concentrations of heavy metals are associated with the use of high performance, modern abatement systems such as a membrane fabric filter provided the operating temperature is correct and the characteristics of the gas and dust are taken into account in the design. The issue is site specific but the following table gives some indication of the effects on the content of metals in dust that will be encountered locally.

Component	Zinc FB Roaster	Zinc refining	ISF process	Lead direct smelting processes	Secondary lead processes	Lead refining
Pb%	0.2 – 2	0.15 – 0.86	10 – 15	30 – 50	20 - 55	14 – 83
Zn%	50 – 60	52 – 76	20 – 50	3 – 5	0.01 - 10	3 – 28
Sb%	n.a	n.a	n.a	–	0.1 - 40	n.a
Cd%	0.2	0.02 – 0.7	0.5	3 – 5	0.01 – 10	n.a
As%	0.004	0.01 - 0.1	n.a	5 - 10	0.01 - 3	n.a
n.a - Means not available						

Table 5.49: Metal content of some dusts from various lead and zinc production processes [tm 25, DFIU 1996]

5.4.3 Wastewater

This is a site-specific issue, existing treatment systems are reported to be to a high standard. The use of sulphide precipitation or combined hydroxide/sulphide precipitation is particularly relevant to metals in this section [tm 171, Steil/Hahre 1999]. All wastewater will be treated to remove metals, solids and oils/tars. Absorbed acid gases (e.g. sulphur dioxide, HCl) and should be reused or neutralised if necessary. The techniques listed in section 2.9 are the techniques to consider. In a number of installations cooling water and treated wastewater including rainwater is reused or recycled within the processes.

For primary and secondary production of the metals in this group, the total emissions to water are based on:

- The slag treatment or granulating system.
- The waste gas treatment system.
- The leaching and chemical purification system.
- The electro-winning process.
- The wastewater treatment system:
- Surface drainage.

The following table gives associated emissions to water after effluent treatment. The data given may not be transposable to all installations.

	Main components [mg/l]				
	Pb	**As**	**Hg**	**Cd**	**Zn**
Process water	<0.1	<0.05	<0.01	<0.05	<0.2
Note: The associated emissions to water are based on a qualified random sample or a 24-hour composite sample. The extent of wastewater treatment depends on the source and the metals contained in the wastewater.					

Table 5.50: Summary of associated emissions to water for some processes

5.4.4 Process residues

The use or recycling of slags, slimes and filter dusts is considered to be part of the processes. The iron precipitation method used (Goethite or Jarosite) depends on local conditions and the composition of the concentrate. The effective washing and precipitation of the leachable metals as sulphides before disposal should be considered. The solubility of the residue should be monitored using a standard leachate test. Disposal should meet the requirements set out in the directive on landfill.

The production processes in this sector have been developed by the industry to maximise the re-use of the majority of process residues from the production units or to produce residues in form that enables them to be used in other non-ferrous metal production processes. An overview of the potential end uses for residues is given earlier in this chapter and some specimen quantities are also given for specific installations.

The quantity of residues produced is strongly dependent on the raw materials in particular the iron content of primary materials, the content of other non-ferrous metals in primary and secondary materials and the presence of other contaminants such as organic materials. The emissions to land are therefore very site and material specific and depend on the factors discussed earlier. It is therefore not possible to produce a realistic, typical table of quantities that are associated with the use of BAT without detailing the raw material specification. The principles of BAT include waste prevention and minimisation and the re-use of residues whenever practical. The production of arsine and stibine from the action of water or water vapour on some residues should be taken into account.

The industry is particularly effective in these practices the use and treatment options for some residues from the production of lead and zinc is given in tables 5.29 to 5.30.

5.4.5 Costs associated with the techniques

Cost data has been compiled for a variety of process variations and abatement systems. The cost data is very site specific and depends on a number of factors but the ranges given may enable some comparisons to be made. The data is provided in an appendix to this note so that costs for processes and abatement systems over the whole of the non-ferrous metal industry can be compared.

5.5 Emerging Technologies

- Zinc concentrates from some newer mines and from proposed developments, provide both opportunities and challenges to the conventional smelters. These fine ground concentrates are often characterised by low iron, elevated silica, high manganese and levels of elements such as germanium, which may cause concern. New processing technology needed to cope with these changes includes: - de-watering and materials handling of ultra-fine concentrate, novel transport systems, siliceous leach circuits, manganese removal cells and front-end smelting [tm 101, NL Zn 1998]. These concentrates are not be available to all producers and the new technology required to treat them may produce other residues that are difficult to deal with.

- Environmental regulations for the disposal of the solid residues can form an incentive to change to the treatment of the iron residue by chemical fixation of the iron residue in the form of a cement (e.g. Jarofix) or other material such as the reaction of Goethite with iron slags (Gravelite). Both processes increase the amount of material produced and will only be effective if the materials are acceptable for civil engineering uses.

- Leaching processes based on chloride for zinc and lead recovery are reported as being at the demonstration stage [tm 206, TGI 1999].

- The thermal treatment of jarosite and goethite has been demonstrated using the Ausmelt and Outokumpu processes [tm 41, Ausmelt 1997; tm 101, NL Zn 1998]. Zinc and other volatile metals are fumed off and recovered, the slag produced could be suitable for construction processes. The processes have not been shown to be economically viable as a general residue treatment method.

- The processing of Jarosite and sewage sludge in an autoclave at 260 °C has been reported [tm 214, Vaartjes 1999]. Limited data is available and viability is not reported. The cellulose in the sewage sludge is the source of energy and the product is a molten material. Zinc, lead and silver are reported to be concentrated and sold and the stony product used for construction.

- The smelting of Jarosite and Goethite has also been demonstrated, but has not been proven to be economic.

- The injection of fine material via the tuyeres of a blast furnace has been successfully used and reduces the handling of dusty material and the energy involved in returning the fines to a sinter plant.

- Control parameters such as temperature are used for melting furnaces and kettles and reduce the amount of zinc and lead that can be fumed from a process.

- Furnace control systems from other sectors may be available for the blast furnace and ISF.

- The EZINEX process is based ammonia/ammonium chloride leaching followed by cementation and electrolysis. It was developed for the direct treatment of EAF dusts and one plant is operational. It may be used for richer secondary zinc feed [tm 120, TU Aachen 1999].

- The BSN process was commissioned in November 1998 and treats pelletised EAF dust by drying, and clinkering followed by the reduction, volatilisation and re-oxidation to produce ZnO. The process claims to produce no waste [tm 120, TU Aachen 1999].

- The Outokumpu Flash Smelting Furnace has been used on a demonstration basis for the production of lead by direct smelting. The use of Waelz kilns for this purpose has also been reported. The literature contains many other potential examples that have not yet been developed beyond the pilot scale.

6 PROCESSES TO PRODUCE PRECIOUS METALS

6.1 Applied Processes and Techniques

Precious metals can be conveniently placed into 3 groups; silver, gold and platinum group metals (PGM's). The most significant sources are precious metal ores, by-products obtained from the processing of other non-ferrous metals (in particular anode slimes from copper production, leach residues and crude metal from zinc and lead production) and recycled material. Many raw materials are subject to the Hazardous Waste Directive and this has an impact on the transport, handling and notification systems. Production processes are common for primary and secondary raw materials and they are therefore described together.

A variety of processes have been developed which exploit the chemical properties of these metals. Although they are relatively inert, their reactivity varies and the various oxidation states of the metal in their compounds allows a variety of separation techniques to be used [tm 5 & 19 HMIP PM 1993]. For example the tetroxides of ruthenium and osmium are volatile and can be separated easily by distillation. Many of the processes use very reactive reagents or produce toxic products, these factors are taken into account by the use of containment, fail safe systems and sealed drainage areas. This is further driven by the high value of the metals.

Many of the process are commercially confidential and outline descriptions only, are available. The processes are usually carried in various combinations to recover the precious metals that are present in a particular feedstock. The other feature of the industry is that generally, the precious metals are recovered on a toll basis, which can be independent of the metal value. Much of the processing is therefore designed to accurately sample and assay the material as well as recover it. Sampling is carried out after the material has been processed physically or from side streams during normal processing. There are over 200 types of raw materials available to the industry and they are normally characterised into five homogenisation types.

Homogenisation category	Type of raw material	Comment
Original	Catalysts, Prepared Sweeps, Solutions.	Direct to process
Sweeps	Mineral + metal, non-fusible carbon catalysts.	Incineration, roasting and pre-enrichment
Scrap	Fusible material.	
Material to be shredded	Film, electronic scrap.	
Materials for dissolution	Material that is dissolved in acid, CN, NaOH etc.	

Table 6.1: Homogenisation categories for sampling

The raw material characterisation is based on the most suitable entrance point into the processing flow sheet (fig 6.1) and is independent of the precious metals that the material contains. The raw materials are usually sampled according to this characterisation and it is reported that most companies use this scheme. The samples are subject to treatment to dissolve the precious metal content or produce a form capable of analysis. Some times this involves all or part of the actual recovery process and so abatement systems are used during the sampling process.

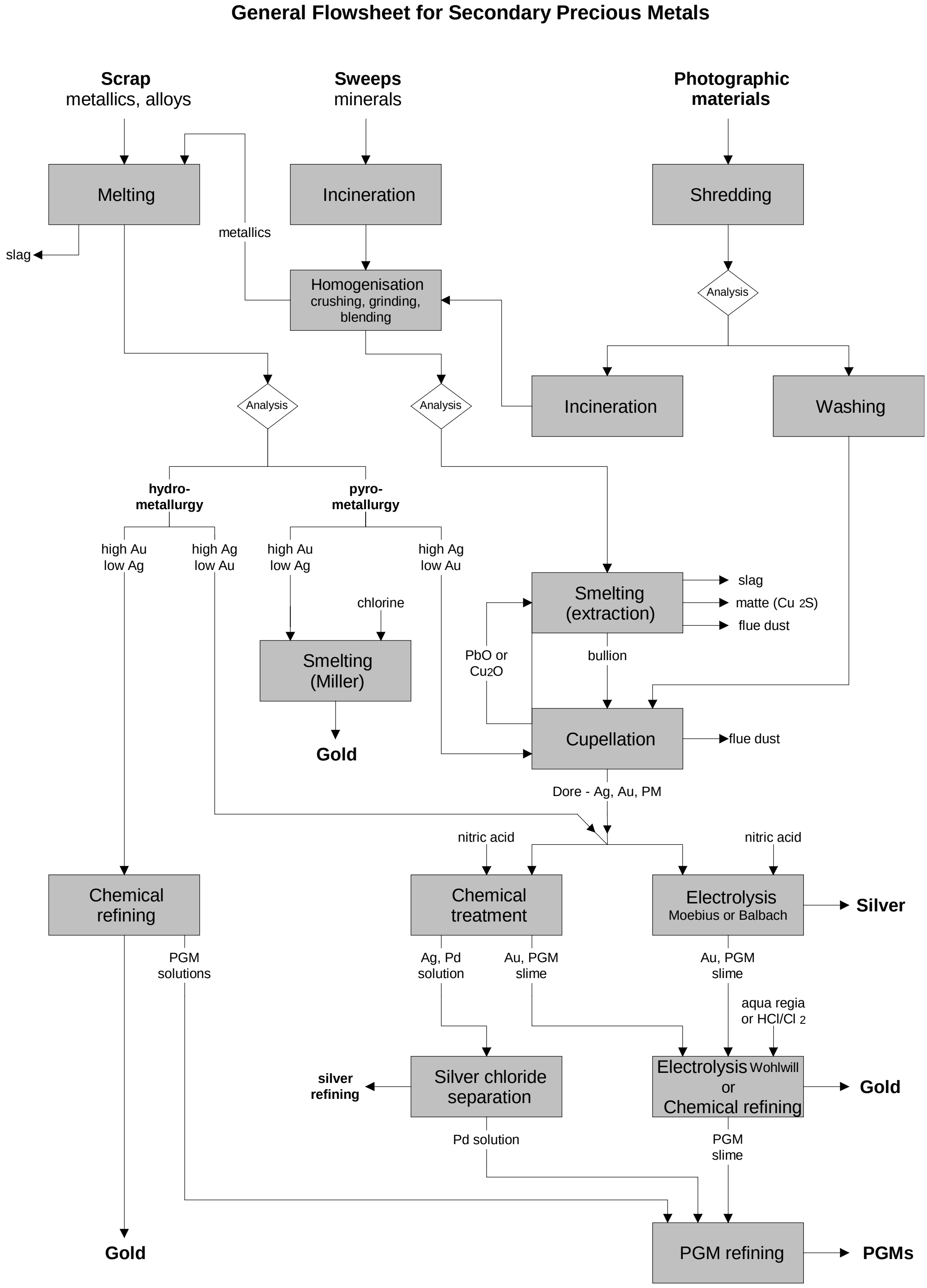


Figure 6.1: General flow-sheet for precious metal recovery

There is also a need to process these materials rapidly and this is reflected in the intentional over capacity of production in this sector. The extensive sampling and analysis also allows the optimum choice of process combinations to be made.

Anode slimes from electrolytic copper refining are a significant source of precious metals and they are treated to remove and recover the precious metals together with other metals such as selenium and tellurium. The process details depend on the proportion of metals that are present.

Pyro-metallurgical or hydro-metallurgical routes are used and solvent extraction stages are also incorporated in some cases. The following figure gives a general example.

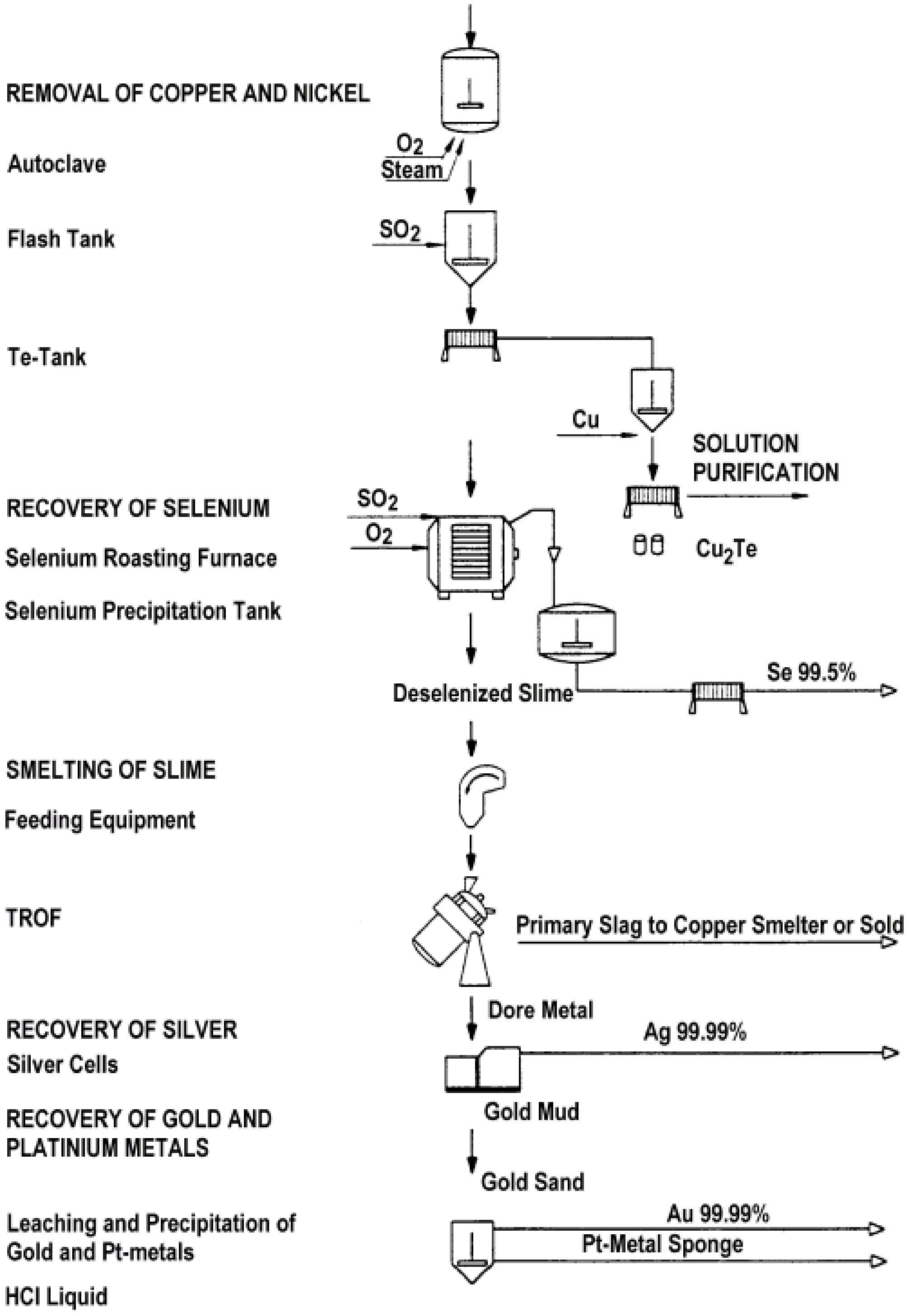


Figure 6.2: Example flow-sheet for anode slime treatment

6.1.1 Silver

The principal sources of silver are scrap (e.g. jewellery, coins and other alloys) concentrates, anode (or tank house) slimes, photographic films, papers and sludges, and ashes, sweeps, sludges and other residues [tm 5 & 19, HMIP PM 1993; tm 105, PM Expert Group 1998].

6.1.1.1 Photographic materials

Photographic film, papers and sludges are incinerated on a batch basis in single hearth furnaces, or on a continuous basis in rotary kilns, to produce a silver-rich ash. Smaller recyclers use box furnaces. The calorific value of the feed is such that fuel is only required during start-up. A fired afterburner, located in a separate chamber, is used to combust the partially burned products in the waste gas as well as filter and caustic scrubber systems. The ash is recovered and treated with other silver bearing material, the gases are filtered and the dust that is collected is also treated to recover silver.

A chemical stripping process in which the silver salts are leached from the emulsion layer is also used. This process treats waste photographic film with a thiosulphate solution that can also contain enzymes. The silver is recovered from the leach liquor by electro-winning and the depleted electrolyte is recycled to the leaching stage. The plastic backing of the photographic film can be recovered in theory but the feed material usually includes quantities of paper such as envelopes and this can inhibit recovery and results in a waste stream [tm 5, HMIP PM 1993].

Silver is recovered from waste solutions from the photographic and other industries by chemical precipitation as sulphide to form a powder which is dried, melted and refined. Alternatively silver thiosulphate solutions are electrolysed at 2 volts to produce silver sulphide, which is insoluble (in practice 5 - 10 ppm Ag in solution is achieved).

6.1.1.2 Ashes, sweeps etc

Ashes, sweeps, printed circuit boards, agglomerated fines, sludges and other materials containing copper and precious metals are blended and smelted in electric, blast, rotary, reverberatory furnaces or top blown rotary converters (TBRC). Lead or copper is used as a collector for the silver and other precious metals; electric power, coke, gas or oil are used as fuel and to generate a reducing atmosphere. In some cases selected plastic waste can be used as a fuel and appropriate after-burning is used to prevent the emission of organic compounds such as VOC and dioxin. Fluxes are added to collect the non-metallic components of the feed materials, which are removed as a slag. Periodically the furnace is run with a slag charge to recover any precious metals in the slag before it is granulated or cast prior to disposal, treatment for depletion or use.

The silver and other precious metals produced in the smelting furnace are collected into molten lead or copper. The lead alloy is transferred to a cupellation furnace where the lead is oxidised to litharge (lead oxide) using air or oxygen. The copper alloy is treated in a similar manner to produce copper oxide [tm 105, PM Expert Group 1998].

These precious metal bearing materials may also be treated in base metal smelters. The metals are then recovered from the lead, Cu or Ni process.

6.1.1.3 Recovery from base metal production

The electrolytic refining of copper anodes produces slimes whose composition is dependent on the feed materials and processes used in the copper smelter. Anode slimes generally contain significant quantities of silver, gold and PGMs and they are sold for their precious metals values [tm 47 to 52, Outokumpu 1997] or recovered at the site of the smelter [tm 92 Copper Expert Group 1999].

Treatment processes vary according to the composition of the slimes and an example is shown above in figure 6.2. The stages can include removal of copper and nickel (and a major portion of tellurium) by acid leaching (atmospheric or under pressure using O_2), roasting to remove selenium unless it has been removed by volatilisation during smelting. Smelting is the carried out with silica and sodium carbonate fluxes to produce Dore metal in reverberatory, electric, TBRC or BBOC furnaces. Dore (silver or gold) is metal that has been concentrated to a form containing more than 60% of the metal [tm 105, PM Expert Group 1998]. Hydro-metallurgy and solvent extraction stages are also used for the recovery of precious metals from anode slimes for example the Kennecott and Phelps Dodge processes.

In the hydrometallurgical production of zinc, the precious metals, if present, in the concentrate are enriched in the Pb/Ag leach residue, which can be processed further in a lead smelter. During lead smelting and refining the precious metals are concentrated in a Pb-Zn-Ag alloy.

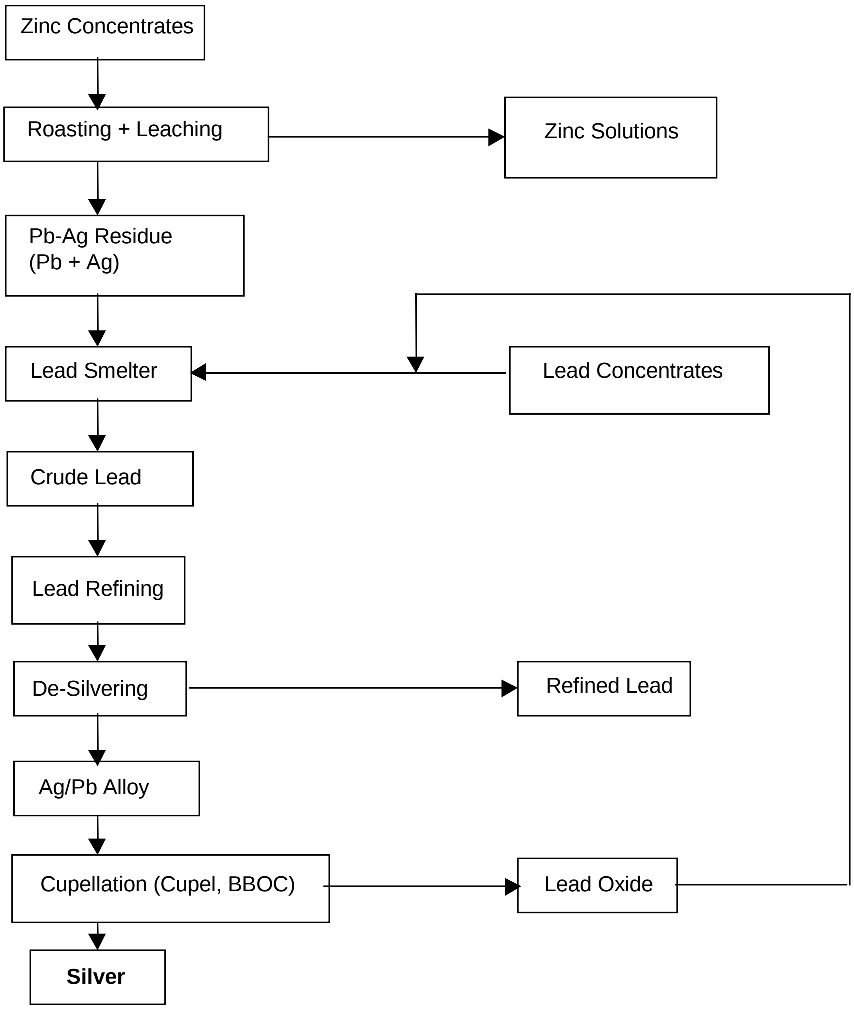


Figure 6.3: Recovery of silver from zinc and lead production

Further treatment can include the removal of the bulk of the lead and zinc by liquation and vacuum distillation and finally cupellation in a reverberatory furnace, TBRC, TROF, cupel or a bottom blown oxygen cupel (BBOC). Lead is oxidised to litharge (lead oxide) using air and oxygen. Some installations that operate copper and lead refineries combine the precious metal enriched phases from the lead and copper lines during the cupellation stage.

In the refining of nickel, the precious metals are recovered from the copper by-product. In the refining of zinc in a zinc-lead shaft furnace the precious metals may be recovered from the lead product. Gold and PGMs are also recovered from these materials, processes vary according to the amount of desired metals and other associated metals e.g. selenium.

6.1.1.4 Refining

The anodes are refined in Moebius or Balbach-Thum electrolytic cells using titanium or stainless steel cathodes in an acidified silver nitrate electrolyte. A direct current applied between the electrodes causes silver ions dissolved from the anode to migrate and deposit as crystals of silver on the cathodes. The crystals are continuously scraped off the cathodes, removed from the cells, filtered and washed. The slimes from the electrolytic cells are treated for their gold and platinum group metals content.

The silver crystals may be melted in a crucible furnace and batch cast into market ingots or grains for rolling down. They can be continuously cast into market bars for rolling down to sheet and strip. Silver is also cast into billet for extrusion into rod for subsequent drawing into wire.

Silver produced by smelting, and high-grade silver residues from manufacturing processes can be refined by dissolution in nitric acid. The resulting solution is purified either by re-crystallisation as silver nitrate suitable for use in the photographic industry or by electrolysis to fine silver for melting and casting into bullion bars.

6.1.2 Gold

The principal sources of gold are impure gold from mining operations, industrial, jewellery, sweeps and dental scrap. Gold is recovered along with silver from the anode slimes from copper electro-refining and other materials using processes described above. Scrap materials may contain significant proportions of zinc, copper and tin.

6.1.2.1 The Miller process

The Miller process can be used to pre-treat the material. In this process the feed materials are melted in an indirectly heated crucible or electric induction furnace while chlorine gas is injected into the melt. At the operating temperature of about 1000ºC, gold is the only metal present that does not react to form a stable molten or volatile chloride. Molten silver chloride rises to the surface of the melt. A borax flux is used to assist collection and skimming of the metal chlorides. Zinc in the feed is converted to zinc chloride which, together with volatile metal chlorides, is exhausted to a gas scrubbing system [tm 5, HMIP PM 1993; tm 105, PM Expert Group 1998].

The Miller process is operated to produce either 98% gold, which is cast into anodes for electro-refining, or 99.5% gold that is cast into bullion bar.

6.1.2.2 Electro-refining

Gold anodes are refined in Wohlwill cells containing gold foil or titanium cathodes. The electrolyte used is an acidic gold chloride solution maintained at about 70 °C. A d.c. electric current applied between the electrodes causes gold ions dissolved from the anodes to migrate and deposit on the cathodes yielding a product containing 99.99% gold.

6.1.2.3 Other processes

Gold is also recovered and refined by dissolving the feed materials in aqua regia or in hydrochloric acid/chlorine. This is followed by the precipitation of high purity gold suitable for melting and casting. Where the feed material contains significant quantities of metallic impurities, a solvent extraction step may be introduced before the gold precipitation stage. Solvent extraction processes and precipitation are also used to recover gold from liquors arising during the production of platinum.

Gold is also removed from solid and liquid cyanide solutions such as plating baths. Solutions of sodium or potassium cyanide can be used to remove gold from surface coated material such as electronic contacts or plated materials. Gold is recovered from the cyanide solutions by electrolysis. Cyanides react with acids to form HCN and therefore careful segregation of these materials is practised. Oxidising agents such as hydrogen peroxide or sodium hypochlorite as well as high temperature hydrolysis are used to destroy cyanides.

6.1.3 Platinum Group Metals

PGMs comprise platinum, palladium, rhodium, ruthenium, iridium and osmium. The principal raw materials are concentrates produced from ores, mattes and slimes from nickel and copper operations. Secondary materials such as spent chemical and auto exhaust catalysts, electronic and electrical component scrap are also significant sources. PGMs can be present in the anode slimes described above and are separated from the gold and silver by a variety of hydrometallurgical processes. Low-grade feedstock may be crushed and blended while metallic feed materials are generally melted to provide a homogeneous product for sampling.

The main stages in the recovery of PGMs are [tm 5 & 19, HMIP PM 1993; tm 105, PM Expert Group 1998]:

- Pre-treatment of the feedstock, sampling and assay;
- Dissolution, separation and purification of the PGMs e.g. by precipitation, liquid/liquid extraction or distillation of tetroxides;
- Recovery of platinum, palladium, rhodium and iridium by reduction (hydrogen), liquid/liquid extraction or electrolytic processes;
- Refining of PGMs for example by hydro-metallurgical techniques such as the use of ammonium-chloro compounds to produce pure metal sponge by pyrolysis.

Specific processes have been developed for carbon based catalysts, using incineration prior to the dissolution stage. Powder based catalysts and sludges are treated in batches, often in box section furnaces. Direct flame heating is applied to dry and then ignite the catalyst that is allowed to burn naturally. The air ingress to the furnace is controlled to modify the combustion conditions and an afterburner is used.

Reforming or hydrogenation catalysts can be treated by dissolution of the ceramic base in sodium hydroxide or sulphuric acid. Prior to leaching, the excess carbon and hydrocarbons are burnt off. PGMs from automotive catalysts can be collected separately in Cu or Ni in plasma, electric or converter furnaces [tm 105, PM Expert Group 1998]. Small operators use open trays to burn off catalysts by self-ignition or roasting, these processes can be dangerous and fume collection and after burning can be used to treat the fume and gases.

PGM refining is complex and individual process stages may have to be repeated to achieve the required purity. The number and order of the stages also depends on the contaminants to be removed and the specific mix of PGMs to be separated from any one batch of feedstock. The processing of secondary materials such as spent chemical and auto catalysts, electrical and electronic scrap in base metal smelters or specific equipment finally produces PGM rich residues or precipitates.

6.2 Present Emission and Consumption Levels

Precious metal refineries are complex networks of main and subsidiary processes. The raw materials used vary greatly in quality and quantity and therefore the equipment used has a variety of capacities and uses. Multi-purpose reactors and furnaces are used extensively and processing steps are often repeated. It is therefore not possible to identify single process steps and their contribution to emissions and consumption.

Some general principles apply to the emissions and consumption of this sector: -

- On average a 10-fold quantity of material has to be treated to isolate precious metals. The concentrations vary from < 1% to nearly pure metal.
- High-energy techniques are used e.g. electric furnaces. Energy recovery is practised if appropriate.
- Residues containing base metals are sold for recovery.
- Many chemical treatments involve the use of cyanide, chlorine, hydrochloric acid and nitric acid. These reagents are reused within the processes but eventually require oxidation or neutralisation with caustic soda and lime. Sludges from wastewater treatment are closely monitored for metals and are recovered if possible.
- A variety of organic solvents are used for liquid-liquid extraction.
- A variety of oxidising and reducing agents are used.
- Acid gases such as chlorine or nitrogen oxides are recovered for reuse.
- Gas volumes vary greatly between cycles. The small scale of the processes usually allows for good containment. Local exhaust ventilation is used.

6.2.1 Material loops in the precious metal recycling industry

One of the characteristics of the PM industry is the need to keep solution volumes small to diminish the losses of precious metals or their compounds. Consequently there are several closed cycles in operation to reclaim materials and these are shown below.

6.2.1.1 The non-metallic cycles

Hydrochloric acid and nitric acid are mainly used for dissolution of metals. Sulphuric acid is used to a lesser extent as part of scrubber solutions for ammonia absorption and electrolyte in silver powder baths. Other materials are used as reagents or are present in the feed materials.

a) The hydrochloric acid loop

For processes involving dissolution, hydrochloric acid, HCl, is used in combination with excess chlorine. By using evaporation and collection in water, an azeotropic acid (in concentrations about 20% w/w) is obtained. This is used in different parts of the refinery.

b) The nitric acid loop

Silver and palladium are often dissolved in nitric acid, HNO_3. A significant quantity of nitrogen oxide off-gases (NO and NO_2) can be captured with oxygen or hydrogen peroxide in special scrubber cascades. The long residence time needed to oxidise small quantities of NO and the reduction of gas absorption by exothermic reactions can produce problems. Therefore cooling and combined scrubbers are necessary to reach the limit values and avoid brown fumes from the stack. The resulting nitric acid from the first scrubber usually has concentrations about 45% by weight and can be reused in several processes.

c) The chlorine loop

Chlorine is used in wet processes to dissolve metals and in dry chlorination steps at elevated temperatures to refine them. In both cases closed systems are used, e.g. using U-tubes with water to produce hypochlorite solutions. Hypochlorite is also used as an oxidising agent in scrubber solutions for various refining processes.

d) The ammonium chloride loop

Ammonia and ammonium chloride are used in the recovery of PGMs. The relatively small solubility of ammonium chloride, NH_4Cl, in evaporated solutions at room temperature makes it possible to reuse crystalline precipitates of this salt.

e) The alumina loop

Heterogeneous catalysts based on alumina, Al_2O_3, are treated in the PM refineries in large quantities for example the reforming catalysts from the oil refining industry. The catalysts are dissolved in caustic soda above 200 °C under pressure and the resulting aluminate solution is sold after separation of the PM as a precipitation aid in water treatment. Alternatively it can be returned to the alumina industry via the BAYER process (dissolution of bauxite). Similar external cycles are possible with aluminium sulphate solutions, which result when the catalysts are dissolved in sulphuric acid.

6.2.1.2 The non-PM-loops

PM-refineries process a lot of materials containing copper, lead, tin, tungsten, rhenium, cadmium, mercury and other special metals. For the separation of all these metals special processes are established which produce concentrates for external non-PM metallurgical plants.

a) Copper

The use of copper as the carrier material for precious metals is becoming more important and copper oxides remain after smelting processes. In hydro-metallurgical stages copper can be precipitated by caustic soda, NaOH, and/or lime, CaO. Copper residues can be recovered in a copper refinery or converted to the sulphate and electro-won if the volume justifies it.

For removing traces of copper, especially in the presence of chelates like ammonia, precipitation with sulphides or harmless mercapto compounds (e.g. TMT 15, a 15% solution of tri-mercapto-triazine) is necessary.

b) Lead

Lead cycles have been known since the middle ages in the refining of silver. The process is still used in the sweep extraction. Liquid lead is a good solvent for the PM, especially in an excess of silver. The PM-enriched lead is oxidised in furnaces or converters by oxygen, producing a nearly quantitative separation of lead and other non-PMs. The resulting oxides are reduced by carbon e.g. in a blast furnace and lead is produced and is used again in the process. Excess lead is sold to lead refineries.

c) Tin

Tin is separated as the metal in solution or as a hydroxide precipitate.

d) Tungsten and other metals

For some metals coming from galvanic processes the base metals such as nickel alloys, tungsten, molybdenum can be recycled by cyanide stripping.

e) Rhenium

For rhenium, ionic exchangers are used. After purification and precipitation as ammonium salt, NH_4ReO_4, it is one of the products of PM-refineries.

f) Cadmium

The cadmium concentration of special alloys, e.g. solders and brazes has decreased over the last years. Cadmium is enriched in flue dusts of special campaigns and sent to external metallurgical plants.

g) Mercury

Mercury may form part of some special materials in small concentrations, e.g. dental amalgam, powders or slimes, residues from battery plants, special Polaroid films. For this kind of material, high temperature distillation, perhaps combined with low vacuum, is the first step of recovery. Average concentrations of the distilled scraps and sweeps are less than 0.1% w/w of mercury concentration limits.

These loops and the separation of non-PM compounds contribute to the avoidance of contamination and optimisation of profitability.

6.2.2 Emissions to air

The main emissions to air from precious metal production are:

- sulphur dioxide (SO_2) and other acid gases (HCl);
- oxides of nitrogen (NO_x) and other nitrogen compounds;
- metals and their compounds;
- dust;
- chlorine;
- ammonia and ammonium chloride;
- VOCs and dioxins.

The relevance of the substances emitted from the major sources is given in the following table.

Component	Incineration or smelting	Leaching and purification	Electrolysis	Solvent Extraction	Distillation
Sulphur dioxide and HCl	••	•	•		
VOC	•	•••		•••	•••
Dioxins	••				
Chlorine		•••	••		
Nitrogen oxides	••	••			
Dust and metals	•••*	•	•	•	•
Note. ••• More significant…………..• less significant Fugitive or non-captured emissions are also relevant from these sources.					

Table 6.2: Significance of potential emissions to air from precious metals production

The sources of emissions from the process are: -

- incineration;
- other pre-treatment;
- smelting and melting furnaces;
- leaching and purification;
- solvent extraction;
- electrolysis;
- final recovery or transformation stage;

Production (tonnes)	Dust kilograms per tonne of metal	Nitrogen Oxides kilograms per tonne of metal	Sulphur Dioxide kilograms per tonne of metal
2155	58	154	232
1200	4.5	68	3.1
2500	2	7	9
1110	18		
102	127	21	

Table 6.3: Emissions to air from a range of large processes

6.2.2.1 Dust and metals

These can generally be emitted from incinerators, furnaces and cupels as fugitive or collected and abated emissions. Furnace sealing and secondary collection from launders is an important factor in preventing fugitive emissions, some electric furnaces use hollow electrodes for material additions to allow improved furnace sealing. Ash from incinerators is usually quenched and the maintenance of the water seal is an important factor in reducing fugitive emissions. Batch incinerators using open trays or boxes present dust and ash containment problems. Collected emissions are usually treated in ceramic or fabric filters, EPs or wet scrubbers [tm 164, Bobeth 1999].

6.2.2.2 Sulphur dioxide

These gases are formed from the combustion of sulphur contained in the raw material or the fuel or are produced from acid digestion stages. Control of the feed stock can be used to minimise emissions and wet or semi-dry scrubbers are used when the concentrations justify it. Electrode mists and gases can be produced during electro-winning. Gases can be collected and reused and mists can be removed de-misters and returned to the process.

6.2.2.3 Chlorine and HCl

These gases can be formed during a number of digestion, electrolytic and purification processes. Chlorine is used extensively in the Miller process and in the dissolution stages using hydrochloric acid/chlorine mixtures. Chlorine is recovered for reuse wherever possible e.g. using sealed electrolytic cells for gold and PMs. Scrubbers are used to remove residual amounts of chlorine and HCl.

The presence of chlorine in wastewater can lead to the formation of organic chlorine compounds if solvents etc are also present in a mixed wastewater.

6.2.2.4 Nitrogen oxides

This is produced to a certain extent during combustion processes and in significant amounts during acid digestion using nitric acid. High concentrations of nitrogen oxides are treated in scrubbers so that nitric acid can be recovered, various oxidising agents are used to promote conversion and recovery as nitric acid.

Residual nitrogen oxides from furnace off-gases can be removed by catalytic means such as selective or non-selective catalysis if very high NO_x concentrations occur continuously [tm 164, Bobeth 1999].

The choice of abatement techniques essentially depends on the variation of the NO_x concentration.

6.2.2.5 VOC and dioxins

VOCs can be emitted from solvent extraction processes. The small scale of the processes usually allows sealing or enclosure of reactors, good collection and recovery using condensers. Collected solvents are reused.

The organic carbon compounds that can be emitted from smelting stages may include dioxins resulting from the poor combustion of oil and plastic in the feed material and from de-novo synthesis if the gases are not cooled rapidly enough. Scrap treatment to remove organic contamination can be practised but more usually afterburners are used to treat the gases produced followed by rapid cooling. In cases where it is not possible to treat the gases from the furnaces in an afterburner they can be oxidised by adding oxygen above the melting zone. It is also possible to identify organic contamination of secondary raw materials so that the most appropriate furnace and abatement combination can be used to prevent the emissions of smoke and fume and the associated dioxins. Organic compounds, including dioxins can be decomposed by catalytic oxidation, often in joint reactors.

	Incineration processes	Pyro-metallurgical processes	Hydro-metallurgical processes
Production range	200 – 1000 kg/d	150 – 1200 t/a	20 – 600 t/a
Dust mg/Nm^3	2 – 10	4 – 10	
Nitrogen Oxides mg/Nm^3	50 – 150	~200	1 – 370
Sulphur Dioxide mg/Nm^3	1 – 25	10 – 100	0.1 – 35
CO mg/Nm^3	10 - 50	80 - 100	
Chloride mg/Nm^3	2 - 5	< 30	0.4 - 5
Cl_2 mg/Nm^3		< 5	2 - 5
Fluoride mg/Nm^3	0.03 - 1.5	2 - 4	
TOC mg/Nm^3	2 - 5	2 - 20	
Dioxins ng ITE/Nm^3	< 0.1	< 0.1	
HCN mg/Nm^3			0.01 - 2
NH_3 mg/Nm^3			0.2 - 4

Table 6.4: Emissions to air from a range of small processes
[tm 164, Bobeth 1999]

6.2.3 Emissions to water

Pyrometallurgical and hydro-metallurgical processes use significant quantities of cooling water. Liquors from leaching cycles are normally recirculated in sealed systems. Other sources of process water are shown in the table below. Suspended solids, metal compounds and oils can be emitted to water from these sources.

All wastewater is treated to remove dissolved metals and solids. Precipitation of metal ions as hydroxides or sulphides is used, a two stage precipitation can also be used. Ion exchange is suitable for low concentrations and amounts of metal ions. In a number of installations cooling water and treated wastewater including rainwater is reused or recycled within the processes.

Special techniques have been developed for precious metal processes to detoxify nitrite (reduction) and cyanide (hydrolysis) in the wastewater [tm 164, Bobeth 1999].

Emission Source	Suspended Solids	Metal Compounds	Oil
Surface Drainage	•••	••	•••
Cooling Water for direct cooling.	•••	•••	•
Cooling Water for indirect cooling.	•	•	
Quenching Water	•••	••	
Leaching (if not closed circuit)	•••	•••	•
Electro-winning (if not closed circuit)		•••	
Scrubbing Systems	•••	•••	
Note. ••• More significant…………….• less significant			

Table 6.5: Significance of potential emissions to water from precious metals production

Production t/a	Effluent [m³/hr]	Main components [mg/l]					
		Ag	Pb	Hg	Cu	Ni	COD
2155	10	0.1	0.5	0.05	0.3	0.5	400
1200	2		< 1	< 0.05	< 2	< 5	
2500	100	0.02	< 0.05	< 0.05	< 0.3	< 0.02	250
1110			3.9 kg/a	0.05 kg/a	194 kg/a	24 kg/a	
102			1260 kg/a		2750 kg/a	1640 kg/a	

Table 6.6: Emissions to water from 5 large processes

Other potential emissions to water may include ammonium, chloride and cyanide ions depending on the individual process stages. No data has been submitted to quantify these components.

6.2.4 Process residues and wastes

The production of metals is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). The most important process specific residues are listed below. Most production residues are recycled within the process or sent to other specialists to recover any precious metals. Residues containing other metals e.g. Cu, are sold to other producers for recovery. Final residues generally comprise hydroxide filter cakes.

Annual waste for disposal tonnes	Waste characterisation
1000	Iron hydroxide, 60% water, (Cat 1 Industrial Waste).
1000	Effluent filter cake
350	Effluent filter cake

Table 6.7: Example of waste quantities

6.2.5 Energy use

Residual energy from incineration processes can be used in various ways depending on the specific site circumstances. Electricity can be produced if more than 0.5 MW/h can be produced.

6.3 Techniques to Consider in the Determination of BAT

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2 “common processes” apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated. Techniques used by other sectors are also applicable particularly those relating to the collection, re-use and scrubbing of organic solvents, nitrogen oxides and chlorine gas.

The use of hoods for tapping and casting is also a technique to consider. These fumes will consist mainly of oxides of the metals that are involved in the smelting process. The design of the hooding system needs to take account of access for charging and other furnace operations and the way the source of process gases change during the process cycle.

The applied processes described above are used to process a wide range of raw materials of varying quantity and composition and are also representative of those used worldwide. The techniques have been developed by the Companies in this sector to take account of this variation. The choice of pyro-metallurgical or hydrometallurgical technique is driven by the raw materials used, their quantity, the impurities present, the product made and the cost of the recycling and purification operation. These factors are therefore site specific. The basic recovery processes outlined above therefore constitute techniques to consider for the recovery processes.

6.3.1 Raw materials handling

The storage of raw materials depends on the nature of the material described above. The storage of fine dusts in enclosed buildings or in sealed packaging is used. Secondary raw materials that contain water soluble components are stored under cover. Storing non-dusty, non soluble material (except batteries) in open stockpiles and large items individually in the open. Separate storage of reactive and flammable materials with segregation of materials capable of reacting together.

Material	Storage	Handling	Pre-treatment	Comment
Coal or Coke.	Open with sealed floors and water collection, Covered Bays, Silos.	Covered conveyors if non-dusty. Pneumatic.		
Fuel and other oils.	Tanks or drums in bunded areas.	Secure pipeline or manual system.		
Fluxes.	Enclosed, Silo If dust forming	Enclosed conveyors with dust collection. Pneumatic.	Blending with concentrates or other material.	
Concentrates.	Enclosed. Drums, Bags. If dust forming	Enclosed with dust collection. Closed conveyor or pneumatic.	Blending using conveyors. Drying or sintering	
Circuit Boards.	Covered Bays, boxes.	Depends on the material	Grinding + density separation., incineration	Plastic content may provide heat input.
Fine dust.	Enclosed. If dust forming	Enclosed with dust collection. Pneumatic.	Blending, Agglomeration (pelletisation).	
Coarse dust (raw material or granulated slag)	Covered Bays	Mechanical loader.	Roasting to remove VOCs.	Oil collection if necessary
Film, catalysts sweeps	Drums, big bags, bales.	Depends on the material	Incineration, roasting	
Plated material.	Drums, boxes.	Depends on the material	Stripping with CN or nitric acid.	
Lump (raw material or slag).	Open	Depends on the material		Oil collection if necessary
Whole Items	Open or Covered Bays	Depends on the material	Milling grinding.	Oil collection if necessary
Reactive materials	Isolated storage	Depends on the material	Crushing or whole feed.	Acid collection
Acids: - Waste acid Recovered acid	 Acid resistant tanks. Acid resistant tanks.		 Sale or neutralisation. Sale.	
Products – Cathodes, billets and ingots. Rod and wire.	Open concrete area or covered storage.			
Process residues for recovery.	Covered or enclosed depending on dust formation.	Depends on conditions.		Appropriate drainage system.
Wastes for disposal.	Covered or enclosed bays, big bags or sealed drums depending on the material.	Depends on conditions.		Appropriate drainage system.

Table 6.8: Material handling and pre-treatment

6.3.2 Metal production processes

As reported above there are many potential processes and combinations of processes that are used for the recovery of precious metals. The exact combination depends on the raw materials and the matrix that contains the metals. The following table shows the generic process stages, the potential problems and the techniques to consider in the determination of BAT for these processes.

Process	Potential problem	Techniques to consider	Comment
Incineration	Dust, VOC, dioxins, SO_2, NO_x	Process control, afterburner and fabric filter	Rotary kiln unless very small scale.
Crushing, blending or drying	Dust	Containment, gas collection and fabric filter	
Pelletisation	Dust	Containment, gas collection and fabric filter	
Smelting and selenium removal/volatilisation	Dust, metals, VOC, NO_x and SO_2	Containment, gas collection and dust removal. Scrubber	Scrubber or wet ESP for selenium recovery.
Cupellation	Lead oxide	Containment, gas collection and fabric filter	Use of the copper route
Acid digestion	Acid gases Acid spillage	Containment, gas collection and recovery/scrubbing system	See also table 6.11
Refining	Acid gases, NH_3 Acid spillage	Containment, gas collection and fabric filter	See also table 6.11
Oxidation or reduction	Chemical components Chemical spillage	Containment, gas collection and scrubbing/treatment	See also table 6.11
Melting, alloying and casting	Dust and metals	Containment, gas collection and fabric filter	
Solvent extraction	VOC	Containment, gas collection and recovery/absorption	See also table 6.11
Dissolution	HCl, Cl_2, NO_x	Containment, gas collection and recovery/scrubbing system	See also table 6.11
Distillation		Containment, gas collection and recovery/scrubbing system	See also table 6.11

Table 6.9: Techniques to consider for metal production stages

EXAMPLE 6.01 INCINERATION OF PHOTOGRAPHIC MATERIAL

Description: - Use of rotary kiln with good process control, gas collection and gas treatment. Rotation and process control allows good mixing of material and air.

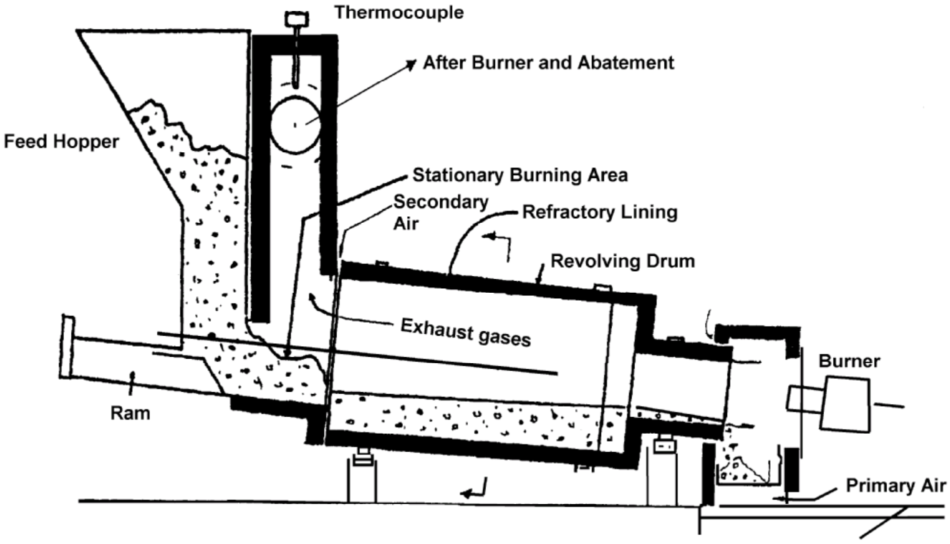


Figure 6.4: Incinerator for photographic film

Main environmental benefits: - Easier fume collection, after burning and gas treatment compared to static or box incinerators.

Operational data: - Non available.

Cross media effects: - Positive effect- good collection efficiency with reduced power consumption, using the calorific value of the film compared to similar systems.

Economics: - Capital cost estimated at ₤450000 for 500 kg/h plant (1988 data).

Applicability: - Incineration of all photographic material.

Example plants: - UK

Reference literature: - [tm 005, HMIP 1993]; [tm 106, Farrell, 1998]

Furnace	Processes used	Advantages	Disadvantages
Blast furnace	Smelting	Established.	Process control needs development. Tuyere injection of fine material is possible.
Rotary furnace	Smelting	High smelting rate with oxygen. Rotation gives good mixing.	Batch process
Electric furnace (resistance, induction, arc)	Smelting	Low gas volumes. Reducing conditions. Through electrode feeding.	Energy cost.
ISA Smelt	Smelting	Range of material. Recovery with other metals e.g. Cu	Minimum size.
Reverberatory furnace	Smelting and cupellation	Established. Processes are combined.	Batch process
Top blown rotary furnace or Tilting rotating oxy fuel (TROF) furnace	Smelting or cupellation	Compact, easy to enclose. Combines processes.	Can be expensive. Batch process
Gas re-circulating roaster	Selenium roasting, smelting	Improved heat transfer	
Bottom blown oxygen cupel	Cupellation	Low fuel consumption. High recovery and process rate. Rising gases are washed by molten layer of litharge	Batch process
Cupel	Cupellation		Relies heavily on fume collection

Table 6.10: Smelting and cupelling furnaces

6.3.3 Fume/gas collection and abatement

The techniques discussed in section 2.7 of this document are techniques to consider for the various process stages involved in the production of precious metals etc. The use of secondary hoods for launders, moulds and charging doors is also a technique to be considered. The processes usually involve small-scale operation and so the techniques such as reactor sealing and containment can be relatively easy and cheap to incorporate.

EXAMPLE 6.02 COLLECTION OF FUME

Description: - Co-incident charging and tapping zone for a rotary furnace.

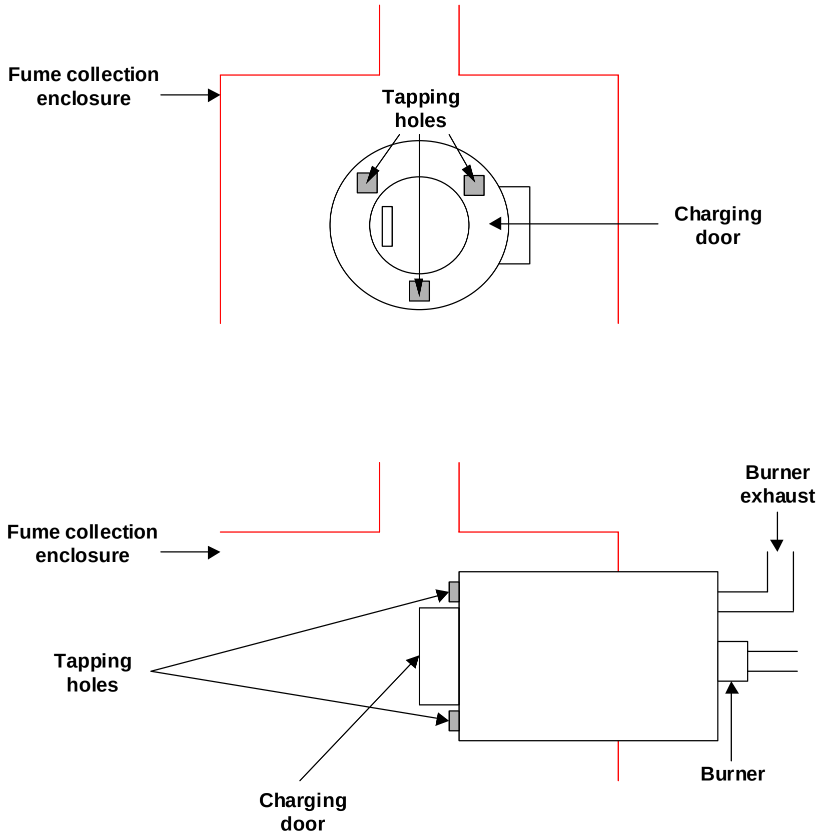


Figure 6.5: Co-incident fume capture system

Furnace lining wear may mean that door end tapping holes may not allow all of the metal to be tapped.

Main environmental benefits: **-** Easier fume collection from a single point.

Operational data: - Non available.

Cross media effects: - Positive effect- good collection efficiency with reduced power consumption compared to similar systems.

Economics: - Low cost of modification, viable in several installations.

Applicability: - All rotary furnaces.

Example plants: - France, UK

Reference literature: - [tm 106, Farrell, 1998]

There are several site-specific issues that will apply and some of these are discussed earlier in this chapter. Essentially the process technologies discussed in this chapter, combined with suitable abatement will meet the demands of stringent environmental protection. Techniques to remove components from some of the off gases are shown below.

Reagent Used	Component in off gas	Treatment Method
Solvents, VOCs	VOC, Odour	Containment, Condensation. Activated carbon, Bio-filter
Sulphuric acid (+ sulphur in fuel or raw material)	Sulphur dioxide	Wet or semi-dry scrubber system.
Aqua Regia	NOCl, NO_x	Caustic scrubber system
Chlorine, HCl	Cl_2	Caustic scrubber system
Nitric acid	NO_x	Oxidise and absorb, recycle, scrubber system
Na or KCN	HCN	Oxidise with hydrogen peroxide or hypochlorite
Ammonia	NH_3	Recovery, scrubber system
Ammonium chloride	Aerosol	Recovery by sublimation, scrubber system
Hydrazine	N_2H_4 (possible carcinogen)	Scrubber or activated carbon
Sodium borohydride	Hydrogen (explosion hazard)	Avoid if possible in PGM processing (especially Os, Ru)
Formic acid	Formaldehyde	Caustic scrubber system
Sodium chlorate/HCl	Cl_2 oxides (explosion hazard)	Control of process end point
Hypochlorite is not permitted in some Regions.		

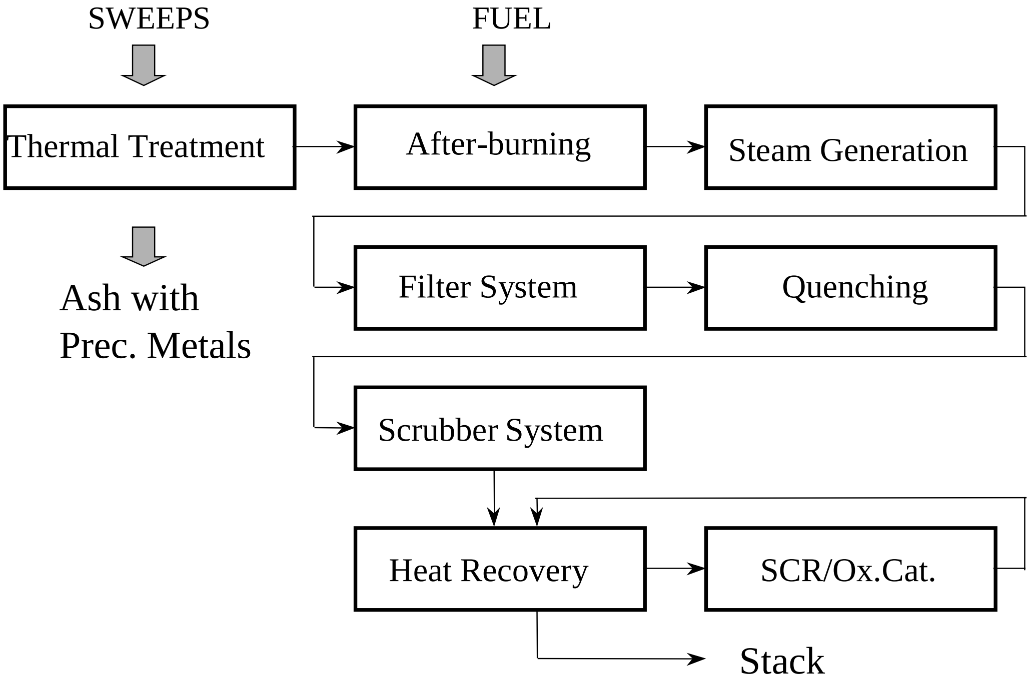
Table 6.11: Chemical treatment methods for some gaseous components

Melting furnaces are also used in the industry. Electric (induction, arc, resistance) furnaces and gas/oil fired furnaces are used. Induction furnaces avoid the production of combustion gases and the associated increase in size of abatement plant.

The hydrometallurgical processes are very important in some production processes. Because the hydrometallurgical processes involve leaching and electrolytic stages, gases evolved such as HCl, need to be recovered or treated. Adequate disposal of leached material and spent electrolyte also needs to be practised. The techniques discussed in section 2.9 to prevent emissions to water for example by containing drainage systems are relevant as are techniques to recover VOCs and use of benign solvents.

EXAMPLE 6.03 USE OF SCR AND SNCR

Description: - Use of SCR or SNCR in precious metal processes.



Main environmental benefits: - NO_x removal.

Operational data: - Non available.

Cross media effects: - Use of reagents and power.

Economics: - Viable in one installation.

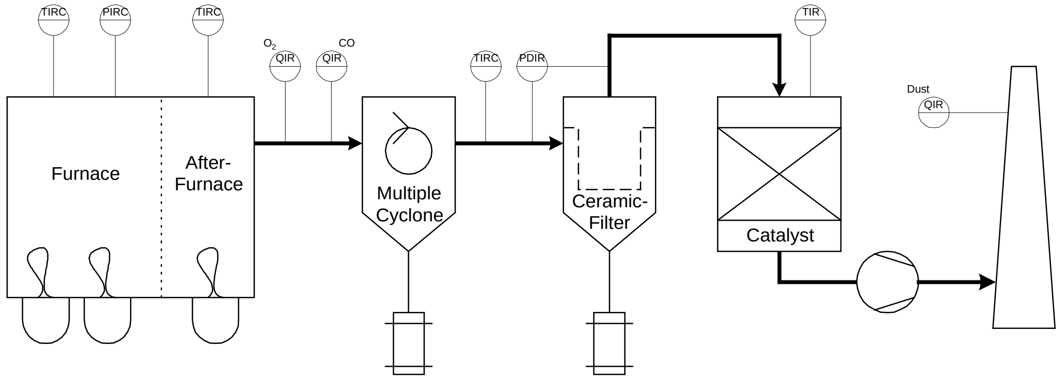
Applicability: - Not reported.

Example plants: - Germany

Reference literature: - [German response to second Draft]

EXAMPLE 6.04 CATALYTIC DESTRUCTION OF DIOXINS

Description: - Use of a catalytic reactor to remove dioxins.



Waste air stream:	800 m^3/h

Ceramic-Filter

Pure-gas:	< 10 mg(Dust)/m^3
Filter-Area:	24 m^2
Drop of pressure:	15 hPa
Temperature:	max. 400 °C

Catalyst

Dioxine/Furane:	< 0,1 ng/m^3
Volume:	170 l
Max. flow through:	1500 m^3/h
Length of stay:	> 0,25 s

Main environmental benefits: - Dioxin removal.

Operational data: - < 0.01 ng/Nm^3 achieved.

Cross media effects: - Power usage.

Economics: - Viable in one installation.

Applicability: - Not reported.

Example plants: - Germany

Reference literature: - [German response to second Draft]

6.3.4 Process control

The principles of process control discussed in section 2.6 are applicable to the production processes used in this Group. Some of the furnaces and processes are capable of improvement by the adoption of many of these techniques.

EXAMPLE 6.05 PROCESS CONTROL FOR THE MILLER FURNACE

Description: - In the Miller process gold is melted at about 1000 °C and chlorine gas is blown through the melt. Metallic impurities form chlorides and form a slag or are fumed off. The initial uptake of chlorine is high and excess chlorine can be emitted easily. Manual control of chlorine addition is difficult. The formation of most of the metal chlorides is exothermic and the use of continuous temperature measurement can be used to control the rate of chlorine addition.
Main environmental benefits: - Prevention of chlorine emission.

Operational data: - Free chlorine release reported be < 1 ppm to air after a venturi scrubber and wet EP.

Cross media effects: - Positive - Prevention of excess consumption of chlorine.

Economics: - Not assessed but the costs are low, viable operation established.

Applicability: - All Miller processes.

Example plants: - UK

Reference literature: - [tm 005, HMIP 1993]

6.3.5 Wastewater

This is a site-specific issue, existing treatment systems are reported to be to a high standard. All wastewater should be treated to remove dissolved metals and solids, cyanide wastes and liquors also need to be treated. Water supply and effluent lines can be separated. The techniques listed in sections 2.9 and 6.2.3 are the techniques to consider. In a number of installations cooling water and treated wastewater including rainwater is reused or recycled within the processes.

6.3.6 General techniques

- Characterisation of raw materials before they are received so that unforeseen impurities and contamination can be identified and the handling, storage and processing difficulties can be taken into account and the material transferred to another processor if appropriate.
- Sampling and analysis of raw materials as soon as possible so that commercial aspects can be confirmed and the process options defined for a particular raw material.
- Raw materials handling systems to minimise leakage of liquids and the emission of dust. Robust packaging should be used during transport and for storage.
- Raw materials storage in enclosed buildings if necessary with separate storage of reactive materials.
- Pre-treatment stages for photographic film and paper using a rotary kiln and afterburner together with an ash quench system that is designed to a high standard. HCl may need to be scrubbed from the exhaust gas and dust removal used. In the case of raw material that contains minor quantities of paper, leaching processes based on sodium thiosulphate and enzymes.
- Pre-treatment stages for catalysts and smaller quantities of material containing PGMs in box incinerators using an afterburner where necessary and fabric filters, scrubbers etc. that are professionally designed and constructed to a high standard so that leakage is prevented. Heat recovery in the form of energy production or re-cuperation should be practised if possible.
- Pre-treatment of small quantities of material in sealed box incinerators using professionally designed collection and abatement equipment including afterburners where necessary.
- Use of techniques such as calcining or leaching/dissolution where possible to recover catalyst support material. The material could be recovered as grinding material, aluminium salts, inert slag or catalyst support material.
- The use of proven precious metal recovery and refining processes in conjunction with proven, efficient abatement systems that are available to the operator, that achieve the environmental standards covered in section 2.8 of this document. The use of copper rather than lead in the smelting circuit.
- Solvent extraction systems using non-toxic solvents as far as possible. Use of containment and VOC recovery and abatement systems.
- Furnace operation control to optimise operating conditions. Key parameters are temperature at various points in the furnace and gas handling system, oxygen and carbon

monoxide concentrations and system pressure. These should be used to control the material feed rate as far as possible.

- Processes control of chemical and hydro metallurgical stages and abatement plant using relevant methods so that it is possible to maintain operating conditions at the optimum level and to provide alarms for conditions that are outside the acceptable operating range.
- The collection and reuse of acid gases such as HCl, HNO_3 and Cl_2. The treatment of CN in gas streams.
- Professional design of dust, acid gas, CN, VOC and metal vapour collection and abatement systems. The operation of these systems to prevent and reduce emissions to the environment. Achievable emission standards are given below.
- Use of contained plant drainage systems where possible. Effluents treated according to their content and analysed before discharge. Scrubbing liquids should also be treated and analysed before discharge.
- Waste materials analysis before transfer to other sites so that the correct disposal or recovery route can be used.
- Plant operators should be trained and given instructions about the correct operating procedures and control parameters.
- Use of good maintenance practice for process plant, abatement systems and other associated processes. A system of inspection should be adopted for these systems.

6.3.7 Energy use

The re-use of energy or the generation of electricity are techniques to consider provided site specific conditions allow this to be achieved economically.

6.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector; which are for the production of precious metals are VOCs, dust, fume, dioxins, odours, NO_x, other acid gases such as chlorine and SO_2, wastewater, residues such as sludge, filter dust and slag;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous section. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this section are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

Best Available Techniques are influenced by a number of factors and a methodology of examining the techniques is needed. The approach that has been used is given below.

First of all the choice of process depends strongly on the raw materials that are available to a particular site. The most significant factors are their composition, the presence of other included metals, their size distribution (including the potential to form dust) and the degree of contamination by organic material. There may be primary materials available from single or multiple sources, secondary raw materials of varying quality or a combination of primary and secondary raw materials.

Secondly the process should be suitable for use with the best gas collection and abatement systems that are available. The fume collection and abatement processes used will depend on the characteristics of the main processes, for example some processes avoid ladle transfers and are therefore easier to seal. Other processes may be able to treat recycled materials more easily and therefore reduce the wider environmental impact by preventing disposal.

Finally, the water and waste issues have been taken into account, in particular the minimisation of wastes and the potential to reuse residues and water within the process or by other processes. Energy used by the processes is also a factor that is taken into account in the choice of processes.

The choice of BAT in a general sense is therefore complicated and depends on the above factors. The varying requirements mean that BAT is influenced mainly by the raw materials available to the site and the required throughput of the plant, the issues are therefore site specific. There are advantages for some primary process that are capable of accepting some secondary materials.

The following points summarise the recommended methodology that has been used in this work: -

- Is the process industrially proven and reliable?
- Are there limitations in the feed material that can be processed?
- The type of feed and other metals contained in it (e.g. Cu, Pb, Zn) influences process selection.
- Are there production level constraints? - e.g. a proven upper limit or a minimum throughput required to be economic.
- Can latest and efficient collection and abatement techniques be applied to the process?
- Can the process and abatement combinations achieve the lowest emission levels? The achievable emissions are reported later.
- Are there other aspects such as safety that are related to processes?

At the time of writing several process and abatement combinations are able to operate to the highest environmental standards and meet the requirements of BAT. The processes vary in the throughput that can be achieved and the materials that can be used and so several combinations are included. All of the processes maximise the reuse of residues and minimise emissions to water. The economics of the processes vary. Some need to operate at a high throughput to achieve economic operation, while others are not able to achieve high throughputs.
The collection and abatement techniques used with these processes were discussed under techniques to consider in the determination of BAT and when applied in combination with the metallurgical process will result in a high level of environmental protection.

As indicated in the general preface to this document, this section proposes techniques and emissions that are considered to be compatible with BAT in general. The purpose is to provide general indications of the emission and consumption levels that might be considered as an appropriate benchmark of BAT based performance. This is done by quoting achievable levels in ranges that are generally applicable to both new and upgraded plants. Existing installations may have factors, such as space or height limitations that prevent full adoption of the techniques.

The level will also vary with time depending on the condition of the equipment, its maintenance and the process control of the abatement plant. The operation of the source process will also influence performance as there are likely to be variations in temperature, gas volume and even the characteristics of the material throughout a process or batch. The achievable emissions are therefore only a basis from which actual plant performance can be judged. Process dynamics and other site-specific issues need to be taken into account at a local level. The examples given in the section on techniques to consider in the determination of BAT give the concentrations associated with some existing processes [tm 137 Copper Expert Group 1998].

6.4.1 Materials handling and storage

The conclusions drawn for Best Available Techniques for the materials handling and storage stages are shown in section 2.17 of this document and are applicable to the materials in this chapter.

6.4.2 Process selection

It is not possible to conclude that a single process can be applied to this group of metals. The pyrometallurgical and hydro-metallurgical processes that are applied at the moment form the basis of BAT but additionally the general factors and fume collection and abatement techniques described above and in Chapter 2 should be used in conjunction with them.

The use of the copper route for smelting precious metals has a lower potential for the emission of lead to all environmental media and should be used if the combination of raw materials, equipment and products allows it.

6.4.2.1 Pre-treatment processes

The pre-treatment processes are described earlier in this chapter and are designed to treat and sample the incoming materials. A wide range of processes have been established for the many materials used and it is not possible to choose a single pre-treatment process. The principles of BAT for pre-treatment are therefore the way materials are handled and transferred, the way process is contained and controlled and the use of robust effective abatement for the materials and reagents used.
These issues are discussed in section 2.3 to 2.10. Chemical treatment methods for some of the products of reactions are shown in table 6.11

6.4.2.2 Pyrometallurgical stages

Applied Technique	Raw Materials	Comments
Miller furnace.	Gold alloy.	Induction or gas oil fired. Temperature control or chlorine metering. Effective collection systems.
Cupelling furnaces. BBOC	Silver alloys (with Cu, Pb).	Oxygen lancing using reverberatory furnace or BBOC has lower energy use and higher recovery rate.
TBRC and TROF	Mixed concentrates, slimes and secondary materials.	With copper/lead materials. Enclosed furnace.
Blast Furnace	Sweeps, Ashes and Concentrate.	Requires modern control, afterburner and efficient abatement. Acid gas removal may be needed.
Gas re-circulating roaster	Anode slimes	Selenium removal and recovery
Rotary Furnace	Ashes and Concentrate.	Oxy fuel used. Efficient fume collection need throughout the process.
Electric Furnace	Ashes and Concentrate.	Sealed furnace. Through electrode feeding. Gas volumes can be lower.
ISA Smelt Furnace	Mixed concentrates and secondary materials.	With copper/lead materials.

Table 6.12: Furnace options for precious metals

6.4.2.3 Hydrometallurgical stages

Essentially the process technologies discussed in this chapter, combined with suitable abatement will meet the demands of stringent environmental protection. An example is given of the collection of chlorine gas that is evolved at the anode during electro-winning, leaching and refining. Other techniques include the containment of solvent vapours using closed solvent extraction reactors and the collection and re-use of solvents and other materials. The use of the collection loops described in 6.2 is particularly relevant and as are the chemical treatments methods for reaction products shown in table 6.11. The significance of the components of any VOC depend on the solvent used and these can only be determined locally.

6.4.3 Gas collection and abatement

The fume collection systems used should exploit furnace or reactor sealing systems and be designed to maintain a suitable depression that avoids leaks and fugitive emissions. Systems that maintain furnace sealing or hood deployment should be used. Examples are through electrode additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems. Secondary fume collection is expensive and consumes a lot of energy but is needed in the case of some furnaces. The system used should be an intelligent system capable of targeting the fume extraction to the source and duration of any fume.

Best Available Techniques for gas and fume treatment systems are those that use cooling and heat recovery if practical before a fabric filter. Fabric filters that use modern high performance materials in a well-constructed and maintained structure are applicable. They feature bag burst detection systems and on-line cleaning methods. Gas treatment for the smelting or incineration stage should include a sulphur dioxide removal stage and/or after-burning if this as considered necessary to avoid local, regional or long-range air quality problems or if dioxins may be present.

Process Stage.	Component In Off - gas.	Abatement option.
Raw materials handling	Dust and metals	Correct storage. Dust collection and fabric filter if necessary
Raw materials pre-treatment	Dust and metals	Correct pre-treatment Gas collection and fabric filter.
Sweeps and film incineration	Organic material*	Process operation, after-burning, correct gas cooling and fabric filter
Roasting and smelting.	Dust and metals. Carbon monoxide and Organic material *. Sulphur dioxide	Process operation, gas collection, cooling and fabric filter. Afterburner, carbon injection. Scrubbing if necessary.
Selenium roasting	Dust and metals. Sulphur dioxide	Process operation, gas collection, cooling and dust removal. scrubbing and wet EP
Dissolution and chemical refining.	Mist, metals and acid gases Other gases	Process operation and gas collection with oxidising scrubber. See table 6.11.
Distillation	Chlorine, bromine and tetroxides.	Enclosed area. Absorber/condenser and scrubber
Solvent extraction	VOC and Odour	Containment, condenser. Carbon or bio filter if necessary.
Electro-winning	Acid mists	Gas collection and scrubbing/ de-misting.
Thermal refining (Miller process)	Dust and metals Chlorine.	Process operation. Gas collection, scrubbing and wet EP.
Melting, alloying and casting.	Dust and metals Organic material*	Process operation. Gas collection cooling and fabric filter. Process operation, after-burning and correct gas cooling.
Slag treatment and cupelling	Dust and metals	Process operation. Gas collection, cooling and fabric filter.
Note. * Organic material can include VOC reported as total carbon (excluding CO) and dioxins.		

Table 6.13: Abatement applications considered as Best Available Techniques

The acid gas and solvent recovery systems and the associated dust and metal recovery stages are those described in section 2.8 of this document. Fume collection systems should follow the best practice out lined in techniques described in section 2.7. The use of or the recycling of acids, slags, slimes and filter dusts are considered to part of the processes.

Other abatement systems are considered to be applicable for other parts of the process and an overview is shown in the above table.

6.4.3.1 Emissions to air associated with the use of BAT

Emissions to air comprise the captured/abated emissions from the various sources, plus the fugitive or uncaptured emissions from these sources. Modern, well operated systems result in efficient removal of pollutants and the information at the time of writing indicates that that the fugitive emissions can be the largest contributor to the total emissions.

For all processes the emissions to air are based on the emissions from:

- The materials handling and storage, drying, pelletising, sintering, roasting and smelting stages.
- Slag or metal fuming processes.
- Chemical refining, thermal refining and electro-winning stages.
- Melting, alloying, casting etc stages.

Fugitive emissions may be highly significant and can be predicted from the fume capture efficiency and can be estimated by monitoring (see section 2.7). They can be expressed in grams per year or grams per tonne of metal produced. Collected emissions can also be expressed in theses terms or more importantly, in terms of concentration.

For most parameters that are emitted to air, the data provided in section 2.8 for the various abatement types will apply (e.g. the achievable dust emission range for a fabric filter), other factors such as metal concentration derive from this. The following tables review the collected and fugitive emissions to air.

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Low SO_2 off-gas streams (~ 1 – 4%)	> 99.1	Single contact sulphuric acid plant or WSA, (tail gas SO_2 content depends on feed gas strength)	For low-grade SO_2 gases. Combined with dry or semi-dry scrubber to reduce SO_2 emission and produce gypsum if a market is available.
SO_2 – rich off-gas streams (> 5%)	> 99.7% conversion factor	Double contact sulphuric acid plant (Tail gas SO_2 content depends on feed gas strength). A de-mister may be appropriate for the final removal of SO_3	Very low levels for other air-borne pollutants will be reached due to intensive gas treatment prior to the contact plant (wet scrubbing, wet EP and, if necessary, mercury removal to ensure H_2SO_4 product quality
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 6.14: Emissions to air associated with the use of BAT from complex metallurgical processes uses for precious metal recovery in conjunction with copper and lead production

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Acid mists Acid gases SO_2 Ammonia	< 50 mg/Nm³ < 5 mg/Nm³ < 50 mg/Nm³ < 5 mg/Nm³	De-mister Wet alkaline/oxidising scrubber. Wet alkaline scrubber. Acidic scrubber	A de-mister will allow the collected acid to be reused.
Chlorine, bromine, Tetroxides	< 2.0 mg/Nm³	Oxidising scrubber	
NO_x	< 100 mg/Nm³	Oxidising scrubber	Recovery of nitric acid followed by removal of traces. The range is not achievable in cases where aqua regia is used.
VOC or solvents as C	< 5 - 15 mg/Nm³	Containment, condenser, carbon or bio filter	
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 6.15: Emissions to air associated with the use of BAT from chemical extraction and refining, electro-winning and solvent extraction for precious metal recovery

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 - 5 mg/Nm^3	Fabric filter Ceramic filter	High performance fabric filters can achieve low levels of heavy metals. The concentration of heavy metals is linked to the concentration of dust and content of the metals in the dust.
Chlorides, fluorides and acid gases	SO_2 < 100 mg/Nm^3 Chloride < 5 mg/Nm^3 Fluoride < 1 mg/Nm^3	Wet or semi-dry alkaline scrubber.	
NO_x	< 100 mg/Nm^3 < 100 - 300 mg/Nm^3	Low NO_x burner, SCR or SNCR Oxy-fuel burner	Higher values are associated with oxygen enrichment to reduce energy use. In these cases gas volume and mass emission are reduced.
Total organic carbon as C	< 5 - 15 mg/Nm^3	Afterburner. Optimised combustion.	Pre-treatment of secondary material to remove organic coatings if necessary.
Dioxins	< 0.1 - 0.5 ngTEQ/Nm^3	High efficiency dust removal system (i.e. fabric filter), afterburner followed by quenching. Other techniques are available (e.g. adsorption by activated carbon, oxidation catalyst).	Treatment of a clean de-dusted gas is required to achieve low levels

Note. Collected emissions only.
Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period.
For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used. For SO_2 or total carbon removal, the variation in raw gas concentration during batch processes may affect the performance of the abatement system.

Table 6.16: Emissions to air associated with the use of BAT from materials pre-treatment (including incineration), roasting, cupelling, smelting, thermal refining, and melting for precious metal recovery

Emissions of metals are strongly dependent on the composition of the dust produced by the processes. The composition varies widely and is influenced a) by the process that is the source of dust and b) by the raw materials that are being processed. For example the dust produced from a smelter is totally different to that produced during incineration. The metal content of the dust can therefore vary widely between processes. In addition for similar furnaces there are significant variations due to the use of varying raw materials. It is therefore not accurate to detail specific achievable concentrations for all of the metals emitted to air in this document. The issue is site specific.

Some metals have toxic compounds that may be emitted from the processes and so need to be reduced to meet specific local, regional or long-range air quality standards. It is considered that low concentrations of heavy metals are associated with the use of high performance, modern abatement systems such as a membrane fabric filter provided the operating temperature is correct and the characteristics of the gas and dust are taken into account in the design.

6.4.4 Wastewater

This is a site-specific issue. All wastewater will be treated to remove solids, metals, oils/tars absorbed components and will be neutralised if necessary.

For primary and secondary production the total emissions to water are based on:

- The ash treatment or quenching system.
- The electro-winning process, leaching and dissolution sections.
- The wastewater treatment system.

The following table summarises the concentrations that can be achieved using suitable effluent treatment methods for example precipitation of metal ions as sulphide.

Main components [mg/l]				
Ag	**Pb**	**Hg**	**Cu**	**Ni**
0.02	0.05	0.01	0.3	0.03
Note: - Associated ranges are daily or hourly averages depending on the method of measurement.				

Table 6.17: Emissions to water associated with the use of BAT

6.4.5 Process residues

The use or recycling of slags and residues is considered to part of the process. The production processes in this sector have been developed by the industry to maximise the re-use of the majority of process residues from the production units or to produce residues in form that enables them to be used in the process and other non-ferrous metal production processes.

The emissions to land are therefore very site and material specific and depend on the factors discussed earlier. It is therefore not possible to produce a realistic, typical table of quantities that are associated with the use of BAT without detailing the raw material specification. The principles of BAT include waste prevention and minimisation and the re-use of residues whenever practical.

6.4.6 Costs associated with the techniques

Cost data has been compiled for a variety of process variations and abatement systems. The cost data is very site specific and depends on a number of factors but the ranges given may enable some comparisons to be made. The data is provided in an appendix to this note so that costs over the whole of the non-ferrous metal industry can be compared.

6.5 Emerging Technologies

- The 'J' process is not operated in Europe but can operate with a lower inventory of gold compared with other gold refining processes. It uses a re-generable iodine solution to dissolve impure gold (< 99.5%). The gold is reduced by potassium hydroxide, separated, washed and dried to a powder containing 99.995% gold. Liquor from the reduction stage is fed to an electrolytic cell where soluble impurities and any unreduced gold iodide are deposited on the cathode and removed for recovery in a precious metals circuit. The solution is then transferred to an electrolytic diaphragm cell fitted with inert electrodes. Iodine solution produced in the anode compartment and KOH solution produced in the cathode compartment are recycled [tm 5, HMIP PM 1993].

- The copper route for smelting silver containing secondary raw material prevents the emission of lead compounds to air. This has been demonstrated at one installation in UK and is the route used inherently in the copper refineries.

- A process has been designed to treat a pyrite concentrate that contains microscopic gold particles (< 1 µm) to produce a gold dore, a lead/silver concentrate and a zinc concentrate [tm 216, Gryllia 1999]. The ore treatment and metallurgical flow-sheets are shown below.

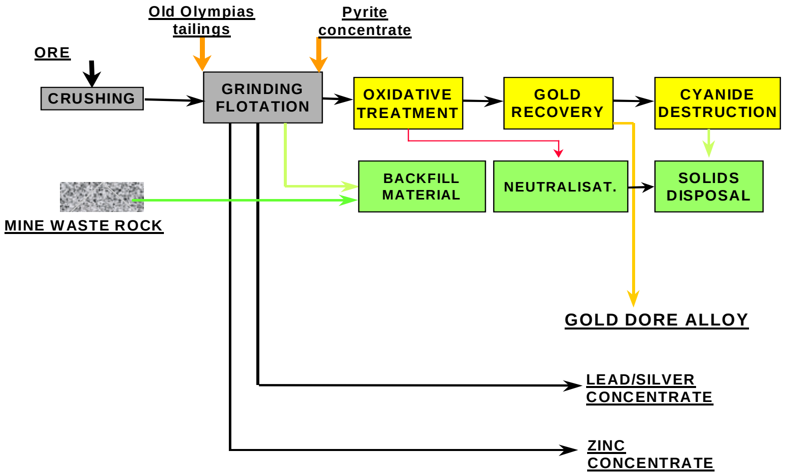


Figure 6.6: Ore treatment flow-sheet

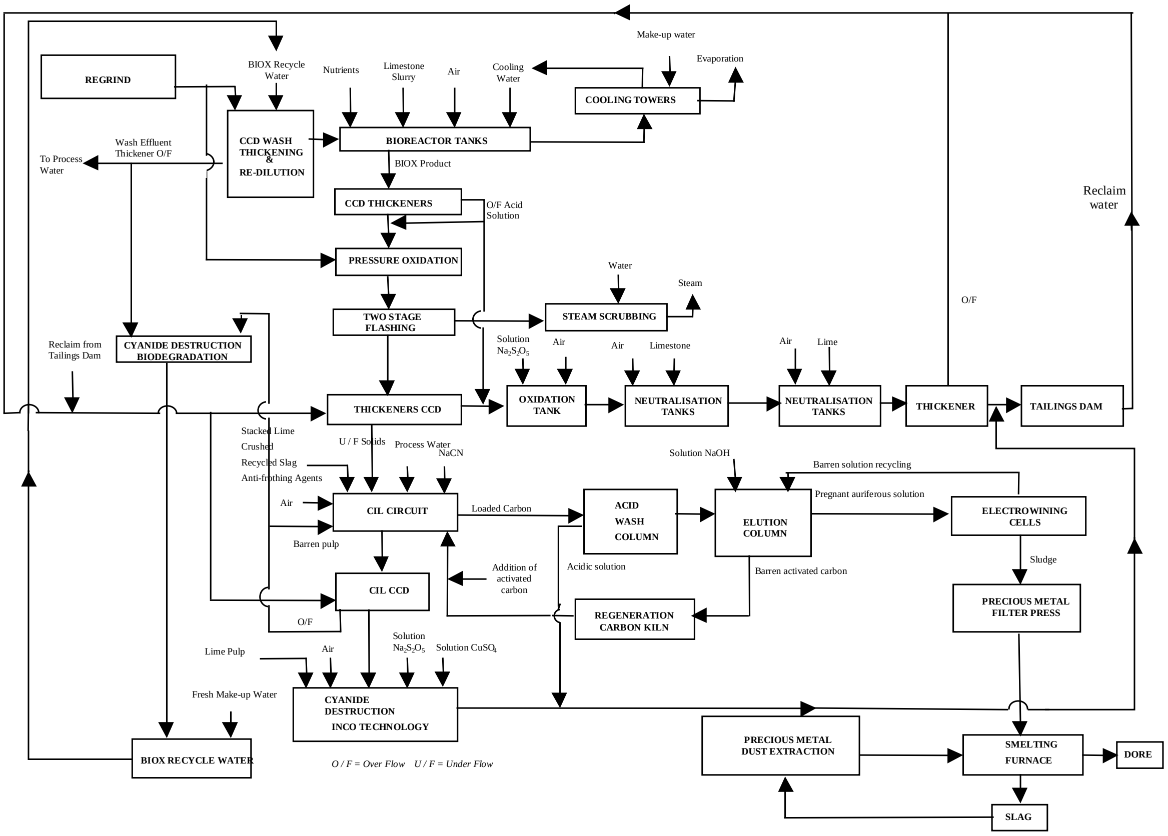


Figure 6.7: Metallurgical process flow-sheet

7 PROCESSES TO PRODUCE MERCURY

7.1 Applied Processes and Techniques

The market for mercury has declined in recent years and this has had a significant affect on the sector. Primary production from ore is now run on a campaign basis over a few months per year. Production from the mercury content of other non-ferrous processes cannot be turned down in this manner and producers of copper, lead and zinc who produce mercury from the scrubber systems prior to sulphuric acid plants can produce calomel from the Boliden-Norzink process, which can be stored or disposed. Secondary mercury production from the treatment of dental amalgam and lamps is now generally performed as a de-mercurising service to produce mercury free feed stock for precious metal recovery or disposal.

7.1.1 Primary production

7.1.1.1 Production from Cinnabar

There is only one producer of mercury from Cinnabar ore in Europe but the process is similar to other worldwide producers. The main difference is the higher mercury content of the European Ore, which means that the ore does not have to be concentrated [tm 70, Mercury Expert Group 1998; tm 71, Mercury Congress 1974].

Rock containing cinnabar (HgS) is crushed in 2 stages to – 25 mm, an extraction system and bag filters are used to treat dust from the crushers and conveyors. The crushed rock is heated to 750 °C in Herreschoff furnaces, which have 8 hearths and use propane fuel [tm 206, TGI 1999]. Cinnabar is oxidised and mercury and sulphur dioxide is driven off in the gas stream. Mercury is condensed in a system comprising 32 water-cooled steel condensers and is collected. Gases are discharged via a stack after passing through a water scrubber, which absorbs some sulphur dioxide. The roasted rock is discharged from the bottom of the furnace and cooled in air, the rock is mercury free and is sold for road building.

The condensed mercury is washed with caustic soda and sodium sulphide and the material pressed in a filter. Mercury is then distilled to give 99.9% purity. The residues from distillation contain 5% mercury and are pelletised with cement and returned to the furnace for recovery [tm 206, TGI 1999].

Cooling water and scrubber water is re-circulated. There is a bleed from the system, which is neutralised with caustic soda and treated with sodium sulphide to precipitate mercury sulphide. The effluent passes through a carbon filter before discharging to the river [tm 70, Mercury Expert Group 1998].

7.1.1.2 Production from the ores and concentrates of other metals

The other significant source of primary mercury is the mercury recovered during the production of other non-ferrous metals. It has been reported that the mercury content ranges from 0.02 to 0.8 kg per tonne of metal (Cu, Zn or Pb) [tm 120, TU Aachen 1999]. These processes remove mercury from the roaster or smelter gas streams prior to the production of sulphuric acid and are described in section 2.8 and in the sections for the production of these metals [tm 26, PARCOM 1996]. It should noted that any mercury that is not captured by the removal stage will be found in the sulphuric acid that is produced, most processes achieve < 0.1 ppm of mercury in sulphuric acid. Mercury is normally recovered from the residues produced from the various scrubbing processes [tm 120, TU Aachen 1999].

7.1.2 Secondary production.

In addition several companies operate mercury recovery systems using dental amalgam and silver oxide batteries as the raw material [tm 16, HMIP Mercury 1993]. These are usually delivered in drums to a reception cupboard that has fume extraction. Batteries and pastes are loaded into suitable receptacles to fit the furnace retort. The temperature of the retort is raised to 700 °C by indirect heating and a vacuum of ~100-mm mercury is applied driving off the mercury from the complex substrate. Heating cycles are up to 18 hours. Gases pass through a steel condenser, a sealed cooling system is used. Mercury is condensed into sealed pots and transferred periodically to storage.

The vacuum can be produced by a variety of means for example a water ejector and a water ring pump can be used which allows wet feed material to be used. Vacuum pumps discharge to a scrubber system to remove mercury.

7.2 Present Emission and Consumption Levels

Emission and consumption data for other non-ferrous metal processes that also produce mercury is given in the relevant chapters on copper and zinc/lead. These processes generally produce mercury or calomel in the range 0.02 to 0.8 kg of mercury per tonne of metal produced depending on the mercury content of the concentrate [tm 120, TU Aachen 1999].

7.2.1 Primary mercury

There are potential emissions of mercury and it’s compounds, sulphur dioxide and particulate matter to air and water. The roasted rock and effluent treatment sludges comprise the solid wastes.

Season	Hg to air mg/Nm^3	Hg kg per tonne of Hg produced	Sulphur Dioxide mg/Nm^3
Winter	10 - 15	5 - 10	
Summer	15 - 20	10 - 20	
Note: The seasonal difference is due to the temperature variation at the condensers. No SO_2 data available.			

Table 7.1: Emissions to air from primary production

Year	Hg to water ppb.	Volume m^3
1993	4	31000
1994	28	11000
1995	66	32500
1996	83	29000
1997	67	45500

Table 7.2: Emissions to water from primary production

7.2.2 Secondary mercury

Year	Hg to air mg/Nm^3	Hg kg per tonne of Hg produced	Sulphur Dioxide mg/Nm^3
1997	7	0.002	

Table 7.3: Emissions to air from secondary production

Year	Hg to water ppb.	Volume m^3
1997	0.3 g/tonne	

Table 7.4: Emissions to water from secondary production

7.2.3 Process residues

The production of metals is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). The most important process specific residues are listed below.

Roasted rock that is free of mercury is used for construction purpose. It represents more than 90% of the quantity of raw material.

Sludges from the wastewater treatment process for both primary and secondary production contain mercury sulphide or calomel. For primary production this material is pelletised and returned to the furnace to recover the mercury. For secondary purposes this is not always possible and small quantities are disposed.

7.3 Techniques to Consider in the Determination of BAT

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2 “common processes” apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

The processes described above are limited in range and represent the technology that is used worldwide. They therefore constitute the techniques to consider in the determination of BAT. However, there are several techniques used by the other non-ferrous metal processes to reduce the emissions of mercury and these techniques are also applicable to the production of mercury from primary and secondary raw materials. The techniques to consider that are described in Chapter 2 “common processes” also apply to the raw materials handling, pre-treatment, process control and abatement systems. The hierarchy of prevention, containment and collection/abatement should be followed as far as possible.

For the production of mercury from secondary raw materials e.g. batteries, the small scale of the process allows equipment to be contained and the gases to be condensed and scrubbed.

7.3.1 Emissions to air

Mercury is volatile at the temperatures encountered in most abatement processes and other techniques are therefore used to remove it [tm 26, PARCOM 1996]. The following techniques are described in section 2.8 and are used for trace concentrations of mercury in copper, zinc and lead smelter gases as part of the gas cleaning train of a sulphuric acid plant. It has been reported that mercury in the condenser gases from the production of mercury from cinnabar is in the form of fine particulate and may not be removed efficiently by some processes. This data needs to be confirmed and the best method of removal defined for this process. Sulphur dioxide is also released during the oxidation of cinnabar and the processes to remove low concentrations outlined in section 2.8 may be applicable.

Boliden/Norzink process. This based on a wet scrubber using the reaction between mercuric chloride and mercury vapour to form mercurous chloride (calomel), which precipitates from the liquor. Mercuric chloride can be regenerated from the calomel in a chlorination stage and mercury can be recovered by electrolysis. The process is reported to have the lowest capital and operating costs [tm 139, Finland Zn 1999]. Mercuric chloride is a very toxic compound of mercury and great care is taken when operating this process.

Sodium thiocyanate process. A wet scrubbing process to precipitate mercury sulphide. Sodium thiocyanate is regenerated.

Outokumpu process. Gases are washed with 90% sulphuric acid in a packed tower to produce mercury sulphate, which is precipitated and removed for recovery. This process also removes selenium.

Systems based on the reaction between mercury and selenium are encountered but selenium is also toxic and great care is needed with disposal of materials. The Outokumpu process removes both mercury and selenium using a sulphuric acid scrubber [tm 46, Outokumpu 1984]. Both metals can be recovered from the precipitate that is formed. The sodium thiosulphate scrubber is also very effective and uses a reactor/scrubber similar to the Boliden Norzink process.

The Boliden-Norzink process is the most widely used technique for removing mercury from emissions to air. The production of calomel from mercuric chloride is straightforward but several processes stop at this stage and accumulate calomel. This is due to the falling price of mercury, which inhibits mercury recovery. The process is capable of achieving emissions in the range 0.05 – 0.1 mg/Nm^3 of mercury in air.

Activated Carbon Filter. An adsorption filter using activated carbon is used to remove mercury vapour from the gas stream.

The activated carbon filter is used in a number of industries to reduce mercury emissions. The break through of mercury from the filter is not easy to predict and consequently a double filter is used with the second filter dealing with breakthrough. When the first filter is exhausted, it is charged with fresh carbon and the second filter becomes the lead unit. Carbon can be regenerated using the Herreschoff furnace and the mercury recovered. Activated carbon filters are capable of mercury concentrations of 0.002 – 0.007 mg/ m^3 provided the double filter arrangement is used.

The use of the air-cooled condenser is reported to be capable of improvement by lowering the operating temperature. No data is yet available for the resulting performance.

EXAMPLE 7.01 BOLIDEN-NORZINK PROCESS

Description: - The gas is scrubbed in a packed bed tower with a solution containing $HgCl_2$. This reacts with the metallic mercury in the gas and precipitates it as calomel, Hg_2Cl_2:

$$HgCl_2 + Hg => Hg_2Cl_2$$

The calomel is removed from the circulating scrubbing solution and partly regenerated by chlorine gas to $HgCl_2$, which is then recycled to the washing stage. The mercury product bleed is either used for mercury production or stored. In the Norzink process part of the precipitate, the calomel, is electrolysed to give metallic mercury and chlorine gas which is reacted with the rest of the calomel to produce the reagent, $HgCl_2$, used in the scrubbing.

An alternative process uses sodium thiocyanate as the scrubbing medium and mercury is precipitated as the sulphide. This can be recovered in a primary mercury roaster.

Main environmental benefits: - Removal of mercury from gases and recovery of the mercury.

Operational data: - For a plant producing with a mercury input in the order of 400 ppm, sulphuric acid is produced with ~ 0.1 mg/l (ppm) of mercury in the acid. This corresponds to about 0.02 mg/Nm^3 in the feed gas to the acid plant.

Cross media effects: - Energy cost of operating the scrubber.

Economics: - Some cost data published indicate that the Boliden-Norzink process (and probably also the Bolchem process) has an investment cost of 200000 $US for about 200000 t/a acid in 1972. The operating costs published are 0.5 DEM/ tonne for the Boliden-Norzink process (1985).

Applicability: - Most mercury removal systems depending on the reagent used.

Example plants: - Germany, Finland, Sweden

Reference literature: - [tm 139 Finland Zn 1999]

7.3.2 Wastewater

Effluents arise from scrubbing and vacuum systems and from spillage and surface run-off. Mercury is universally removed from aqueous effluents by precipitation as mercury sulphide. Sodium sulphide is used as the regent and the pH of the effluent is controlled. Mercury sulphide is not soluble and is precipitated. Activated carbon is also used to remove final traces of mercury from effluents. Emissions to water of 0.05 mg/l are easily achievable provided that solids are removed efficiently, in some cases sand filters are used for this purpose. Sludges and spent carbon from primary mercury production are returned to the furnaces [tm 70, Mercury Expert Group 1998].

Another main effluent stream arises from the removal of mercury from some roaster off-gases. The mercury-removal step involves a gas-liquid contact tank with a solution of mercury chloride ($HgCl_2$). This mercury chloride reacts with metallic mercury from the gas to form a solid Hg_2Cl_2-precipitate ("calomel"). The precipitated slurry is removed and oxidised with Cl_2 to form a new $HgCl_2$ washing solution. Some of the slurry is de-watered by a filter press and sold as Hg_2Cl_2 for mercury recovery or disposed of as a special waste.

Effluents from the process are pre-treated locally for mercury-removal by reaction with zinc dust or by precipitation as HgS before processing in a final effluent treatment plant. Mercury sulphide can be recovered in the primary process.

7.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector; which for the production of mercury are mercury vapour, dust, fume, odours, SO_2, other acid gases, wastewater, residues such as sludge, filter dust and slag;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous section. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this section are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

Best Available Techniques are influenced by a number of factors and a methodology of examining the techniques is needed. The approach that has been used is given below.

First of all the choice of secondary process depends strongly on the raw materials that are available to a particular site. The most significant factors are their composition, the presence of other included metals, their size distribution (including the potential to form dust) and the degree of contamination by organic material.

Secondly, the process should be suitable for use with the best gas collection and abatement systems that are available. The fume collection and abatement processes used will depend on the characteristics of the main processes, for example some processes are easier to seal. Other processes may be able to treat low-grade materials more easily and therefore reduce the wider environmental impact by preventing disposal.

Finally, the water and waste issues have been taken into account, in particular the minimisation of wastes and the potential to reuse residues and water within the process or by other processes. Energy used by the processes is also a factor that is taken into account in the choice of processes.

The choice of BAT in a general sense is therefore complicated and depends on the above factors. The varying requirements mean that BAT is influenced mainly by the raw materials available to the site and the required throughput of the plant, the issues are therefore site specific.

The following points summarise the recommended methodology that has been used in this work: -

- Is the process industrially proven and reliable?
- Are there limitations in the feed material that can be processed?
- The type of feed and other materials contained in it influences process selection.
- Are there production level constraints? - e.g. a proven upper limit or a minimum throughput required to be economic.
- Can latest and efficient collection and abatement techniques be applied to the process?
- Can the process and abatement combinations achieve the lowest emission levels? The achievable emissions are reported later.

- Are there other aspects such as safety that are related to processes?

The collection and abatement techniques used with these processes were discussed under techniques to consider in the determination of BAT and when applied in combination with the metallurgical process will result in a high level of environmental protection.
As indicated in the general preface to this document, this section proposes techniques and emissions that are considered to be compatible with BAT in general. The purpose is to provide general indications of the emission and consumption levels that might be considered as an appropriate benchmark of BAT based performance. This is done by quoting achievable levels in ranges that are generally applicable to both new and upgraded plants. Existing installations may have factors, such as space or height limitations that prevent full adoption of the techniques.

The level will also vary with time depending on the condition of the equipment, its maintenance and the process control of the abatement plant. The operation of the source process will also influence performance as there are likely to be variations in temperature, gas volume and even the characteristics of the material throughout a process or batch. The achievable emissions are therefore only a basis from which actual plant performance can be judged. Process dynamics and other site specific issues need to be taken into account at a local level. The examples given in the section on techniques to consider in the determination of BAT give the concentrations associated with some existing processes [tm 137 Copper Expert Group 1998].

The pyrometallurgical and hydro-metallurgical processes that are used form the basis of BAT but additionally the factors described in Chapter 2 should be used in conjunction with them.

7.4.1 Materials handling and storage

The conclusions drawn for Best Available Techniques for the materials handling and storage stages are shown in section 2.17 of this document and are applicable to the materials in this chapter. In addition because of the vapour pressure of mercury, storage of the product in sealed and isolated flasks is considered to be BAT.

7.4.2 Process selection

For primary mercury production from cinnabar the use of a Herreschoff furnace is considered to be BAT. For other production either from gas treatment systems for other non-ferrous metals or from secondary raw materials it is not possible to conclude that a single production process is BAT.

7.4.3 Gas collection and abatement

The gas or fume collection systems used can exploit furnace-sealing systems and be designed to maintain a suitable furnace depression that avoids leaks and fugitive emissions.

Best Available Techniques for gas and fume treatment systems are those that use the BAT for mercury removal described in section 2.17. At the time of writing the performance of the scrubber based processes are uncertain for fine mercury particles and it is concluded that further investigation of the techniques in this application is needed before BAT can be confirmed and associated emissions given. For dust forming process stages a fabric filter is considered to be BAT. Fabric filters that use modern high performance materials in a well-constructed and maintained structure are applicable. They feature bag burst detection systems and on-line cleaning methods.

The sulphur recovery systems and the associated dust and metal recovery stages are those described in section 2.8 of this document.

Fume collection systems follow the best practice outlined in techniques described in section 2.7. The abatement systems that are considered to be BAT for the components likely to found in the off gases are summarised in the following table. There may be variations in the raw materials that influences the range of components or the physical state of some components such as the size and physical properties of the dust produced, these should be assessed locally.

Process Stage	Abatement option	Component in the off-gas
Ore grinding and conveying	Dust collection and fabric filter.	Dust.
Handling secondary material	Enclosed handling, scrubbing of ventilation gases.	Dust, Hg vapour Handling free Hg and dried material –
Primary or secondary roasting	Mercury condenser and mercury scrubber system *. Removal of sulphur dioxide.	Dust, SO_2, Hg vapour or mist. Depends on gas collection from furnace and condensers
Product handling	Enclosed filling station, scrubbing of ventilation gases.	Hg vapour. Depends on gas collection from furnace and launders –
Note * It has been reported that mercury from the condenser gases of the production from cinnabar are in the form of fine particulate and mat not be removed efficiently by some processes. It is concluded that further investigation is needed so that reliable data can be considered		

Table 7.5: Summary of abatement methods for components in the off-gas

7.4.3.1 Emissions to air associated with the use of BAT

The techniques listed above when used in appropriate combination are capable of preventing emissions to the environment. For all processes the total emissions to air are based on the emissions from:

- The materials handling and storage, drying, pelletising, sintering, roasting and smelting stages.
- Refining stages, distillation and packaging stages.

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 - 5 mg/Nm^3	Fabric filter.	A wet EP may be applicable to gases from slag granulation
SO_2	50 - 200 mg/Nm^3	Wet or semi-dry scrubber and fabric filter	Raw gas concentration and temperature may vary widely during a process and can affect the final SO_2 content.
Mercury	To be determined	To be determined	An investigation is needed to establish the most effective techniques when particulate mercury is present as a fine mist.
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 7.6: Emissions to air from ore grinding, roasting, distillation and associated processes for primary production of mercury

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Mercury	0.02 mg/Nm³	Mercury scrubber (Boliden, thiosulphate etc)	
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 7.7: Emissions to air from secondary production and production from base metals associated with the use of BAT in the mercury sector

The techniques able to remove fine mercury particles from the gas stream from a condenser system need to be investigated and reported.

Fugitive emissions are highly significant and can be predicted from the fume capture efficiency and can be estimated by monitoring (see section 2.7).

7.4.4 Wastewater

The emissions to water are based on a bleed from the scrubber and cooling systems.

Wastewater is neutralised with caustic soda and treated with sodium sulphide to precipitate mercury sulphide. The effluent passes through a carbon filter before discharge [tm 70, Mercury Expert Group 1998]. The achievable emission to water is < 50 ppb mercury.

7.4.5 Process residues

Roasted rock that is free of mercury is used for construction purpose. Other raw materials that have been roasted to remove mercury e.g. batteries, are used in precious metal recovery processes.

Sludges from the wastewater treatment process for both primary and secondary production contain mercury sulphide or calomel. For primary production this material is pelletised and returned to the furnace to recover the mercury. For secondary purposes this is not always possible and small quantities are disposed.

7.5 Emerging Technologies

A process integrated with primary mercury production is being developed to recover mercury that is removed from processes that are substituting other materials for mercury. This development will include the abatement of fine mercury particles and this technique will be available for primary mercury production. Details are not available at the time of writing.

8 REFRACTORY METALS

Refractory metals are high melting point metals that are characterised as well by other special physical and chemical properties, such as high density, inertness, corrosion and acid resistance etc. Zirconium has even the ability to capture slow neutrons, which gives this metal an important role by building nuclear power reactors. Refractory metals are produced both as metal ingot (buttons) by using electron beam furnaces and as metal powder that serves as raw material for powder metallurgical treatments like pressing and sintering.

8.1 Applied Processes and Techniques

The following sections will define the applied processes and technologies for the production of the most common and most important refractory metals. The production of ferro-alloys, which normally contain the same metals, will be discussed in detail in the next chapter of this document.

8.1.1 Chromium

Besides the use of chromium as an alloying element in the steel industry chromium metal is also widely used in other industrial sectors. In the chemical industry for instance chromium is needed in large quantities to manufacture pigments that are used to produce paints and inks. Another considerable amount of chromium is consumed as an electroplated protective coating, because chromium is corrosion resistant to a variety of corrosive materials at room temperature.

Chromium metal can either be made from chromite ore and concentrates by carbo- and metallo-thermic reductions or by electrolysis from chromic acid. In order to get chromic acid the chromite ore is roasted with sodium carbonate followed by a leaching process with sulphuric acid to produce sodium chromate that can further be transformed to chromic acid.

8.1.1.1 Production of chromium metal by metallo-thermic reduction

The thermic process uses carbon, silicon or aluminium as a reducing agent. The charge is automatically weighed and loaded into a bin at a computerised weighing station. The station utilises various abatement techniques to prevent airborne emissions. Once the charge is complete, the bin is taken to an enclosed room to mix the contents. To minimise dust in the workplace, a negative pressure is maintained by the ventilation fan within the blender room, which feeds through a filter unit to atmosphere. The bin is finally located on an automatic feed platform at the firing station

The firing pot is prepared by ramming refractory sand around a central former. Sand is fed from a storage hopper via a "sand slinger" and mixed with water. The pot is then vibrated in order to compact the sand. The feed hopper is fitted with an integral dust extraction and filter unit.

After ramming the firing pot, the inner surface is coated with a weak binder solution and dried under a gas fired hood before being transferred to the firing station. Combustion fumes from the drying hood are fed via a stack to atmosphere using natural convection.

The firing pot is located inside a firing chamber, which has a travelling fume hood, and integral feed chute above it. The raw material mix is automatically fed at a controlled rate into the firing pot, where the exothermic reaction takes place. Fume generated by the reaction is ducted to the main bag filter plant. After the evolution of fume has subsided, a reduced volume of extraction is provided to the firing chamber.

When the metal has solidified following the reaction, the firing pot is removed and transferred by crane to a cooling conveyor. This is partially enclosed by a hood and is ventilated by a number of extraction fans, which discharge to atmosphere outside the building. Disposable fibreglass filter panels protect the fan inlets.

On removal from the cooling conveyor (by crane), the firing pot is placed on a stripping bogie for transferral to a stripping booth. Inside the closed booth, the pot casing is hoisted off the solidified metal/slag. Debris from the pot lining falls into a hopper and is transferred to a vibratory sieve. Cartridge filter extraction units control emissions during these operations.

The stripped metal/slag and firing pot casing are retrieved by means of the stripping bogie. The firing pot casing is removed and returned to the pot preparation station for reuse. The slag is separated from the Chromium metal 'button' and sent to a despatch storage area. The button is lifted by crane from the stripping bogie and transferred to a bosh tank where water is used to reduce button temperature to below 100 °C. Extraction of the steam generated by boshing is by means of a fan and ductwork which discharges to atmosphere outside the building.

After cooling the metal button is transferred to other departments on site for cleaning, breaking, crushing and grinding to achieve the desired product size. Packaging of the material is carried out in accordance with customer requirements and may utilise FIBC's, drums and plastic bags. A process flow-sheet of the thermic chromium process is presented in the following figure.

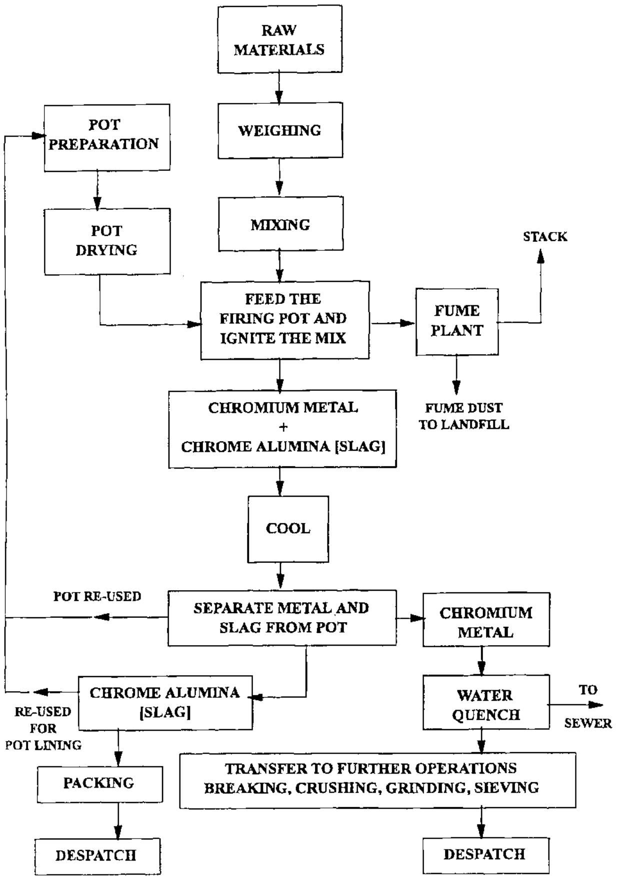


Figure 8.1: Production of chromium metal by the metallo-thermic process

The silico-thermic reduction is not sufficiently exothermic to be self-sustaining and must therefore be performed in an electric arc furnace. If the carbo-thermic process is used, the chromium oxide will be reduced by carbon in an electric arc furnace. The chromium metal produced by this process contains high amounts of carbon.

8.1.1.2 Production of chromium metal by electrolysis

In the electrolytic process normally high carbon ferrochrome is used as the feed material which is then converted into chromium alum by dissolution with sulphuric acid at temperatures at about 200 °C. After several process steps using crystallisation filtration ageing, a second filtration and a clarifying operation the alum becomes the electrolyte for a diaphragm cell. The process is very sensitive, however to a number of parameters, the most important being pH, catholyte temperatures, catholyte recirculation and density, current density and cathode preparation [tm 8 HMIP 1993]. The following table presents a schematic process flow-sheet of the electrolytic process using ferro-chrome as a raw material.

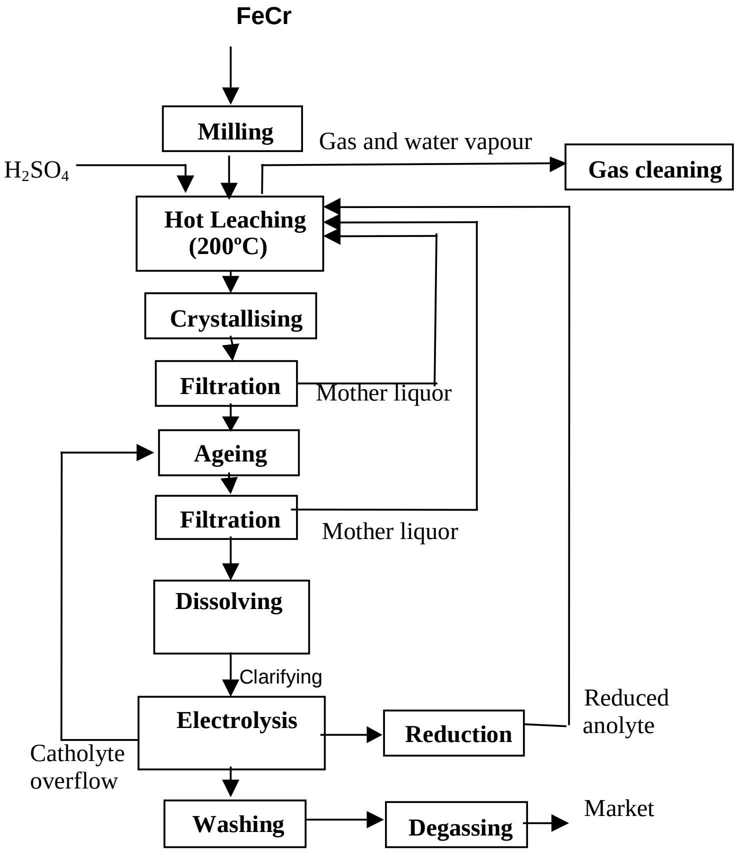


Figure 8.2: Production of chromium metal by electrolysis

The additional de-gassing stage is necessary because the carbon content of the electrolytic chromium is sometimes too high for further industrial applications. The cooled chromium metal is fragmented with a breaker prior to crushing and drumming. The generated slag can be reused as refractory lining or sold as abrasive or refractory material.

8.1.2 Manganese

Manganese metal is mainly used in the iron, steel and aluminium industry. In aluminium production for instance manganese is used as an alloying element improving the product hardness. For the production of pure manganese metal several processes are known [tm 107 Ullmanns 1996]:

- Electrolysis of aqueous manganese salts
- Electrothermal decomposition of manganese ores
- Silico-thermic reduction of manganese ores or slag
- Alumino-thermic reduction of manganese ores or slag
- Distillation of ferro-manganese
- Electrolysis of fused salts

From the above listed processes the first two are the most important ones. The other processes are not economically significant.

8.1.2.1 Electrolysis of aqueous manganese salts

The production of manganese metal by the electrolysis of aqueous manganese salts requires at first a milling of the manganese ore. Milling increases the active surface and ensures sufficient reactivity in both the reduction and the subsequent leaching steps. After milling the manganese ore is fed to a rotary kiln where the reduction and calcination takes place. These process is carried out at about 850 - 1000 ºC in a reducing atmosphere. As a reducing agent, several carbon sources can be used e.g. anthracite, coal, charcoal and hydrocarbon oil or natural gas. The calcined ore needs to be cooled below 100 ºC to avoid a further re-oxidation.

The subsequent leaching process is carried out with recycled electrolyte, mainly sulphuric acid. After leaching and filtration the iron content is removed from the solution by oxidative precipitation and the nickel and cobalt are removed by sulphide precipitation. The purified electrolyte is then treated with SO_2 in order to ensure plating of γ-Mn during electrolysis. Electrolysis is carried out in diaphragm cells [tm 8 HMIP 1993]. The cathode is normally made of stainless steel or titanium. For the anode lead-calcium or lead-silver alloy can be used. After an appropriate reaction time the cathodes are removed from the electrolysis bath. The manganese that is deposited on the cathode starter-sheet is stripped off mechanically and then washed and dried. The metal is crushed to produce metal flakes or powder or granulated, depending on the end use.

8.1.2.2 Electrothermal decomposition of manganese ores

The electrothermal process is the second important process to produce manganese metal in an industrial scale. The electrothermal process takes place as a multistage process. In the first stage manganese ore is smelted with only a small amount of reductant in order to reduce mostly the iron oxide. This produces a low-grade ferro-manganese and a slag that is rich in Mn-oxide. The slag is then smelted in the second stage with silicon to produce silico-manganese. The molten silico-manganese can be treated with liquid slag from the fist stage to obtain relatively pure manganese metal. For the last step a ladle or shaking ladle can be used. The manganese metal produced by the electrothermal process contains up to 98% of Mn.

8.1.3 Tungsten

Tungsten is the refractory metal with the highest melting point, which is due to the extremely high bonding energy. This consequently leads to other extended properties, such as a very low vapour pressure, compressibility and thermal expansion.

Tungsten is used for a variety of different industrial applications. According to the amount of metal required, tungsten is mainly used to produce hardmetal and metal carbide powder that can further be treated by powder metallurgical methods to produce hardmetal tools. Tungsten is also consumed in considerable amounts as an alloying element in the steel industry. Another major field is the use of tungsten as an alloying element with other non-ferrous metals and as tungsten compounds in the chemical industry.

The high melting point of tungsten precludes the use of smelting techniques. Beneficiated ores and concentrates are therefore processed by hydrometallurgy using acid or alkaline digestion to produce an intermediate, chemically refined salt. This is then calcined to oxide and reduced to metal powder. Powder metallurgy techniques, in particular compacting and sintering are then employed, following by a range of fabrication processes including extrusion, forging and rolling. Carburisation of metal powder to form tungsten carbide may be further cemented with cobalt to form hardmetal [tm 8 HMIP 1993]. Due to the available raw materials, tungsten can either be made from primary or secondary materials. A typical tungsten flow-sheet is presented in the next figure.

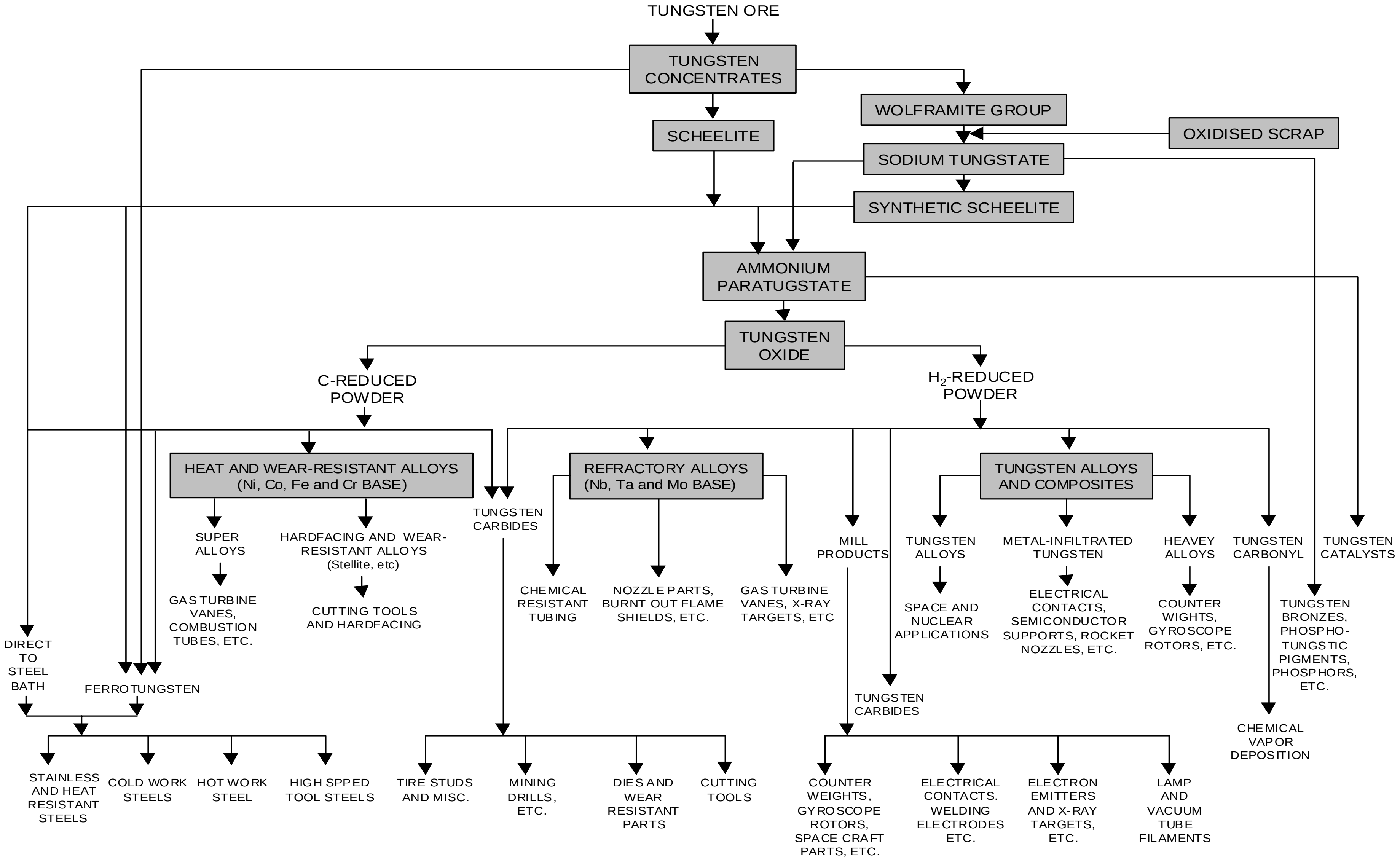


Figure 8.3: Tungsten flow-sheet
[tm 008, HMIP 1993]

8.1.3.1 Production of tungsten metal powder from primary raw material

The first step for the production of tungsten, which is normally carried out directly at the mining site, is crushing and milling of the raw material in order to liberate the tungsten mineral from the gangue material. The next stage is the production of ammonium paratungstate (APT) by hydrometallurgical methods.

The Scheelite and Wolframite concentrates that are mostly used are dissolved by pressure leaching to produce a sodium-tungsten solution. The leaching process dissolves also other elements such as silicates, thiomolybdate as well as elements like As, Sb, Bi, Pb and Co that need to be removed from the solution by purification. Thiomolybdate can further be used for molybdenum production. The purified sodium tungstate solution is then converted into ammonium tungstate solution. The conversion of the sodium tungstate solution can be carried out either by a solvent extraction or an ion exchange process. In the subsequent crystallisation step, the water and ammonia are distilled. At the same time as the distillation takes place the pH-value decreases and the APT crystallises out of the solution. The solid APT is then calcined commonly in a rotary kiln in order to obtain tungsten oxides.

The two oxidic forms utilised for tungsten powder production are yellow and blue oxides (WO_3 and W_4O_{11}). Yellow oxide is produced by heating APT in air at temperatures above 250 ºC. Blue oxide can be produced if the calcining step is carried out with exclusion of air at temperatures from 400 to 800 ºC. The production of blue oxide is usually preferred, because a smaller amount of reducing agent is then required in the subsequent reduction stage.

The reduction of tungsten oxides (blue or yellow tungsten oxide) to tungsten metal powder is today normally carried out by hydrogen reduction. For the reduction either a rotary furnace or a pusher furnace is used, in the latter case the powder passes through the furnace in boats. Today also modern automated band furnaces are used for the production of tungsten powder. Hydrogen passes counter-currently to the oxides through the furnace, water vapour is formed in the reduction process in the furnace. The hydrogen is partly recirculated. Possible occurring dust is recovered by e.g. bag filter, wet scrubber or similar equipment The important process parameters are the furnace temperature, the amount of oxides charged to the furnace per unit time, the rate of hydrogen circulation and the depth and the porosity of the bed or boat. The process of producing tungsten metal powder is presented in the next figure.

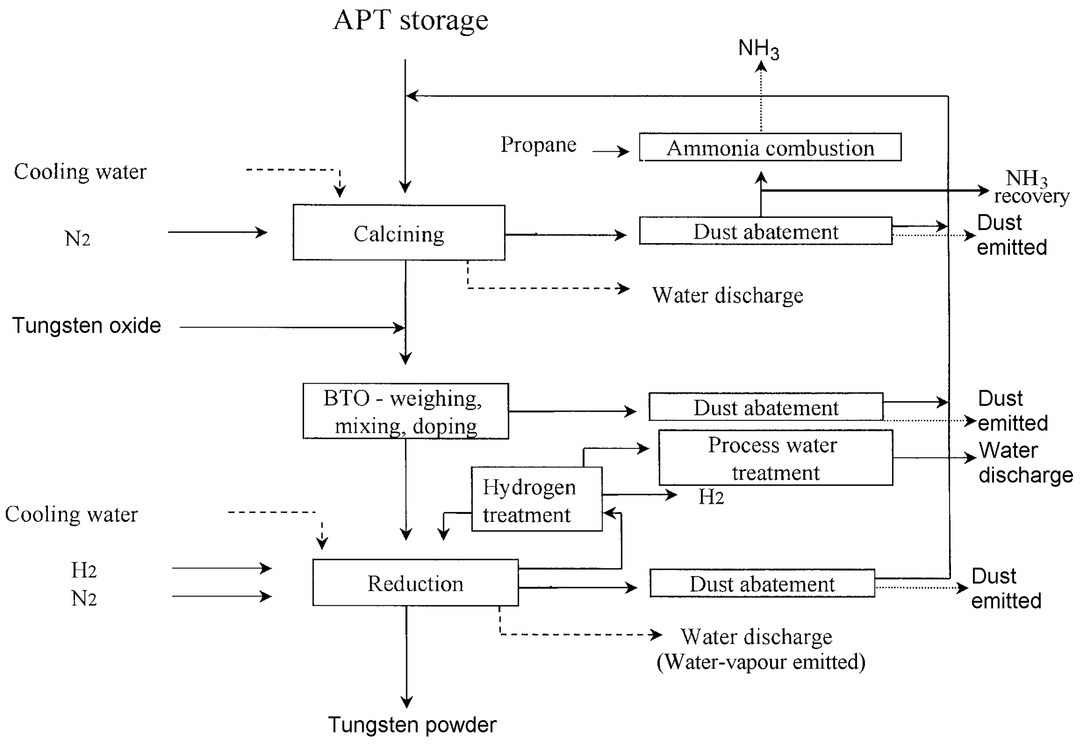


Figure 8.4: Production of tungsten metal powder
[tm 182, ITIA 1999]

Most of the tungsten powder is converted to tungsten carbide. The tungsten powder is mixed with black carbon in a ratio giving the monocarbide after the reaction. Pusher or batch furnaces can be used for the carburisation.

- **Pusher furnace:** The mixture of W and C is charged into graphite boats or crucibles and passes through the furnace continuously. Hydrogen is used as a protective atmosphere and passes through the furnace counter-currently and is flared off after exit using a propane flare as ignition control. The furnaces are electrically heated and operate in the temperature range of 1100 – 2000 °C.
- **Batch furnace:** The mixture of W and C is loaded into paper cylinders or other suitable container and densified by tapping. The material is heated by induction in a water-cooled coil with hydrogen as protective atmosphere. Hydrogen is flared off when leaving the furnace. The process takes place at a temperature range of 1800 – 2000 °C.

The process of carburisation tungsten metal powder is shown in the following flowsheet.

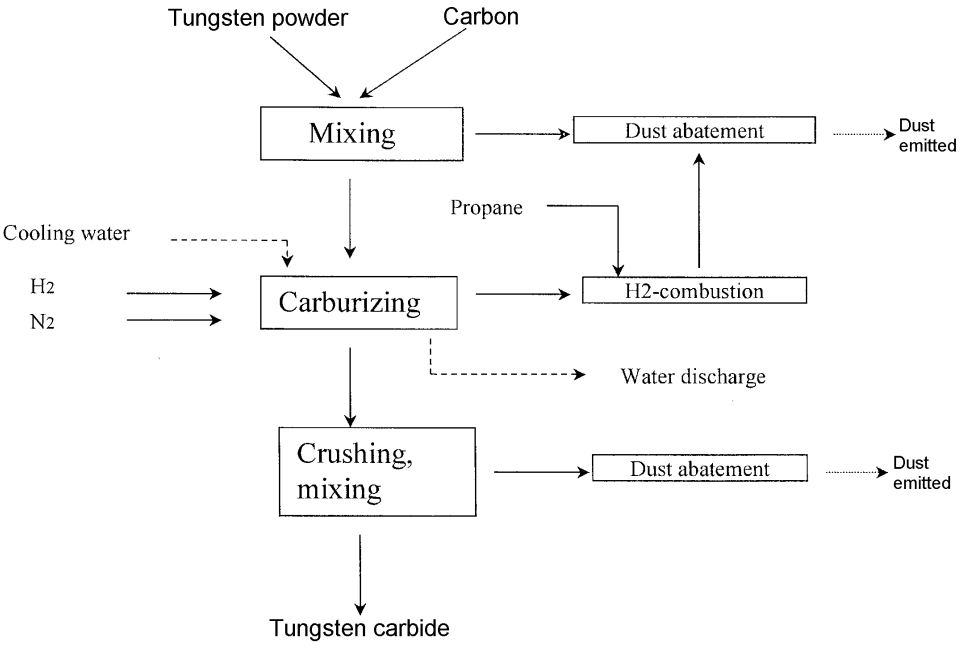


Figure 8.5: Production of tungsten carbide
[tm 182, ITIA 1999]

8.1.3.2 Processing of tungsten secondary raw material

The increasing availability of tungsten scrap from various sources led to the development of different processes for processing tungsten secondary raw material (tungsten hardmetal scrap). The three major processes for the recycling of tungsten scrap (tungsten carbide that contains some cobalt as a binder) are the Goldsteam process, the Zinc process and the Leach-Milling process [tm 8 HMIP 1993].

In the **Goldsteam process** the fragmented carbide is carried in a stream of air at high velocity and collides with a stationary target. The impact at below ambient temperatures creates adiabatic cooling and breaks the embrittled carbides. The products are air classified and the fines collected, the oversize being recirculated. The process is limited in its application with hardmetal as very high cobalt levels render the material ductile, although this may be mitigated by preheating and rapid quenching of the hardmetal.

In the **Zinc process** the scrap is contacted with molten zinc, which forms an amalgam with the cobalt and effectively breaks up the cemented carbide. After full penetration of the scrap, the zinc is removed by vacuum distillation, leaving the hardmetal as a spongy material, which can easily crushed. After crushing, milling and sieving the powder can be used as a raw material in the manufacture of graded, ready to press powder. The limitations of the process are on the size of the pieces to be retreated and the need for double zinc distillation. The zinc process is operated batchwise, with the scrap and zinc placed in a reactor or in graphite crucibles. After around 12 hours at 900 ºC the pressure is reduced and the zinc distilled, requiring typically a further 15 hours.

In the **Leach-Milling process** the pieces of scrap are leached with batches of mineral acid in a lined mill. The cobalt dissolution reaction is slow and the recovered carbide has undesirable high oxygen content. Further processing to recover the cobalt is necessary, and the process now finds little usage in modern plants.

Contaminated cemented carbide scrap, turnings, grindings and powder scrap are oxidised and chemically processed to APT in a way similar to that used for the processing of tungsten ores. If present , cobalt tantalum and niobium are recovered in separate processing lines.

8.1.4 Vanadium

Vanadium is consumed in general as an alloying component for the production of the iron-vanadium alloy called ferrovanadium. The development of vanadium technology started at the beginning of the fifties effectively and was essentially related to ferrovanadium and to certain vanadium compounds. Another major and important metallurgical application was developed in the 50s. Vanadium became the vital constituent of the multi-component titanium alloys for aerospace applications. The major potential and applications of alloys can be found in nuclear reactors and superconductors. The use of vanadium in the chemical industry is based on the properties of vanadium, especially its changing of oxidation states in vanadium salts. Thus the most important behaviour of vanadium compounds in the chemical industry can be used in catalysts of key processes, such as the production of Sulphuric acid, EPDM, Adipinic- (Nylon), Maleinic- or Phthalic acid. Furthermore vanadium oxides, as the active component in DeNOx-catalysts, has been used for the reduction of nitrogen-oxides in the emission control of power plants (incineration facilities). New developments of vanadium salts are concentrated in the production of alternative yellow and orange pigments to replace ecologically critical chromium pigments.

8.1.4.1 Production of vanadium metal from primary raw material

The majority of vanadium metal used today is produced from vanadium slag, which is obtained from a pre-reducing process of titanomagnetite ore in an electric arc furnace. The electric arc furnace produces pig iron that is oxidised further in an oxygen blown converter in order to transfer the vanadium into the slag. The vanadium containing slag is then used as the worlds major raw material source to produce vanadium oxide, which can further be transformed by reduction to vanadium metal, especially vanadium containing alloys.

In the first step of the process the vanadium slag is ground and liberated from the iron granulates. After grinding, commonly alkali metal salts are blended and fed to a multiple hearth furnace or rotary kiln where roasting, a disintegration of the slag under oxidising conditions, takes place at about 700 – 850 °C. Thus, both the oxidation of vanadium to V(V) and the formation of a water-soluble salt, can be achieved. Afterwards, the roasted vanadium slag is leached to form high concentrated vanadium containing liquid phase. The separation and purification of the vanadium from the liquid phase can be usually done by precipitation of an ammonium-containing vanadate by controlling pH-value and temperature. The achieved precipitate is filtered, dried and can be alternatively transformed in several process steps to high purity vanadium oxides, such as vanadium pentoxide, vanadium tetroxide or vanadium trioxide as function of temperature and reduction/oxidation conditions.

In order to gain vanadium metal, the vanadium oxides can either be treated by carbo- or metallo-thermic reduction. The carbo-thermic reduction forms vanadium metal with high oxygen and carbon contents, which is the reason for the rare use of this process. The more common method is the metallo-thermic process using calcium or aluminium as the reducing agent. By using calcium as a reductant the reaction takes place in a closed pressure furnace that is lined with pure magnesium oxide. The alumino-thermic process of exclusively vanadium pentoxide is a self-sustaining process without additional requirements of energy. The process is carried out in temperature resistant equipment where a mixture of high purity vanadium pentoxide is reduced by aluminium powder.

Melting in an electron beam furnace allows both the direct purification of the vanadium metal and the use of reduced vanadium oxides by the alumino-thermic process.

8.1.4.2 Processing of vanadium secondary raw material

Vanadium is present in a variety of natural materials such as vanadium containing crude oil or bauxite that is used for the alumina production. If these sources are used for energy generation or as raw material in technical processes, vanadium is sometimes transferred to the residues e.g. boiler ashes or by products e.g. salts from the alumina production. During the last twenty years several different processing technologies had been developed in order to gain purified vanadium oxides from these secondary raw material sources. The recovery of vanadium from scrap is sometimes related to the recovery of other refractory metals, for instance by using spent catalysts either vanadium or molybdenum can be recovered.

Residues like vanadium containing oil or spent catalysts can be digested with sulphuric acid and further transformed by an extraction step into an acid solution of vanadyl sulphate. In the subsequent process step the solution is treated by oxidation and precipitation, which produces a precipitate that is called red cake, a vanadium polyvanadate. The red cake can then be calcined to form an alkali containing vanadium pentoxide.

Another method for processing vanadium-containing residues presents a combination of a pyrometallurgical and hydrometallurgical method. The vanadium content of the residues is oxidised at elevated temperatures to produce a water leachable alkali metal vanadate. After the leaching step the vanadium is precipitated and calcined in order to generate vanadium pentoxide.

In the production of alumina, which is described in detail in Chapter 4 of this document, a salt is generated as a residue or by-product. If the alumina production is based on bauxite that contains high levels of vanadium, the salt can further be used to obtain vanadium pentoxide. In comparison to the other vanadium pentoxide production using vanadium slag as raw material this process causes a wastewater problem because the salt contains also arsenic that it transported into the leach liquor and further to the wastewater.

The vanadium pentoxide produced either from primary or secondary raw material can be reduced by a variety of different metallurgical processes to produce metallic vanadium. The following flow-sheet demonstrate the different production routs of vanadium pentoxide and the subsequent processes to produce vanadium metal.

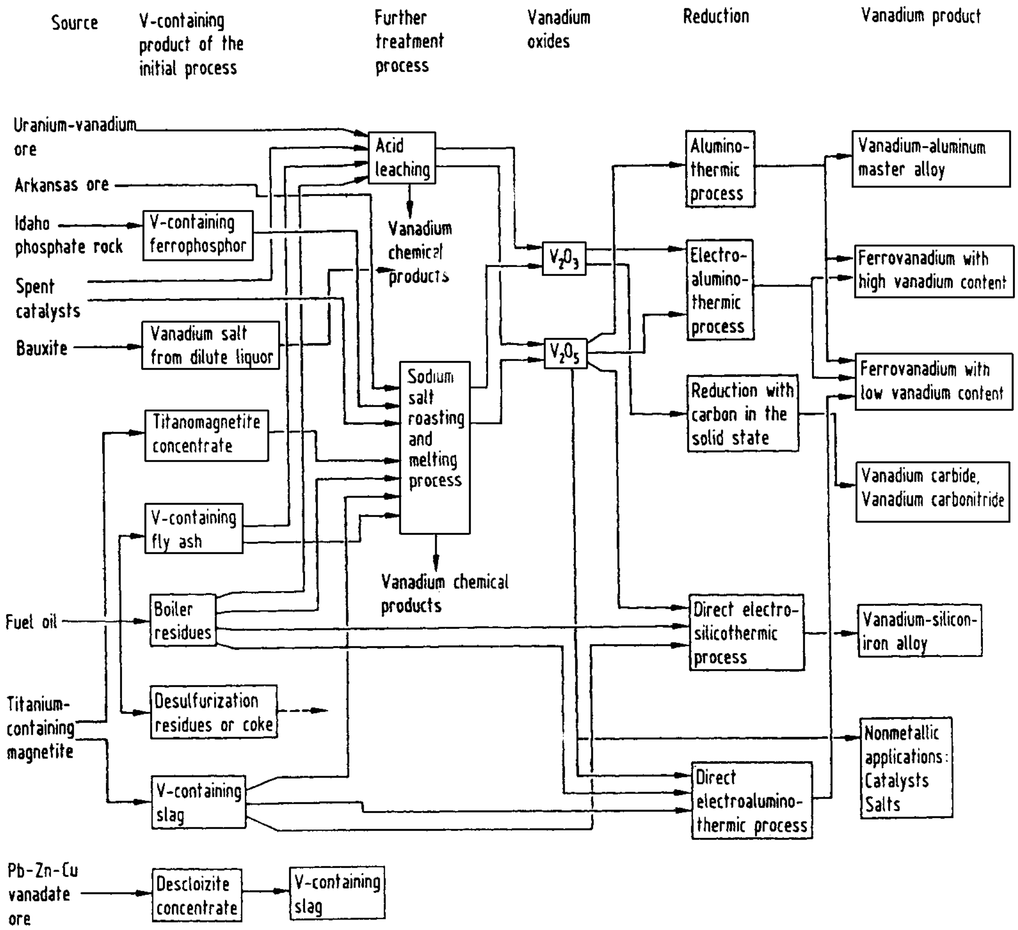


Figure 8.6: Production of vanadium pentoxide and vanadium metal [tm 008, HMIP 1993]

8.1.5 Molybdenum

Molybdenum in its pure stage is a lustrous grey metal that can be used for a wide range of industrial applications. The use of molybdenum starts with its demand as an alloying element in the steel production combines the use of molybdenum compounds in the chemical industry and ends with a product used by lubricant manufacturers.

Molybdenum can even be obtained from primary ore sources or from secondary ores that means molybdenum is also produced as a by-product by copper mining. The molybdenum-containing mineral is first ground and floated in order to separate the molybdenite from the host rock. The molybdenite ore is then roasted to remove the sulphur and change the sulphide to oxide. Besides the use of technical grade molybdenum trioxide (MoO_3) in the production of ferro-alloys, it is also the starting compound for all other molybdenum containing products such as ammonium dimolybdate, sodium molybdate and molybdenum metal [tm 107, Ullmanns 1996]. The conversion of concentrated molybdenite ore (molybdenum sulphide) into technical grade molybdenum trioxide for the metallurgical or chemical industry is performed by calcination and roasting. The process of molybdenite roasting is described in detail under the production of ferro-alloys in Chapter 9 of this document.

8.1.5.1 Production of molybdenum metal powder

Molybdenum metal powder can be produced in a two-stage process by reducing molybdenum trioxide (MoO_3) with hydrogen. Besides molybdenum trioxide compounds like ammonium hexamolybdate and ammonium dimolybdate may also be used for the powder production. In the first step of the process MoO_3 is reduced at about 600 ºC in an exothermic process to molybdenum dioxide (MoO_2). The second reduction stage, in which the metal powder is produced, takes place at ca. 1050 ºC. The process can carried out either in a pusher furnace, a walking beam furnace or a rotary kiln where the hydrogen is led in an countercurrent flow. Pressing and sintering in order to get compact molybdenum metal can then be used to process the powder. Melting of molybdenum in a vacuum arc furnace or an electron beam furnace is another way to produce compact molybdenum metal.

8.1.5.2 Processing of molybdenum secondary raw material

Molybdenum is used in large scale as a catalyst in the petrochemical industry. Spent catalysts are therefore a valuable source of secondary raw material, which can be used for molybdenum recovery. The recovery of molybdenum and the recovery of the vanadium content can follow the following process steps. [tm 107 Ullmanns 1996].

- Initial heat in air at 600 ºC to remove the residual sulphur, carbon and hydrocarbons and to oxidise the metals to soluble molybdate and vanadate.
- A leaching step resulting in preferential solubilisation of molybdate and vanadate, leaving the nickel-cobalt- alumina as a solid.
- Separation of the molybdenum and vanadium.
- Treatment of the Ni-Co-alumina residue to recover the nickel and cobalt content.

8.1.6 Titanium

Titanium is consumed by the industry mostly as titanium dioxide (TiO_2) that is used as pigments in the paint, plastic and paper industry, and as titanium metal. Titanium metal even as a pure metal or alloys is used in applications where the relatively high cost of the metal is justified by its outstanding characteristics. Due to the high strength-to-weight ratio of its alloys and their corrosion resistance, titanium is important and widely used for high performance aircraft engines and airframes.

There are commonly two applied processes established for the production of titanium metal. The Kroll-process, where titanium-tetrachloride (TTC) is reduced with molten magnesium to produce pure titanium metal as well as titanium sponge. The Hunter-process uses molten sodium for the reduction of TTC. Due to the reactivity of molten titanium the production of titanium ingots is then carried out in special vacuum furnaces

Titanium-tetrachloride can be manufactured from titanium oxide containing ore and from titanium rich slag that is generated by the metallurgical treatment of ilmenite ore. The chlorination is today exclusively carried out by a fluidised–bed process. The choice of a fluidised bed reactor is due to its higher reaction rate and the improved heat-transfer and therefore the higher achievable reaction temperatures. After the chlorination a subsequent separation and purification process is normally necessary in order to obtain a titanium-tetrachloride of a purity of about 99.9%.

8.1.6.1 Production of titanium metal sponge

As already mentioned above the production of titanium metal sponge can be carried out either by the Kroll- or the Hunter-process. In the Kroll-process, pure titanium–tetrachloride (TTC a colourless, fuming liquid) is reduced by reaction with molten magnesium under an inert gas atmosphere. The reaction takes place in a reaction vessel that is constructed of stainless or carbon steel, sometimes with titanium coated interior. A typical rector for the production of titanium sponge is shown in the next figure.

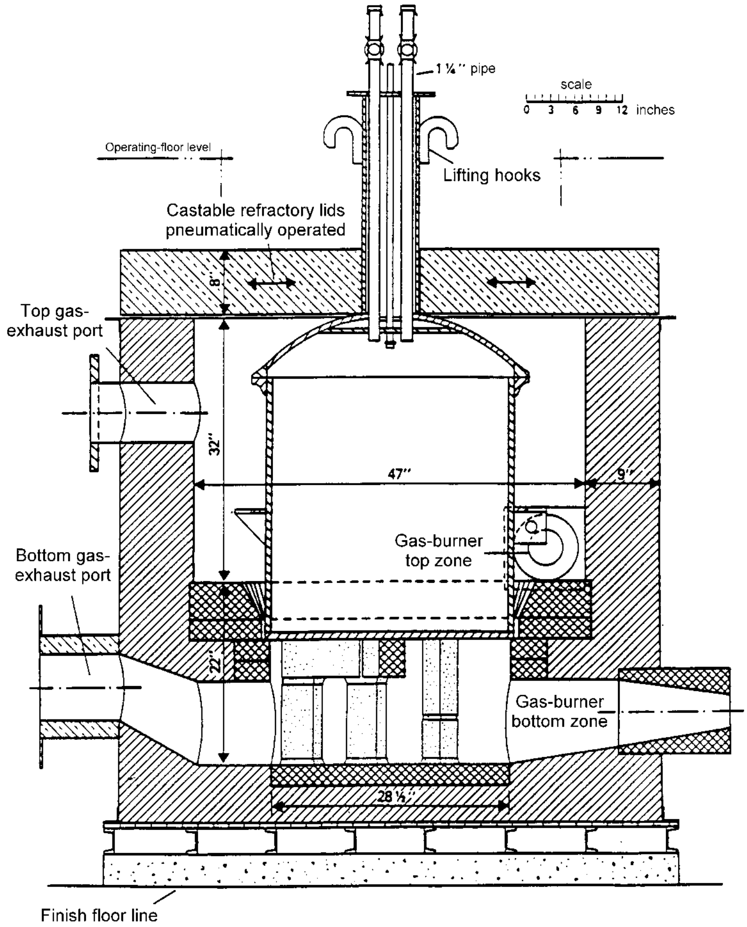


Figure 8.7: Reaction vessel of the titanium production using the Kroll process [tm 008, HMIP 1993]

The rector is first charged with oxide free magnesium and argon gas. When the magnesium is molten by using external heating, TTC is carefully charged to the reactor. Due to the exothermic nature of the reaction, the process can be operated and controlled by the rate of adding TTC to the reactor. The temperature range goes from 850 to 950 °C, where the lower temperatures gives longer reaction times but purer titanium sponge. The process produces titanium metal sponge intimately mixed with magnesium chloride and other impurities such as unreacted magnesium, TTC and some sub chlorides of titanium. These impurities can be removed by using the following techniques [tm 008 HMIP 1993].

- Acid leaching with dilutes nitric or hydrochloric acid
- Purging the reaction vessel and its contents with argon at 1000 ºC, thus the volatilising and removing the impurities.
- Vacuum distillation at a pressure of 0.2 mm mercury and a temperature of about 960 - 1020 ºC for 30 – 60 hours.

The Hunter-process, in which TTC is reduced with metallic sodium has lost its importance and is now mostly replaced by the Kroll-process.

The titanium sponge can be melted in order to obtain titanium ingots by using the consumable electrode vacuum arc melting process.

8.1.6.2 Processing of titanium secondary raw material and titanium sponge

The growing titanium production has consequently increased also the availability of titanium secondary raw material. The melting operation to produce titanium ingots by reusing titanium secondary raw material but as well melting titanium sponge is conducted in vacuum in specially designed furnaces. Batches of titanium scrap and titanium sponge are mixed and pressed in order to form blocks. The blocks are welded together to produce a consumable electrode. The electrode is then installed in the furnace chamber in a manner, where a cooled copper crucible, which collects the molten titanium, encloses the bottom end of the electrode. An arc is struck between the lower end of the electrode and the bottom of the crucible and the electrode is moved downwards as it is consumed.

Untreated titanium scrap can also be used directly as an additive to steel, nickel, copper, aluminium or other metals, and for the production of ferro-titanium.

8.1.7 Tantalum

Tantalum metal plays an important role in the production of electronic components, chemical equipment and the aerospace technology e.g. manufacture of electronic capacitors or heat shields for rocket boosters. Tantalum is also used in the fabrication of corrosion resistant process equipment like heat exchangers for acid liquids, columns, diaphragms etc.

8.1.7.1 Production of metallic tantalum from primary raw material

The production of metallic tantalum can be based on both, tantalum-containing minerals or tantalum rich slag that arises from smelting of tin concentrates. The recovery of tantalum from tin slag has increase in resent years and present today about 30% (worldwide) of the total tantalum production. The production of tantalum and niobium oxides from tin slag is presented in the next figure.

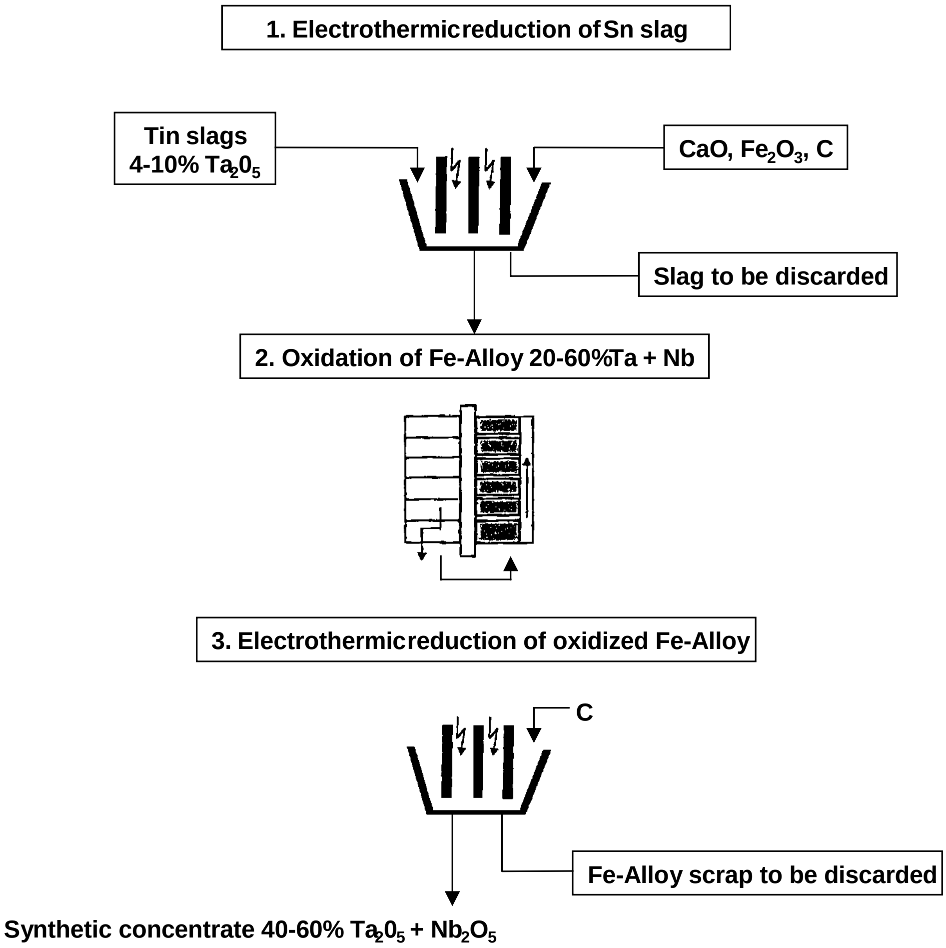


Figure 8.8: The production of tantalum and niobium oxides from tin slag

The tantalum-containing mineral is first crushed and treated by flotation and subsequent leaching and concentrated by flotation or other benefaction processes. The concentrate is digested in hydrofluoric acid. Ta and Nb subsequently is extracted by organic solvents in order to obtain potassium heptafluorotantalate as an intermediate product. The potassium heptafluorotantalate is then reduced by sodium to tantalum powder. To produce a pure metal powder normally two processes can be used. The first process is carried out by de-oxidation of the tantalum powder with magnesium or a vacuum thermal treatment under protective gas. The second process takes place by melting the powder in an electron beam furnace (EBM). Due to the high melting point of tantalum, most of the impurities presented in the powder are volatilised and captured by the furnace off-gas. The purified powder can then further be used for the production of semi-finished products or the fabrication of tantalum capacitors. The tantalum process is summarised in the next figure.

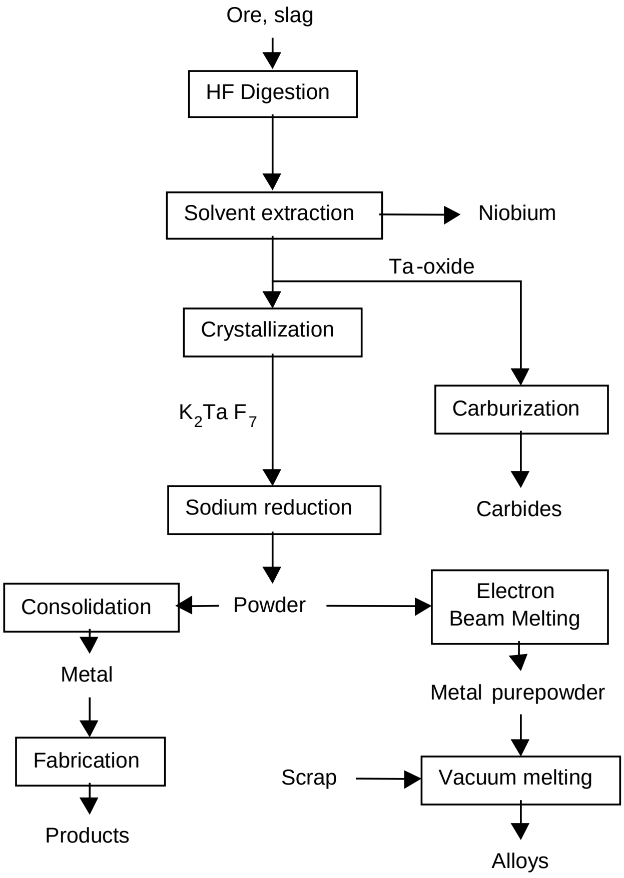


Figure 8.9: Production of pure tantalum metal powder

8.1.7.2 Processing of tantalum secondary raw material

The secondary raw materials used to produce tantalum are scrap consisting of unoxidised tantalum and oxidised tantalum related with other oxidised metals. The unoxidised tantalum scrap e.g. sintered parts, can be re-melted in an electron beam furnace or treated by de-hydrogenation in an vacuum furnace in order to re-produce tantalum powder. The second type of scrap represents the oxidised tantalum, for instance oxidised tantalum anodes coated with manganese dioxide or with conductive silver [tm 107 Ullmanns 1996]. This scrap can be treated with nitric or hydrochloric acid and results in a residue containing of oxidise tantalum. Alternatively the scrap that contains manganese dioxide can be melted directly by reducing the oxides in argon-hydrogen plasma to tantalum metal.

8.1.8 Niobium

Niobium is a refractory metal that is closely related to tantalum, and offers therefore nearly the same corrosion resistance as tantalum but a melting temperature, which is close to the melting point of molybdenum. Niobium is used as tubing in nuclear reactors because of its resistance to neutron bombardment. Niobium is as well used for rocket nozzles and jet engines because of the extended strength and oxidation resistance at the low weight of niobium.

8.1.8.1 Production of niobium from primary raw material

In primary raw material like columbite and tantalite niobium always occurs together with tantalum and other elements. In order to separate both metals the production of niobium needs the same separation process as it is used by the production of tantalum. After a series of different unit operations the pre-treatment process end up with niobium pentoxide as an intermediate product. Niobium pentoxide can be used in the chemical industry or further be reduced to niobium metal powder and niobium carbide. The processing of niobium and tantalum compounds is shown in the following figure.

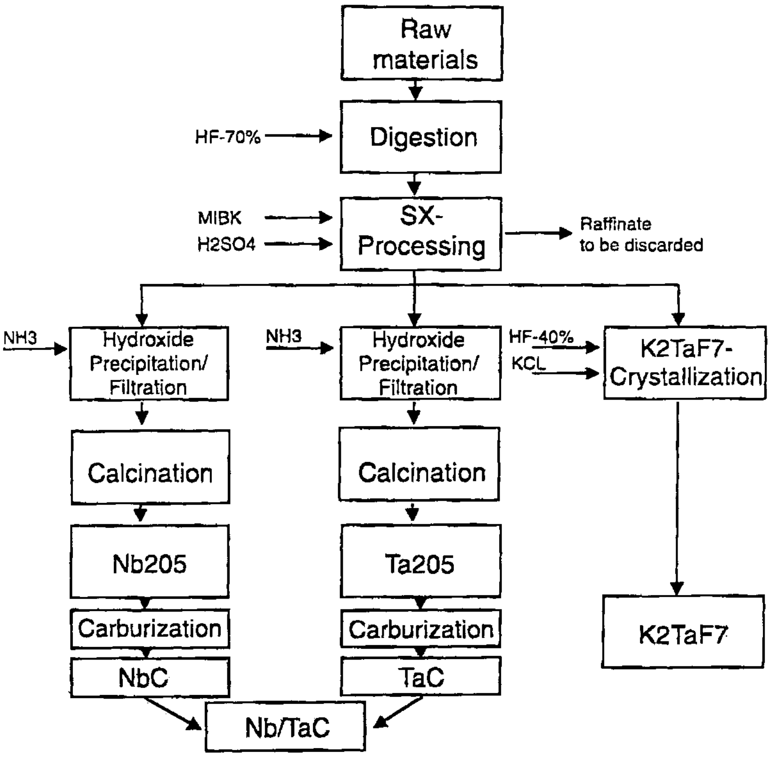


Figure 8.10: Processing of niobium and tantalum compounds

The production of niobium metal can be carried out by carbo-thermic or metallo-thermic reduction of niobium pentoxide, whereas the most important process is the reduction of niobium pentoxide with aluminium. The alumino-thermic process today produces almost 90% of niobium metal. The process is carried out under vacuum in an electric arc furnace and produces a low-oxygen and carbon free niobium metal.

For the carbo-thermic reduction, niobium pentoxide is mixed with carbon, pelletised and reduced in a vacuum furnace. The process that takes place at about 1950 °C and produces a niobium metal with a high carbon and oxygen content that needs a further refining step.

The refining step is necessary in order to remove the impurities, which are carried into the process by the raw material or introduced during the process. The refining takes place at high temperatures using an electric arc or electron beam furnace. Due to the high melting point of niobium most of the impurities are removed from the melt by vaporisation. To obtain a sufficient refining result the crude niobium needs a second refining cycle. The refining and electron beam melting process generates a highly purified niobium metal that can be used for high-frequency superconductors.

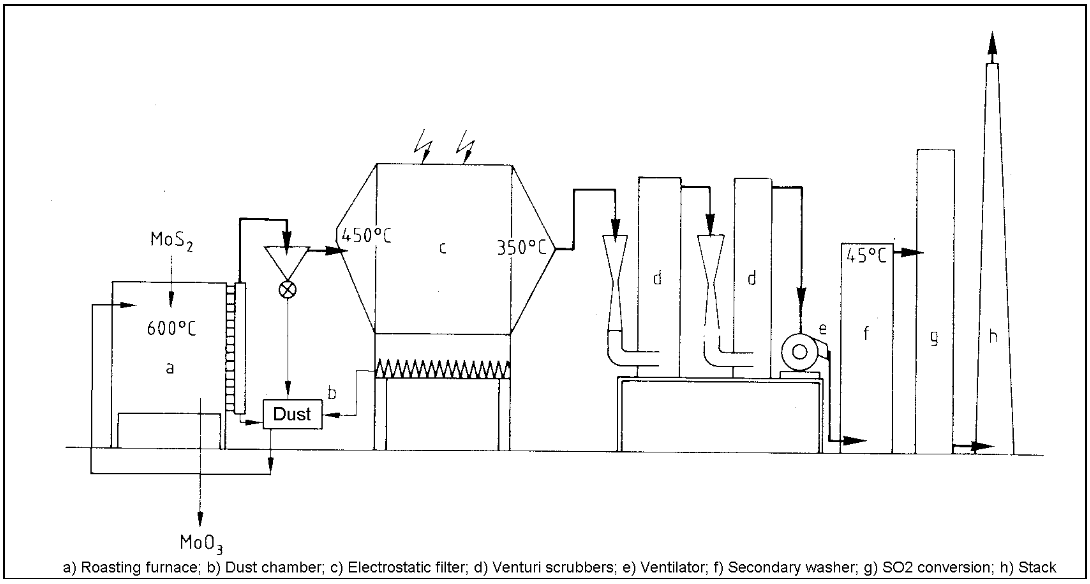
8.1.9 Rhenium

Rhenium, the refractory metal with the third highest melting point has only recently being exploited for a commercial use. Less than one quarter of the consumption of rhenium is in the form of alloys in which rhenium is a very small but important constituent. The biggest application is in platinum-rhenium catalysts used to produce lead free patrol. Other uses include thermocouples, reforming catalysts and a variety of electrical applications.

Rhenium metal is exclusively produced as a by-product from the molybdenite roasting process, where rhenium is volatilised and exits with the roaster off-gas. The rhenium can then be recovered from the off-gas steam be high-energy scrubbers.

8.1.9.1 Rhenium recovery by molybdenite roasting

The roasting process of molybdenite ore generates large amounts of dust and sulphur dioxide and also vaporised rhenium in the form of rhenium heptoxide (Re_2O_7). The rhenium escapes with the roaster off-gas because of its high vapour pressure. Rhenium heptoxide and selenium oxide present in the off-gas can be removed from the waste gas stream be using a wet scrubbing operation. The recovery of rhenium from the flue gases in the roasting of molybdenite is shown schematically in the next figure [tm 107 Ullmanns 1996].



a) Roasting furnace; b) Dust chamber; c) Electrostatic filter; d) Venturi scrubbers; e) Ventilator; f) Secondary washer; g) SO2 conversion; h) Stack

Figure 8.11: The recovery of rhenium from the flue gases in the roasting of molybdenite

Because of the ability of rhenium heptoxide to dissolve in water it is transferred easily into the scrubbing liquor. The scrubbing water is recirculated to the scrubber in order to get a higher rhenium concentration. The concentrated scrubbing liquor that contains about 0.2 to 1.5 g/l of rhenium can then be treated by chemical precipitation or preferable by the use of ion exchangers in order to obtain rhenium metal.

8.1.9.2 Production of rhenium metal

After removal of the rhenium content from the roaster off-gas it can be recovered from the scrubbing liqueur by precipitation as its sparingly soluble sulphide or the use of ion exchangers. Further treatment with strong mineral acids leads to the intermediate product ammonium per-rhenate. Ammonium per-rhenate can then be reduced with hydrogen in order to obtain rhenium metal powder. The reduction process occurs as a two-stage process. In the first stage that takes place at about 300 – 350 ºC rhenium dioxide will be produced. The second stage reduces the rhenium dioxide at 800 ºC to rhenium metal that can be obtained from the process at pure metal powder. The metal powder can then further be compressed and sintered in order to get pellets or large workpieces.

8.1.10 Zirconium and Hafnium

The sister metals zirconium and hafnium both have an important role in the nuclear industry because of there excellent metallurgical and corrosion resistant properties in the extreme environment of the nuclear core while having exactly the opposite effect on thermal neutrons. Besides this zirconium is also used in the chemical industry as well as Zircon bricks are needed as furnace linings.

The production of zirconium and hafnium metal starts with mixing together zircon concentrates and carbon. The mixture can then be chlorinated in a fluidised bed reactor. The zirconium-chloride can be removed from the reactor off-gas by condensation that is controlled by the temperature. Dissolution in a low melting fused salt eutectic followed by vaporisation of a zirconium-hafnium-chloride. Separation of zirconium and hafnium is carried out by solvent extraction where zirconium or hafnium can selectively be extracted depending on the extractant that is used. Metal production uses the Kroll-process, where the zirconium/hafnium tetra-chloride is sublimed and reduced with magnesium and magnesium-chloride. The product of this process step can then be treated by vacuum arc refining to the final metal.

8.2 Present Emission and Consumption Levels

The manufacturing of refractory metals normally takes place at high temperatures. The environmental impact on air, water and land can be classified as follows.

- Consumption of raw material and energy
  - Raw material and energy consumption

- Emissions to air
  - Dust and fume emissions from smelting, hardmetal and carbide production
  - Other emissions to air are ammonia (NH_3), acid fume (HCl), hydrogen fluoride (HF), VOCs and heavy metals.
  - Emissions of noise and vibrations

- Solid residues, wastes and by-products
  - Dust, fume and sludge
  - Slag

- Wastewater emissions
  - Overflow water from wet scrubbing systems
  - Wastewater from slag and metal granulation
  - Blow down from cooling water cycles

8.2.1 Consumption of raw material and energy

The available data of the consumption of raw material and energy for the production of refractory metals are presented in terms of specific input factors based on a tonne of produced product in the following tables.

	Cr	**W**
Ore and concentrates kg/t	Chrome oxide	n.a.
Energy consumption kWh/t	139	1000 - 1500 (APT-production) 3500 - 12000 (Carbide production) 1500 - 2500 (Zinc process)
Gas m^3/t	6	n.a.
Water m^3/t	2 (N 1)	n.a.
Aluminium powder kg/t	n.a.	n.r.
Calcium powder kg/t	n.r.	n.r
Others kg/t	n.a.	n.a.

Notes:
(N 1) The presented figure on water consumption can only give an indication.
n.a = data not available n.r = not relevant in this production process

Table 8.1: Consumption data for the production of refractory metals as specific input factors

The next table presents some information on process data for smelting refractory metals in an electron beam furnace. In electron beam furnaces electron guns produce high-energy electrons, which impact their energy to the furnace charge to affect its melting.

Electron beam furnaces are used to melt and/or refine refractory metals such as vanadium, niobium and tantalum, metals such as molybdenum and tungsten as well as reactive metals like zirconium and hafnium [tm 107, Ullmanns, 1996].

Metal	Crucible capacity [t]	Furnace power [MW]	Throughput [t/h]	Energy consumption [kWh/t]
Niobium	0.5 - 2	< 1.2	0.02 - 0.4	6000 - 15000
Tantalum	0.5 - 2	< 1.2	0.02 - 0.4	6000 - 15000
Molybdenum			0.02 - 0.1	< 5000
Tungsten			0.02 - 0.1	< 5000
Titanium			0.2 - 1	1000

Table 8.2: Process data for smelting refractory metals in an electron beam furnace [tm 107, Ullmanns 1996]

8.2.2 Emissions

8.2.2.1 Emissions to air

According to the raw material that is needed and the unit operations used, e. g. crushing, drying, smelting firing, metal and slag separation, calcining, hydrogen reduction, carburisation and product handling one of the most important sources of environmental input are dust and fume emissions. The dust emissions either as stack or fugitive emissions are important because harmful metal compounds, such as manganese and cobalt may be part of the dust.

Unloading and storage of raw material can generate dust when the material is feed from packaging containment’s such as drums, plastic bags or Flexible Intermediate Bulk Containers (FIBC) into bins.

The dust and fume that is generated by smelting or melting for instance chromium or titanium metal or from the production of hardmetal powder, is collected by hoods and transferred to an abatement system and de-dusted (e g. by a fabric filter or a wet scrubber). Stack emissions are normally monitored continuously or periodically and reported by on-site staff or off-site consultants to the competent authorities. Fugitive losses can also be measured as shown in Chapter 2, which gives an overview of common techniques used by producing non-ferrous metals.

Heavy metals are carried into the process as trace elements in the primary or secondary raw material. The metals with boiling points below the process temperature will escape as gases in the form of metal vapour, which partly condenses and oxidises to form part of the dust and fume from the firing chamber. The metal vapour and off-gases generated by melting or refining of refractory metals in an electron beam furnace are collected by a vacuum system and then condensed by intensive cooling.

Another environmental impact of the production of refractory metals such as tantalum, zirconium and hafnium are the radioactive levels of some raw materials. Also the toxicology of some refractory metals for instance chromium, manganese and vanadium should be taken into account. This is as well the case if cobalt takes part of the hardmetal powder, where then the occurrence of “hardmetal disease” has been found [tm 008, HMIP, 1993].

8.2.2.2 Emission to Water

For the production of refractory metals the emissions to water are very dependent on the process and the abatement system as well as the type of wastewater treatment used. There exist a variety of different water collection and wastewater treatment systems. Some plants use a central wastewater treatment plant in which water from different production processes as well as surface run-off water will be cleaned together. Other facilities are using a separate treatment system for rainwater and special treatment processes for the different process wastewater streams. The main water pollutants are suspended solids and metal compounds. The wastewater is treated in order to remove dissolved metals and solids and is recycled or reused as much as possible in the process. The possible wastewater streams are:

- Surface run-off and drainage water
- Waste water from wet scrubbers
- Waste water from slag and metal granulation
- Cooling water

The contaminated water is normally led to a thickener or a settling pond to settle out the suspended solids. Precipitation steps are often used to remove metal compounds from the water. The particles mostly consist of very fine particles, it may therefore be necessary to add flocculent to assist settling in thickeners. After the treatment in a thickener or a settling pond the suspended solids are usually below 20 mg/litre, which allows reuse in scrubbers, as cooling water or as process water for other purposes.

8.2.2.3 By-products, process residues and wastes

The production of refractory metals is related to the generation of a number of by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). The most important process specific residues are filter dusts, sludge from wet scrubbers, slag form the smelting process, used furnace linings and packaging material like drums or big-bags. These residues are partly sold as by-products, recycled to the process or in cases of wastes without economic utility transported to a deposit or a landfill.

8.2.2.4 Summary of emissions by producing refractory metals

Taking into account the different processes used in the production of refractory metals, the following table will give an overview about the environmental input in terms of emission to air, water and land. The table will as well make a distinction between the use of primary and secondary raw material

Refractory Metal	**Emission to air**			**Emission to water**	**Generation, recycling and reuse of process residues**	**Remarks**
Chromium			mg/Nm^3			
Primary raw material	Dust	From raw material storage handling and preparation cleaned by a bag filter	5 - 10	• Effluent from the water quench tank (bosh tank)	• Dust collected in the abatement system • The Chrome Alumina slag is sold as a raw material for use mainly in the -steel refractory industry or, as stated previously, re-used to line the firing pots. • Slag recovered from the boshing tanks, debris from the stripping booth and that from stripping used reaction pots is disposed to a licensed landfill	
	Dust	From the firing chamber cleaned by a bag filter	< 5			
	Dust	Fugitive emissions from smelting and metal and slag separation	n.a.			
	Cr	The amount of chromium and its compounds as part of the total dust emissions is reported as be less then	< 2.			
Secondary raw material						• Chromium metal scarp is commonly used directly in steelworks or for the production of ferro-chrome
Manganese			mg/Nm^3			
Primary raw material	Dust	From raw material storage handling and preparation cleaned by a bag filter	< 10	• No information are available for the generation of wastewater	• Electrolyte purification waste • Waste electrolyte • No information are available for the generation of other residues	
	Mn	Manganese fume Manganese tetroxide and manganese organic compounds	n.a.			
Secondary raw material						• No information available for the production of secondary manganese

Table 8.3: Emissions by producing chromium and manganese metal

Refractory Metal	**Emission to air**			**Emission to water**	**Generation, recycling and reuse of process residues**	**Remarks**
Tungsten			mg/Nm^3			
Primary raw material	Dust	Raw material storage and handling (charging boats)	< 10	• Cooling water systems are designed as closed loops and are not in contact with the processed material • Wastewater resulting from scrubbing is checked for W and NH_4 contents and if necessary, treated to reduce these.	• Dust that is collected in the abatement system is recycled to the production process. • Residues from crystallisation and drying of APT	• The dust emissions are normally well below the reported ELV (20 mg/Nm^3) because W-powder is a valuable material. • The only available measured dust emission concentrations that has been reported are exclusively in the range of 1 - 3 mg/Nm^3 • This data are due for the production of tungsten metal powder and tungsten carbide. • Ammoniac is a very odour intensive substance, which may easily results in odour problems.
	Dust	Calcining	1 - 6			
	Dust	Hydrogen reduction	< 5			
	Dust	Powdering	< 10			
	Dust	Product handling	< 10			
	Dust	Fugitive emissions from furnace loading and unloading. Carry over of fine particles	n.a.			
	NH_3	Fugitive ammoniac decomposition fumes from calcination	< 60.			
	H_2	Possible fire risk from hydrogen fumes				
Secondary raw material	Dust	Same as for primary production	< 10	• Cooling water systems are designed as closed loops and are not in contact with the processed material • Wastewater resulting from washing is treated in a special wastewater treatment facility	• Dust that is collected in the abatement system is recycled to the production process	• Cobalt is normally added to the hardmetal powder. This can cause “hardmetal disease” therefore the emission concentration of Co is less than 1 mg/Nm^3.
	Zn	Zinc fume from the distillation process	n.a.			
	Co	Cobalt fume from the distillation process (C0 is part of the hardmetal scrap)	< 1			

Table 8.4: Emissions by producing tungsten metal and tungsten metal powder

Refractory Metal	Emission to air			Emission to water	Generation, recycling and reuse of process residues	Remarks
Vanadium			mg/Nm^3			
Primary raw material	Dust	From raw material preparation like grinding	< 10	• No information are available for the generation of wastewater	• Dust collected in the abatement system • leach tailings • No information are available for the generation of other residues	• Calcium powder that is used as a reductant should be stored very carefully because of the high risk of fire hazards.
	Dust	From mixing with alkali metal salts for the roasting process	< 3			
	Ca	Calcium fines may be emitted be using calcium powder as a reductant	n.a.			
	Al	Aluminium fines may be emitted be using aluminium powder as a reductant	n.a.			
Secondary raw material	Different emissions of process chemicals are possible, but dependent on the used raw material and the process. Data are not available			No information are available for the generation of wastewater	Vanadium decomposition sludge No information are available for the generation of residues	
Molybdenum			mg/Nm^3			•
Primary raw material	Dust	From raw material storage handling and preparation cleaned by a bag filter	< 10	• No information are available for the generation of wastewater	• No information are available for the generation of residues	• According to international classification, Molybdenum trioxide (MoO_3) is classified as harmful (XN)
	Dust	Fugitive emissions from loading and unloading, carry over of fine particles	n.a.			
	Mo	Fumes	n.a.			
	H_2	Possible fire risk from hydrogen fumes				
Secondary raw material	Different emissions of process chemicals are possible, but dependent on the used raw material and the process. Data are not available			• No information are available for the generation of wastewater	• No information are available for the generation of residues	

Table 8.5: Emissions by producing vanadium and molybdenum metal

Refractory Metal	Emission to air			Emission to water	Generation, recycling and reuse of process residues	Remarks
Titanium			mg/Nm^3			
Primary raw material	Dust		< 10	• Liquid effluents are generated by using wet scrubbing systems. These effluents may contain Hydrochloric acid, TTC and sodium hydroxide. • Liquid effluents arise from the use of cooling water on a once –through basis or as blowdown from closed circuit cooling water systems serving reactor vessels and crucibles in melting furnaces. • Scarp detergent wash water • Acid leachate and rinse water • Sponge wash water • Titanium chloride purification effluent	• Dust collected in the abatement system. • The dust contains titanium, titanium dioxide and sodium oxide. • Some melting furnace crucibles are cooled with liquid sodium-potassium alloys (NaK) and small quantities of oxidised material of this source are generated in form of sludge. The sludge is reacted with water and the resulting liquid is discharged to the effluent treatment plant.	• Particulate titanium consists of relatively coarse particles, which settle quickly and represent a fire hazard. • Frequent cleaning ensures that accumulation do not occur and the dust can normally sold as a by-product. • TTC (Titanium-Tetrachloride)
	Dust	Dust, containing titanium fines, salt and possibly small quantities of sodium are produced during the crushing of the melt removed from the reaction vessel.				
	Dust	Fugitive emissions	n.a.			
	Acid fume	Hydrochloric, hydrofluoric and nitric fumes	n.a.			
	TiOCl	TTC vapour hydrolyses in contact with moist air producing a fog containing titanium dioxide, titanium oxychloride (TiOCl) and Hydrochloric acid				
	TTC	The argon gas used to provide an inert atmosphere in the reactor vessel picks up traces of TTC and sodium				
	TiO_2 NaO	Fumes from cleaning the reactor lids contain titanium dioxide and sodium oxide				
	Cl		< 5.			
Secondary raw material	Emissions that are comparable to the above mentioned air emissions			Similar effluents than for the primary production	Same residues than for the primary production	

Table 8.6: Emissions by producing titanium metal

Refractory Metal	Emission to air			Emission to water	Generation, recycling and reuse of process residues	Remarks
Tantalum			mg/Nm^3			
Primary raw material	Dust	Raw material storage and handling (charging boats)	< 10	• Cooling water systems for the electron beam furnace are designed as closed loops and are not in contact with the processed material • No information are available for the generation of other wastewater sources	• Dust that is collected in the abatement system is recycled to the production process. • No information are available for the generation of other residues	• This data are due for the production of tantalum metal powder and tantalum carbide. • Tantalum in non-toxic and bioinert. Allergic reactions are unknown [tm 108, Ullmanns, 1996] • Ammoniac is a very odour intensive substance, which may easily results in odour problems. • Some tantalum raw materials may have high levels of radioactivity. • HF (Hydrogen fluoride) is highly toxic and can easily be absorbed by a skin-contact.
	Dust	calcining	< 5			
	Dust	Hydrogen reduction	< 5			
	Dust	Carburisation	< 5			
	Dust	Powdering	< 10			
	Dust	Product handling (fine powder)	< 10			
	Dust	Fugitive emissions from furnace loading and unloading. Carry over of fine particles	n.a.			
	NH_3	Stack and/or fugitive ammoniac decomposition fumes from calcination	< 60.			
	HF	Hydrogen-fluoride	< 1			
	H_2	Possible fire risk from hydrogen fumes				
Secondary raw material	Dust	Same as for primary production		• Cooling water systems for the electron beam furnace are designed as closed loops and are not in contact with the processed material • Tantalum alloy leach and rinse • Tantalum sludge leach and rinse • Tantalum powder acid wash and rinse • Capacitor leach and rinse	• Dust that is collected in the abatement system is recycled to the production process • No information are available for the generation of other residues	• HF (Hydrogen fluoride) is highly toxic and can easily be absorbed by a skin-contact. • Storage and handling of HF should take this into account • Cobalt is normally added to the hardmetal powder. This can cause "hardmetal disease" therefore the emission concentration of Co is less than 1 mg/Nm^3.
	H_2	Possible fire risk from hydrogen fumes				
	NH_3	Stack and/or fugitive ammoniac decomposition fumes from calcination	< 60.			
	HF	Hydrogen-fluoride	< 1			
	Trace metals like Co, MnO, Ni and Ag can be presented in tantalum scrap and may be emitted		Ni < 1 Co < 1			

Table 8.7: Emissions by producing tantalum metal

Refractory Metal	Emission to air			Emission to water	Generation, recycling and reuse of process residues	Remarks
Niobium			mg/Nm^3			
Primary raw material	Dust	From all sources cleaned by a bag filter	< 10	• No information are available for the generation of wastewater	• Dust collected in the abatement system • Slag from the reduction in the vacuum furnace • It is known that pyrochlore, which is a significant raw material source may contain high radioactive levels and the thermal smelting process is thus potentially environmentally polluting with respect to disposal of slag. • No information are available for the generation of other residues	• Niobium and its compounds have very low toxicity • HF (Hydrogen fluoride) is highly toxic and can easily be absorbed by a skin-contact. • Storage and handling of HF should take this into account levels.
	Dust	From handling fine powders	< 5			
	Dust	From the production of Niobium carbides	< 5			
	Dust	Fugitive emissions	n.a.			
	VOC	From solvent extraction	n.a.			
	HF	Hydrogen-fluoride emissions	< 1			
	HCl		< 5			
	Al	Aluminium fines may be emitted by handling aluminium powder that is used as a reductant				
	Other emissions are dependent on the used raw material and the process. Additional data are not available					
Secondary raw material	Dust	From all sources cleaned by a bag filter	< 10	No information are available for the generation of wastewater	No information are available for the generation of residues	• HF (Hydrogen fluoride) is highly toxic and can easily be absorbed by a skin-contact. • Storage and handling of HF should take this into account
	HF	Hydrogen-fluoride emissions from digestion	< 1			
	Other emissions are dependent on the used raw material and the process. Data are not available					

Table 8.8: Emissions by producing niobium metal

Refractory Metal	Emission to air			Emission to water	Generation, recycling and reuse of process residues	Remarks
Rhenium			mg/Nm^3			
Primary raw material	Dust	From all sources cleaned by a bag filter	< 10	• Production wastewater • No information are available for the generation of wastewater	• Dust collected in the abatement system • Sludge as a residue from the removal of rhenium from scrubbing liquor • Refining residues • Sludge treatment solids • Rhenium raffinate	• Rhenium and its compounds have very low toxicity levels.
	Dust	From handling fine powders	< 5			
	Dust	Fugitive emissions	n.a.			
	Other emissions are dependent on the used raw material and the process. Additional data are not available					
Secondary raw material	Emissions are dependent on the used raw material and the process. Data are not available			No information are available for the generation of wastewater	No information are available for the generation of residues	
Zirconium and Hafnium			mg/Nm^3			•
Primary raw material	Dust	From all sources cleaned by a bag filter	< 10	• No information are available for the generation of wastewater	• Zr and Hf are also associated with radioactive metals (uranium, polonium and thorium) which can be present in residues • Acid leachate from zirconium metal and alloy production. • Leaching rinse water from zirconium metal and alloy production. • Waste acid	• Zirconium processing has significant environmental risk associated with its residual radioactivity from radioactive metals (uranium, polonium and thorium) being presented in the heavy sand that is used as raw material. Radiation levels are not published.
	Dust	Fugitive emissions	n.a.			
	F	Fluoride emissions	n.a.			
	Radioactivity from Zircon		n.a.			
	The chlorination process for parting zircon concentrate and volatilisation of zirconium tetrachloride requires strict containment procedures. Other emissions are dependent on the used raw material and the process. Additional data are not available					
Secondary raw material	Emissions are dependent on the used raw material and the process. Data are not available			• No information are available for the generation of wastewater	• No information are available for the generation of residues	

Table 8.9: Emissions by producing rhenium, zirconium and hafnium metal

8.3 Techniques to Consider in the Determination of BAT

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2 "common processes" apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

Due to the fact, that only a very few companies in Europe produce refractory metals and many of the processes are commercially confidential, with the exception of chromium metal only outline descriptions focused strongly on environmental issues can be presented.

EXAMPLE 8.01 PROCESS OF ALUMINO-THERMIC PRODUCTION OF CHROMIUM METAL

Description: - The following description gives details of a new plant installed in UK, for the production of Alumino-thermic Chromium metal. The plant was built to replace an existing Chromium metal production plant, which had been in operation for more than 40 years. The plant was commissioned in 1997

1. Raw Materials Storage: - Raw materials such as chromic oxide and aluminium powder as well as various oxidising and conditioning agents are stored at one end of the building in separate areas to prevent cross-contamination. The oxidising agents are stored in a secure compound to avoid the risk of fire.

2. Weighing Operation: - The Chromic Oxide F.I.B.C's are attached to discharge stations situated above weighing hoppers mounted on load cells at floor level. Screw feeders transfer the raw materials into the weighing hoppers. The discharge stations are connected to cartridge filters situated outside the building. The aluminium powder discharge stations are not connected to cartridge filter units. They have anti-static vent socks fitted because of the explosion risks associated with this material.

The minor additions are added from a mezzanine floor via sack/drum-tip stations. Each individual station has its own integral dust extraction unit. Vacuum lifting equipment allows the operator to empty the containers at a comfortable working height, All material caught by the dust extraction is shaken from the filter media periodically and is collected in an integral storage hopper below.

The weighing bin for each batch sits on an electrically driven bogie, which travels on a rail track situated in a pit beneath each discharge point. The various raw materials are automatically dispensed into the weighing bin. This process and the positioning of the bin on the track are computer controlled.

3. Mixing Operation: - The weighing bin is transferred to a separate enclosed room where the contents are mixed in a rotating blender. Ventilation of this room is provided by an axial flow fan, which discharges to atmosphere. Disposable fibreglass filter panels protect the fan inlet.

4. Firing Pot Preparation: - The firing pot base is prepared with granular refractory on a stand placed at a comfortable working height. The pot is secured on to the base and transferred to a vibratory turntable situated in an adjacent pit. Refractory material is screw fed from a storage hopper around a central former placed in the firing pot, which is rotated slowly. The lining is compacted by the vibratory turntable.

The refractory storage hopper is fitted with an integral dust extraction and filter unit.

The rammed lining is sprayed with a binder solution and dried in one of several gas-firing units. Emissions are ducted out of the shop at roof level by natural convection.

5. Firing Operation: - The firing pot is located inside one of several firing chambers situated below ground level. Travelling fume extraction hoods are moved forward to cover the firing pot and to connect with the main extraction ducting.

The weighing bins are located on an automatic vibratory feeder platform. The feed rate of material into the firing pots is computer controlled. Once the mixture is ignited and the reaction is underway, the fume generated is ducted to the main bag filter plant. The filter plant is located outside the main building in an extension adjacent to the firing chambers.

After the reaction fume has subsided, a reduced extraction volume is provided to each chamber containing a cooling pot. Powered dampers isolate the ducting to a firing chamber when it is empty.

6. Firing Pot Cooling : - When the metal has solidified, the firing pot is removed and transferred by crane to a long, slowly moving, cooling conveyor. The latter is partially enclosed by a hood and is ventilated by a number of extraction fans which discharge to atmosphere outside the building. The fan inlets are protected by disposable fibre glass filter panels.

7. Button Stripping Operation: - The cooled firing pot is transferred by a jib crane onto a bogie for transporting into a stripping booth. Inside the closed booth, the pot casing is automatically lifted off the base, The bogie is then rotated and a scraper bar removes the refractory lining. A cartridge filter plant provides dust extraction from the stripping booth.

The debris from the pot lining falls into a collection hopper and is transferred to a vibrator sieve. The sieved refractory material is collected in pans and recycled. A filter unit provides dust extraction from the sieve and sieve discharge.

8. Quenching Operation: - The Chromium button and slag are removed from the stripping booth on the bogie. The slag is separated from the metal button, cooled and sent to a despatch area. The Chromium button is transferred to a quenching tank for final water-cooling. Steam generated in this quenching operation is extracted by fans and ducted to atmosphere outside the building.

The cooled Chromium button is transferred to other departments for cleaning; breaking; crushing and grinding, prior to packing and final despatch.

Main environmental benefits:

The Main filter plant: - Firing can only take place in one chamber at a time due to a system of interlocks on the travelling hoods and firing feed conveyor.

During the firing process when large amounts of fume are generated for a relatively short period of time, the extraction volume is at its maximum. During this period a lower ventilation volume is available at the other remaining chambers [one or more of which may contain a pot which is cooling but emitting little fume].

When no firing is taking place, the fume plant is automatically shut down to the lower extraction rate in order to minimise the energy consumption of the filter unit.

The filter plant comprises 4 compartments, with 132 filter bags per compartment. The cleaning cycle is fully automated with each chamber cleaned 'off-line' in turn by means of a reverse air pulse system.

A monitoring and recording system is installed on the fume plant to continuously monitor particulate emissions. This comprises of a probe mounted in the exhaust stack and a combined control unit/microprocessor based datalogger. Emissions from the stack are continually monitored and any deviation above a pre-set level will signal an alarm. The fume plant operates with a total particulate emission levels below 5 mg/Nm^3.

Emissions to air:- Total particulate emissions are below 5 mg/Nm^3 where the part of chromium and its compounds is less then 1 - 2 mg/Nm^3.

Emissions to water [sewer]: - The only liquid emission is from the water quenching tanks.

Emissions to land: - Waste fume dusts from the process are taken to a licensed landfill site. The quantity of fume dust generated will depend upon the quantity of chromium metal being produced.

Operational data: - The plant uses the following utilities:

Electricity	-139 kWh/tonne of Cr metal
Gas	-6m^3/tonne [calorific value of gas is 39.2 MJ/Nm^3]
Water	-2 m^3/tome

Cross media effects: - The nature of the operation is such that most of the releases are to air rather than to either of the other two environmental media.

For most applications, the metals industry has generally standardised on a bag filter plant to control airborne emissions. A bag filter plant [i.e. a dry system] was chosen for this application, as it would provide good filtration with the lowest environmental impact.

Wet scrubbing systems were considered, but rejected. A wet type of abatement such as a Venturi scrubber would result in a sludge waste, which would be more difficult and costly to dispose of, and would contain a significant proportion of water. The plume from the main stack would also be wet and not so well dispersed.

Economics: - The total cost of the project was in the order of about 4.35 MEuro included in which were the following:

Weighing Station	0.72 M €
Firing Chambers/Feeders	0.29 M €
Cooling Conveyor/Stripping Booth	0.36 M €
Pot Preparation	0.24 M €
Main Fume Plant	0.65 M €
Building and Civil Work	1.88 M €

Applicability: - The above presented technique is as a whole applicable to a new plant, but it can partly also be applied to existing plants.

Reference literature: - [tm 162, London and Scandinavian Metallurgical CO Limited 1999]

8.3.1 Materials, storage and handling

The raw materials used for the production of refractory metals are basically metal oxides, reducing agents such as aluminium or calcium powder, hydrogen, and additives. The main environmental impact by storage and handling of these materials are fugitive dust emissions and sometimes, depending on the produced metal and the used process, contamination of surface waters and soil cased by wash out from rainwater. There are several productions that are based to a large extent on the recovery of refractory metals from scrap. In this case the scrap need to be monitored in order to avoid radioactive or otherwise contaminated metals to be processed without any precautions. High levels of radioactivity play as well an important role by processing several raw materials such as zircon.

To prevent soil contamination, raw materials are preferable stored in a closed containment on hard surfaces indoor. To keep the materials clean the storage area can also be divided in different storage-bays. Dry fine-grained materials should be handled in closed silos, bins and hoppers to prevent fugitive emissions to the environment as well as to the workspace.

Closed conveyors and transfer systems are used for handling of dusty fine materials like metal powders, where extraction and filtration equipment is used for dusting delivery points. The dust leaden air from the silos, closed conveyors and charging systems are cleaned by using bag filters, which may be monitored by measuring the pressure drop to control the cleaning mechanism. The collected dust is normally fed back to the storage because raw materials for producing refractory metals (hard metals) are valuable minerals.

Metal scrap, turnings and swarf for the production of secondary titanium metal sometimes have to be liberated from oil and cutting liquids, which may take place by drying in a rotary kiln. Ducting carries the oil-bearing gases away from the dryer and through a cyclone to remove dust and carry over. The gases then pass through an afterburner, which is heated by a gas-fired burner. Combustion gases/fumes are either recirculated through the dryer or are ducted to a second cyclone. After passing through the cyclone, sorbent (sodium bicarbonate) is introduced to neutralise the gas stream. Finally the gas passes through a ceramic filter unit before being discharged to the atmosphere via a stack. A detailed example of this technology is presented in the ferro-alloy part of this document.

Hydrofluoric acid is used in several processes to produce refractory metals such as Ta and Nb. The handling of HF requires precautionary measures in respect of health and safety at work, since HF is recognised as aggressive and very toxic. An essential requirement for health and safety of workers for example is the permanent availability of a calcium di-gluconate solution as a first aid in cases of skin contact.

8.3.2 Smelting, firing, hydrogen reduction and carburisation processes

In the production of refractory metals, hardmetal powder and carbides one of the most important stage is the reduction of metal oxides. Depending on the reducing agent, different types of smelting respectively reducing systems (such as reaction crucibles or pusher furnaces using hydrogen as a reducing agent) are considered techniques. The next table will give an overview of these furnaces

Firing, smelting or reduction system	Produced metal	Gas collection and abatement	Advantages	Disadvantages
Electric arc furnace			- Remelting of secondary metals	
Firing pot (crucible)	Cr	movable closed hood connected with a bag filter	-	
Pusher furnace	Ta-, W-powder Ta, W-carbides	bag filter Wet scrubber	- Production of refractory metal powder - Production of refractory metal carbides by carburisation - Quasi continuous production	- The raw material needs to be charged in small containment's called boats
Band furnace	Ta-, W-powder Ta, W-carbides	bag filter Wet scrubber	- No loading and unloading of the boats - Continuous production - Fully automated	
Rotary furnace	W-powder	bag filter Wet scrubber	- Production of tungsten metal powder	
Batch furnace	Ta- and W-carbides-	bag filter Wet scrubber	- Production of refractory metal carbides by carburisation	- The raw material needs to be charged in containment's
Electron beam furnace	Melting of Nb, Ta, Mo, W and Ti.	vacuum extraction condenser and scrubbing system	- High power density - Very high temperature - Water cooled inert crucible - Controlled atmosphere - Low off-gas volume	- High specific energy consumption - Low melting rate
	Refining of V, Nb, Ta, Hf and Zr	vacuum extraction condenser and scrubbing system	- Removing of C, O, N, H and divers other impurities	

Table 8.10: Summary of advantages and disadvantages of the used smelting systems in the production of refractory metals

Example 8.02 Production of tungsten metal powder and tungsten carbide

This paragraph demonstrates good practice for the production of tungsten metal powder and tungsten carbides. The same technique can be used as well to produce tantalum metal or other refractory metal powder

Description: - The installation produces tungsten metal powder. Ammonium paratungstate (APT) is used as raw material and calcined to yellow and blue oxide (WO_3 or $W_{20}O_{58}$). Subsequently the yellow and blue oxide is reduced to tungsten metal powder by using hydrogen as a reducing agent. The reduction takes place in a modern automated band furnace, which is equipped with a closed system where excess hydrogen is being directly recycled. A condenser is used for removing water and dust carry-over. The dust (hardmetal powder) is recycled. The tungsten metal powder can further be transformed by carburisation into tungsten carbide.

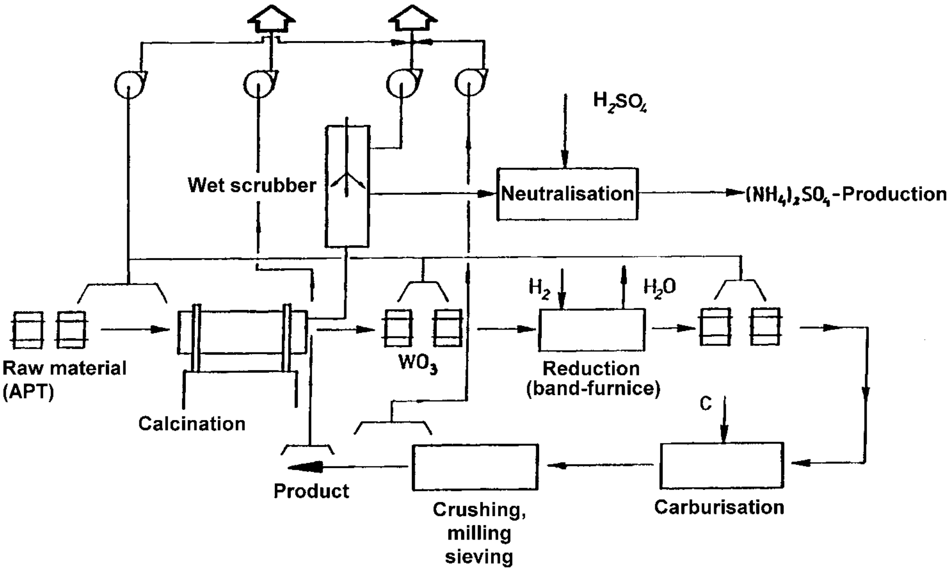


Figure 8.12: Production of tungsten powder and tungsten carbide

Main environmental benefits: - Two bag filters cleans the suction air that is collected by appropriate hoods and the process equipment. The dust that is collected by the filter consists nearly to a 100% of tungsten powder and is recycled to the production process.

Process step	**Dust after abatement mg/Nm^3**
Raw material handling	< 4
Calcining	< 4
Reduction furnace (band furnace)	< 2
Powdering	< 4
Product handling	< 4

Table 8.11 Dust emission after abatement

Operational data: - Not available

Cross media effects: - A small amount of washing liquid from the wet scrubber needs to be neutralised and treated. No other important cross media effects.

Economics:- Not available

Applicability: - To all new and existing hardmetal powder and carbide productions

Reference literature: - [tm181, UBA Wien 1999]

8.3.3 Gas collection and abatement

The techniques for fume collection and abatement discussed in Chapter 2 of this document are techniques to consider for the production of refractory metals. Bag filter and wet scrubbers are normally used for de-dusting the process off-gases.

There exist a number of different bag filter designs using different kinds of filter materials, which in principle all achieve for the production of refractory metals very low emission values that means dust emissions below 5 mg/Nm^3. The use of modern filtration techniques, like the membrane filter (surface filtration) results additionally in an increasing bag life, high temperature limit (up to 260 ºC) and relatively low maintenance costs combined with very low dust emissions. Due to the low off-gas volume in the hardmetal powder and metal carbide production, emission concentrations of dust in the range of less than 1 - 4 mg/Nm^3 are possible to reach with modern filter materials. Low dust emissions are both environmental and economically interesting, because hardmetal powder and carbides are valuable products. Never the less low dust emissions of hardmetal especially by recycling cobalt containing tungsten scrap are important to protect the working area in order to minimise the risk of health damage.

Bag house filters are in many cases in the metallurgical industry pressure filters with fans on the dirty fume/gas side. Recent developments led to a closed suction filter with fans on the clean-gas side. This combines the advantages of gentle bag cleaning that means longer bag life, low operating and maintenance costs and due to the closed filter a defined gas volume [tm 144, Elkem, 1998].

Hooding systems are used to collect process off-gases, especially fume from metal smelting and dust where hardmetal powder and metal carbides are produced. Hooding systems are therefore techniques to consider also with the aim to minimise fugitive emissions. The design of the hooding system needs to take account of access for charging and other furnace operations and the way the source of process gases change during the process cycle.

8.3.4 Process control

The principles of process control discussed in Chapter 2 are applicable to the production processes used in this Group.

8.3.5 Wastewater

Existing treatment systems are reported to be to a high standard. All wastewater should be treated to remove dissolved metals and solids. The techniques listed in Chapter 2 are the techniques to consider. In a number of installations cooling water and treated wastewater including rainwater is reused or recycled within the processes.

A water treatment is needed in the processes with wet scrubbers and granulation processes, because suspended solids should be removed before the water is recirculated. To reach acceptable values of harmful components, it may in some cases be necessary to polish the bleed that has to be taken from the scrubbing water cycle. This may take place by using sand filters, carbon filters or by adding suitable chemicals to precipitate harmful compounds.

8.3.6 Process residues

The processes and recycling routes that were discussed earlier in the section on present emission and consumption levels for the different refractory metals are techniques to consider in the determination of BAT. The most important factor to reduce the environmental impact of discharging residues as waste are process-integrated measures that result in the generation of fewer residues. If the amount of process residues is minimised by using primary measures, the extended amount should be recycled or reused as much as possible. The specific feed materials will influence the final process choice. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes.

8.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector; which are for the production of refractory metals, hardmetal powder and metal carbides, dust and fume, solid hardmetal and metal compounds, wastewater, residues such as filter dust, sludge and slag. Process chemicals such as hydrogen fluoride (HF) that is used for processing tantalum and niobium are highly toxic, which need to be taken into account by handling and storage of these materials;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous section. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this section are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

8.4.1 Materials handling and storage

The conclusions drawn for Best Available Techniques for materials handling and storage are shown in section 2.17 of this document are applicable to the materials in this chapter. In addition the following techniques for materials storage and handling are also BAT for this sector.

- Characterisation of raw materials before they are received so that handling, storage and processing difficulties can be taken into account.
- The pure titanium tetrachloride needs to be off-loaded from rail or road tankers with argon and stored under a blanket of argon. The storage tanks need to be vented to an argon gas-holder via a cold trap to recover any TTC in the vent system.
- Acid fumes vented from storage tanks should be treated prior being discharged to atmosphere.
- Sampling and analysis of raw materials so that the process options can be defined for a particular raw material and radioactive raw materials can be identified.
- Hydrofluoric acid is used in several processes to produce refractory metals such as Ta and Nb. The handling of HF requires precautionary measures in respect of health and safety at work, since HF is recognised as aggressive and very toxic. An essential requirement for health and safety of workers for example is the permanent availability of a calcium di-gluconate solution as a first aid in cases of skin contact.

8.4.2 Process selection

8.4.2.1 Smelting, firing, hydrogen reduction and carburisation process

According to the different refractory metals produced and the environmental impact of the processes, which are widely be influenced by the used smelting, reduction and carburisation system, the following production systems are considered to be BAT for this sector. The considered furnaces are in general all applicable to new and existing plants. For the production of hardmetal powder from secondary raw material and hardmetal scrap the zinc process is economically attractive and environmentally of low potential risk.

Furnace type	Produced metal	Gas collection and abatement	Remarks
Reaction chamber (firing pot)	Cr produced by metallo-thermic reduction	movable closed hood connected with a bag filter	• Recovery of heat energy will not be practised, because the metallo-thermic reduction takes place as a batch process, which needs only a short reaction time.
Pusher furnace	Ta-, W-powder Ta, W-carbides	bag filter Wet scrubber	• The reduction furnace of metal oxides is equipped with a closed system where excess hydrogen is being directly recycled. A condenser is used for removing water and dust carry-over. The dust (metal- or carbide powder) is reused • Each furnace needs a nitrogen purge • The stoker arm has to be sealed to seal the tube entrance. • Boats are emptied over a screen into drums
Band furnace	Ta-, W-powder Ta, W-carbides	bag filter Wet scrubber	• The reduction furnace of metal oxides is equipped with a closed system where excess hydrogen is being directly recycled. A condenser is used for removing water and dust carry-over. The dust (hardmetal powder) is reused • Each furnace needs a nitrogen purge
Rotary furnace	W-powder	bag filter Wet scrubber	• The kiln is sealed to prevent egress of fume and dust. • By producing tungsten powder in the rotary furnace the discharge is into a closed chamber where the powder is purged with nitrogen. The powder is then discharged into churns which are kept under nitrogen
Batch furnace	Ta- and W-carbides-	bag filter Wet scrubber	• The extraction system needs to be able to handle variable off-gas volumes
Electric vacuum furnace	melting of secondary refractory metals from scrap e.g. titanium	bag filter Wet scrubber	• Energy recovery may only be possible from the cooling water cycle
Electron beam furnace	Melting of Nb, Ta, Mo, W and Ti.	vacuum extraction condenser and scrubbing system	• High energy consumption • Energy recovery may only be possible from the cooling water cycle • Zr and Hf are also associated with radioactive metals (uranium, polonium and thorium) which can be present in residues
	Refining of V, Nb, Ta, Zr and Hf	vacuum extraction condenser and scrubbing system	

Table 8.12: Furnaces considered as BAT for the production of refractory metals

8.4.2.2 Process control

The techniques presented in the different sections of Chapter 2 describing possibilities to control the process by computerised systems will be part of BAT for this sector. The most important are considered being.

- Furnace operation control to optimise operating conditions. Key parameters are pressure and temperature at various points in the furnace and gas handling system, hydrogen and oxygen concentrations, residence time and system pressure.
- Process control using relevant methods so that it is possible to maintain operating conditions at the optimum level and to provide alarms for conditions that are outside the acceptable operating range.
- Plant operators should be trained and given instructions about the correct operating procedures and control parameters.
- Use of good maintenance practice for process plant, abatement systems and other associated processes. A system of inspection should be adopted.

8.4.3 Gas collection and abatement

The techniques presented in Chapter 2 for off-gas collection techniques as well as air abatement techniques will be part of BAT for this sector. According to the techniques to consider that are presented for fume/gas collection and abatement, BAT for this sector is as follows.

- An extraction system to take fumes and dusts from, calcining smelting reduction and carburisation furnaces.
- Bag filters are BAT for cleaning off gases from reaction chambers and the raw material and product handling stages by producing chromium metal where a residual particulate matter concentration of less than 5 mg/Nm^3 is reachable. The part of chromium and its compounds is less then 1 - 2 mg/Nm^3
- Bag filter are BAT for cleaning off gases from the calciner, the reduction and carburisation furnaces and the raw material and product handling stages, where the associated range of residual particulate matter concentration of metal and carbide powder is less than 1 - 5 mg/Nm^3.
- For metal compounds such as nickel, vanadium, chrome, manganese etc. as part of the total fume and dust, the emissions are according to the harmful nature of the metal much lower than the associated dust emissions**.** Several secondary raw materials have or contain also toxic metals and metal compounds that may be emitted from the process and so need to be reduced The associated level for nickel and cobalt compounds for instance is less than 1 mg/Nm^3.
- By producing metal powder or metal carbides, the off-gas system can be designed as a closed system, where dust can only escape by periodic removal from the capture system. The small amount of dust can then be recycled completely back to the process.
- If a wet scrubber is used to clean the off-gas from the metal powder production, the amount of powder removed is separated from the water by decantation, dried and recycled. Due to the additional energy and the wastewater that needs to be treated the dry system should preferably be used.
- Ammonia emissions from calcining furnace can be reduced by wet scrubbing and a subsequent neutralisation with H_2SO_4. Ammonia can also be recovered for the ATP production.
- Ammonia fume from the APT calcining in a sealed reactor can only escape due to a seal failure, at which point the feed and heating are switched of and the seal repaired.

Ammonia fume will escape to atmospheric vent if there is an undetected heater failure, but this is avoided by the use multiple burners and burner alarms.

- Ammoniac emissions from the tantalum production, which are also very odour intensive can be reduced by acid scrubbing where the associated emissions levels are below 60 mg/Nm^3.
- Hydrogen fluoride (HF) is a very toxic chemical substance and need therefore handled and utilised carefully. By using modern techniques the associated emission level of hydrogen fluoride is below 1mg/Nm^3.
- Appropriate hooding systems connected with a bag filter are preferably used for collecting and cleaning fumes and dust from all raw material handling, powdering and product handling stages

The following table summarises the captured emission associated with the use of best available technique and the techniques that can be used to reach these levels.

Pollutant	Emissions associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	< 5 mg/Nm^3	Fabric filter	
Heavy metals	Cr and its compounds 1 - 2 mg/Nm^3 Ni and Co < 1 mg/Nm^3	Fabric filter	High performance fabric filters (e.g. membrane fabric filters) can achieve low levels of heavy metals. The concentration of heavy metals is linked to the concentration of dust and the proportion of the metals as part of the dust.
NH_3	< 60 mg/Nm^3	Wet scrubbing and a subsequent neutralisation with H_2SO_4	For the production of Tantalum In the production of tungsten metal powder and metal carbide NH_3 can also be recovered for the APT production
HF	< 1 mg/Nm^3	Wet scrubbing system	Hydrogen fluoride (HF) is a very toxic chemical substance and need therefore handled and utilised carefully.
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 8.13: Emission levels to air associated with the use of BAT

8.4.4 Wastewater

The techniques presented in Chapter 2 for effluent treatment and water reuse will be part of BAT for this sector. According to the techniques to consider that are presented for water treatment, BAT for this sector is defined as follows:

- Closed water cycles are suitable for wet scrubbers, and cooling systems.
- The bleed form closed water cycles need to be treated to remove particulate matter and metal compounds from the water.
- Treated waste waster should be recycled and reused as much as possible.
- Scrubbing liquids should also be treated and analysed before discharge.
- Containment of plant drainage systems where possible and treatment of effluents according to their content with analysis before discharge.

8.4.5 Process residues

The techniques presented in Chapter 2 for waste minimisation will be part of BAT for this sector. According to the processes that were defined as applied techniques the following ways of recycling and reuse of slag, filter dust and sludge are considered as BAT for this sector:

Refractory metal	Residue	Recycling, reuse and discharge
Chromium	Dust Slag	• Dust might partly be reused • Slag can be reused for a variety of purposes • Chrome-alumina slag can be sold as raw material to the steel and refractory industry
Manganese	Dust	• Dust is partly recycled back to the process
Tungsten	Dust	• Dust is recycled back to the process
Vanadium	Dust	• Dust is recycled back to the process
Molybdenum	Dust	• Dust is recycled back to the process
Titanium	Dust	• Dust is recycled back to the process • Some melting furnace crucibles are cooled with liquid sodium-potassium alloys (NaK) and small quantities of oxidised material of this source are generated in form of sludge. The sludge is reacted with water and the resulting liquid is discharged to the effluent treatment plant
Tantalum	Dust	• Dust is recycled back to the process
Niobium	Dust	• Dust is recycled back to the process • Slag from the reduction in the vacuum furnace • It is known that pyrochlore, which is a significant raw material source may contain high radioactive levels and the thermal smelting process is thus potentially environmentally polluting with respect to disposal of slag
Rhenium	Dust	• Dust is recycled back to the process • Sludges as a residue from the recovery process of rhenium from scrubbing liquor that was generated by a molybdenum roasting process. The sludge need to be treated.
Zirconium	Dust Slag	• Zr and Hf are also associated with radioactive metals (uranium, polonium and thorium) which can be present in residues. This have to be taken into account be using or discharging these residues.
Hafnium		

Table 8.14: Recycling and reuse of residues from the production of refractory metals

8.5 Emerging Techniques

Due to strategic and environmental considerations the recycling of hardmetal scrap becomes more and more important, therefore a lot of research have been done in recent years in this field. Selective electrolytic dissolution has been researched for the recycling of hardmetal scrap but not detailed information is available to describe the current stage of the developments.

Further information on the development of new processes and furnace improvements are very difficult to get, because process developments and improvements are sometimes carried out directly be the hardmetal producing companies, which will then be covered by commercial confidentiality.

9 FERRO-ALLOYS

Ferro-alloys are mainly used as master alloys in the iron and steel industry, because it is the most economic way to introduce an alloying element in the steel melt. Besides this, special ferro-alloys are also needed for the production of aluminium alloys and as starting material in specific chemical reactions.

As an additive in the steel production ferro-alloys improve the properties especially the tensile strength, wear and corrosion resistance. The effect of improved properties of steel by using ferro-alloys as an alloying element depend more or less on the following influences [tm 107, Ullmanns 1996]:

- a change in the chemical composition of the steel;
- the removal or the tying up of harmful impurities such as oxygen, nitrogen, sulphur or hydrogen;
- a change in the nature of the solidification, for example, upon inoculation.

Depending on the raw material that is used (primary or secondary raw material), the production of ferro-alloys can be carried out as a primary or secondary process. The principal chemistry of both processes can be shown as follows.

Primary Processes:

Oxidic metal ore + iron ore/scrap + reductant → ferro-alloy + reductant oxide + slag

Secondary Processes:

Metal scrap + iron scrap → ferro-alloy

Today, primary ferro-alloys are principally produced either by the carbo-thermic or metallo-thermic reduction of oxidic ores or concentrates. The most important process is the carbo-thermic reduction in which carbon in the form of coke (metallurgical coke), coal or charcoal is normally used as a reducing agent. When a blast furnace is used coke is also needed as an energy source.

The metallo-thermic reduction is mainly carried out with either silicon or aluminium as the reducing agent. The following chemical equations show the basic principles of the carbo and metallo-thermic production routes.

Carbo-thermic reduction: **Metal-oxide + Carbon → Metal + Carbon-monoxide**

Silico-thermic reduction: **Metal-oxide + Silicon ↔ Metal + Silicon-oxide**

Alumino-thermic reduction: **Metal-oxide + Aluminium → Metal + Aluminium-oxide**

9.1 Applied Processes and Techniques

Depending on the production rate, ferro-alloys can be divided into two main categories, bulk alloys and special alloys. Bulk ferro-alloys (ferro-chrome ferro-silicon, ferro-manganese silico-manganese and ferro-nickel) account for about 90% of the total production of ferro-alloys in the European Union.

Compared to bulk ferro-alloys, the production rate of special ferro-alloys is rather small. Special ferro-alloys (ferro-vanadium, ferro-molybdenum, ferro-tungsten ferro-titanium ferro-boron, and ferro-niobium) are mostly used in the iron, steel and cast-iron industry. Besides this some special ferro-alloys are increasingly used also in other industry sectors e.g. aluminium and chemical industries.

9.1.1 Ferro-chrome

Ferro-chrome, along with nickel (ferro-nickel) is the major alloying element in the production of stainless steel. Stainless steel is used in a variety of areas from cutlery to aircraft engine turbine blades.

The chromium content of ferro-chrome normally varies from 45 to 75% together with various amounts of iron, carbon and other alloying elements. The use of ferro-chrome depends widely on the carbon content, ferro-chrome can therefore be classified as follows.

1. **High-carbon ferro-chrome (HC FeCr)** with 4 – 10% C (“*ferro-chrome carburé*”)
2. **Medium-carbon ferro-chrome (MC FeCr)** with 0.5 – 4% C (“*ferro-chrome affiné*”)
3. **Low-carbon ferro-chrome (LC FeCr)** with 0.01 – 0.5% C (“*ferro-chrome suraffiné*”)

9.1.1.1 Raw materials

The main raw material to produce ferro-chrome is chromite ore, which is an iron oxide and chromium oxide containing mineral. The ratio between Cr and Fe in the chromite ore determines the chromium content of the alloy produced, e.g. a high Cr/Fe ratio is advantageous for the production of a ferroalloy with high chromium content. Chromite ore and concentrates are used in the form of hard lumpy and friable lump types, as well as chromite fines.

Depending on the different production routes and the desired carbon content of the ferro-chrome, carbon or silicon is used as a reducing agent. For the production of HC FeCr, carbon is added to the process as a reductant in form of metallurgical coke, coal or charcoal. Metallurgical coke is the most common reductant. It is important that a coke with a low phosphorous and sulphur content is used because 60 - 90% of the phosphorous and 15 - 35% of the sulphur is transferred into the metal. For the production of LC FeCr ferro-silico-chromium and ferro-silicon are used in a silico-thermic reduction as reducing agents and raw material.

In order to achieve the right metal analysis, a good metal recovery and a satisfactory furnace operation, auxiliary materials such as quartzite, bauxite, corundum, lime and olivine can be added to the burden as fluxing agents.

9.1.1.2 Pre-treatment techniques

Chromite is used as a raw material for the ferro-chrome production in the form of lumpy ore, fines and concentrates. It has to be noted that about 70 - 80% of the world’s chromite sources are available as fines (< 10 mm). To convert ore fines and concentrates to furnaceable material, they need first to be agglomerated by briquetting, pelletising/sintering or sintering.

Agglomeration is necessary to achieve good recoveries and also to give a permeable burden, which allows the gas from the reaction zone to escape.

Briquettes are made by pressing or shaping an ore mix with added binder to a suitable shape and size. The briquettes are used in the furnace after hardening of the added binder, but without thermal treatment. This method can be used for materials with a relatively wide grain size range of less than 5mm.

Green pellets are made by rolling fine grained moist ore with an addition of a binder and fine grained coke breeze into balls in a rotary drum or on a disc. These are later sintered in a steel belt or shaft furnace to hard, porous pellets with constant physical and chemical properties. The coke breeze in the pellets with an addition of furnace gas is used as fuel for the sintering.

Sintering is suitable for particle size in the range of 0.1 - 3 mm. Coke breeze is added to the ore mix but no binder. The mix is placed on a grate and the coke breeze ignited. The heat from burning the coke breeze will produce a sinter cake by melting of the gangue minerals in the ore. This cake must later be crushed to lump material of a suitable size.

Where thermal treatment (sintering) is involved, process off-gases must be cleaned in cascade scrubbers or bag filters. For all the agglomeration processes, collected raw material dusts from these processes, or from other raw material handling processes can be recycled.

9.1.1.3 Production of ferro-chrome and silico-chromium

9.1.1.3.1 High-carbon ferro-chrome

High-carbon ferro-chrome (HC FeCr) is produced almost exclusively by direct carbo-thermic reduction of chromite ore in three-phase submerged electric arc furnaces (EAF) with continuous operation. The smelting charge can be pre-heated in a shaft or rotary kiln by using the CO-gas from the smelting process. Pre-reduction in a rotary kiln is also possible. In both cases the specific consumption of electrical energy will be reduced. Closed, semi-closed or open submerged electric arc furnaces including three-phase AC (Alternating Current) operation and single phase DC (Direct Current) plasma furnaces are used. The DC arc furnace includes a single hollow graphite electrode.

The submerged arc furnaces use Søderberg electrodes where the electrode may be formed by hot paste, briquettes, blocks or paste cylinders. The electrode paste is charged on top of the electrode in accordance with its consumption. The material is subject to increased heat as it moves downwards in the electrode column. It melts at about 80 ºC and bakes at 500 ºC. To control the smelting process the furnace operation can be based on resistance or current control, so that the electrodes are lifted and lowered when necessary to keep resistance or current constant. This means certain requirements to the electrode sealing to prevent air leakage into the furnace. As an alternative another practice is commonly used where the electrode moves only during slipping and otherwise stand in place.

During the smelting process the metal oxides are reduced by the coke, with metal carbides as the final product The reduction produces large volumes of CO gas from the reaction zone under the electrode tips. In an open furnace the CO gas is burned at the surface of the furnace. By using a closed, sealed furnace the volume of the off-gas can be reduced by a factor of 50 - 75 and by the factor of 10 - 20 in case of a semi-closed furnace. The investment cost for the off-gas cleaning systems for closed furnaces are much lower than for open furnaces, The cleaned CO-gas can be used as fuel for raw material preheating, coke drying and similar processes, substituting oil or other fossil fuels. Energy can be recovered from semi-closed furnaces in the from of steam or hot water.

Ferro-chrome and the slag are tapped off at regular intervals from tap holes near the bottom of the furnace. Slag and metal are tapped through the same tap hole by using cascade tapping into the same metal vessel. The lower density slag will float at the top and eventually overflow through the ladle spout to the slag-pot or via secondary launder to a slag pit, granulating basin or other slag vessel. Less frequently metal is tapped directly to the casting area. After the slag is skimmed off, the molten metal is cast. Bed casting and layer casting are the most frequently used methods of casting ferro-chrome because of the simplicity and the low costs of these methods. The cooled castings are crushed and screened on the product handling line to produce the commercial lot specified by the customers. If it is possible the molten ferro-chrome can also be transferred directly to an adjacent stainless steel making plant.

The slag can either be granulated with a high pressure water jet or cast outdoors in layers, cooled, crushed and screened. Slag that contains metal is also crushed and the metal content recovered by means of slag-metal separation. Recovered slag-free lump metal can be sold, while slag contaminated metal and fines are generally recycled to the smelting process. Both the granulated and the lumpy slag are reused as building and road construction material.
An example of a High-carbon ferro-chrome production process using a closed submerged electric arc furnace is shown in the following figure.

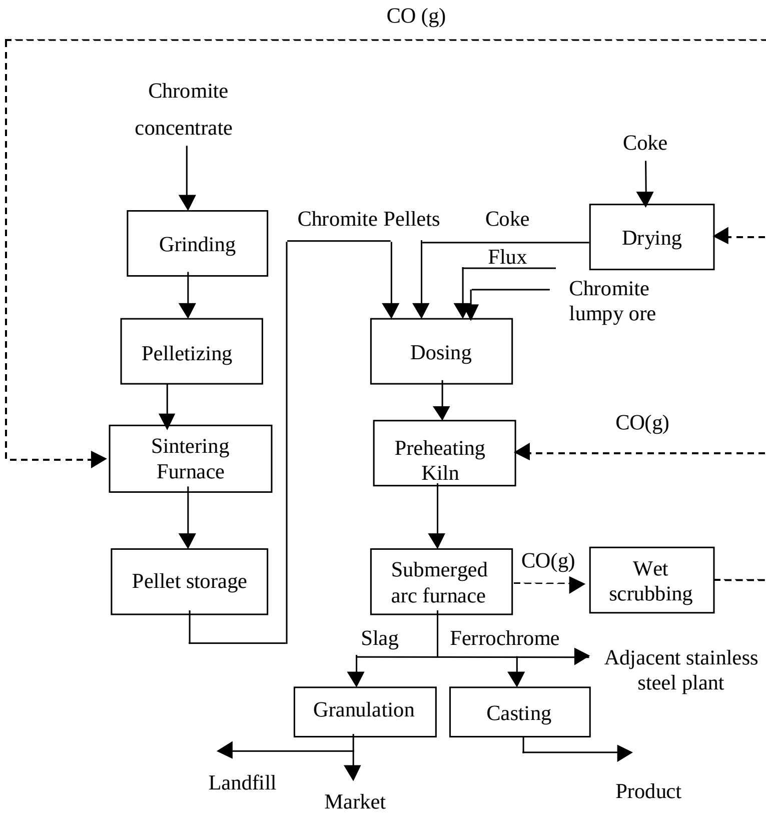


Figure 9.1: High-carbon ferro-chrome production by using a closed furnace

Due to the high availability of chromite fines the DC (Direct Current) arc technology has been developed for smelting of chromite fines without prior agglomeration. The principle is a transferred arc open bath process where the furnace is equipped with a single hollow graphite electrode for the charging of chromite ore fines, reductant fines and fluxes. The chrome ore can efficiently preheated for example in a fluidised-bed system. The use of off-gas energy can decrease the electric energy consumption per unit produced.

9.1.1.3.2 Medium-carbon ferro-chrome

Medium-carbon ferro-chrome (MC FeCr) can be produced by the silico-thermic reduction of chromite ore and concentrates or by the de-carburisation of HC FeCr in an oxygen-blown converter. The Oxygen can be introduced in the molten metal from top of the melt by using water-cooled lances or by injection from the bottom of the converter. The bottom-blowing process has the advantage that a high de-carburisation rate can be achieved together with a high chromium recovery. The high bath temperature in a bottom-blown converter affects the high de-carburisation and chromium recovery rate.

The silico-thermic route is more economic and therefore more important today for producing MC FeCr. The reason may be the small amount of MC FeCr that is needed compared with the high demand of HC FeCr together with the fact that Low-carbon ferro-chrome can be produced by the same process as well.

9.1.1.3.3 Low-carbon ferro-chrome

In order to get the desired low carbon content in the Low-Carbon ferro-chrome a carbo-thermic process can not be used. The most commonly used processes are therefore metallo-thermic reductions known as the Duplex, Perrin or Simplex processes.

At the time of writing the only process used in the European Community to produce LC FeCr is the Duplex process. In this process LC FeCr is produced by the silico-thermic reduction of a lime-chromite slag. The slag-smelting process takes place in a tiltable AC arc furnace with Søderberg electrodes. The furnace is operated at about 1750 ºC. The liquid melt is tapped in regular intervals into a first reaction ladle.. When SiCr, ore and lime is added to the ladle the reacting mixture is converted into LC FeCr and an intermediate slag. During this process the ladle is covered by a smoke hood. About 70% of the intermediate slag is transferred to a second reaction ladle, which is also covered by a fume collection hood. Adding Si, FeSi, sand and boric acid to the mixture produces a final slag and a metal. The metal is recycled back to the first ladle. A fabric filter cleans the off-gas of the furnace and from both reaction ladles. The dust from the bag house is recycled into the smelting furnace. The Perrin process is similar but uses two arc furnaces.

LC FeCr can also be produced by the so-called Simplex process. In the Simplex process HC FeCr is crushed in a ball mill in order to get a ferroalloy powder. After briquetting the HC FeCr-powder together with Cr_2O_3, Fe_2O_3 the mixture can be de-carburised by annealing at about 1350 ºC in a vacuum furnace.

9.1.1.3.4 Silico-chromium

Silico-chromium is also used as an alloying element in the steel industry. It can be produced in the same kind of three phase submerged electric arc furnaces as used for HC FeCr production. The reduction of SiO_2 to Si is combined with the generation of huge amounts of CO gas. The high generation rate of CO makes it important to use a porous burden (e.g. gas coke), a semi-closed or closed furnace with an appropriate energy recovery system.

9.1.2 Ferro-silicon and silicon alloys

Ferro-silicon, silicon metal and silico-calcium (SiCa) are used as additives in different industrial activities. As an alloying element, ferro-silicon increases the strength of steel and is therefore used to melt steel that is needed to produce for instance wire-cords for tyres or ball-bearings. High purity FeSi is used to produce high permeability steel for electric transformers. Silicon metal is important as alloying element in aluminium and for the production of chemicals and electronic equipment. The major user for silico-calcium is also the steel industry. The above mentioned metals can be classified by their silicon-content as follows.

1.	**Ferro-silicon**,	silicon content less than 96%
2.	**Si-metal**	silicon content above 96%
3.	**Silico-calcium**	silicon content about 60 – 65% and calcium content of 30 – 35%

9.1.2.1 Raw materials

The raw materials that are commonly used for the production of ferro-silicon, silicon metal and silico-calcium are listed in the following table.

Raw material	Ferro-silicon	Si-metal	Silico-calcium
Quartz	■	■	■
Coke	■		■
Petrol coke		■	
Coal	■	■	■
Charcoal	■	■	
Woodchips	■	■	
Limestone			■
Iron-ore/steel scrap	■		
Amorphous carbon		■	
Graphite electrodes		If a combined graphite/ Søderberg-electrode is used	
Søderberg electrode paste	■		■

Table 9.1: Raw material for the production of ferro-silicon, Si-metal and silico-calcium

In order to achieve good process results the selection of the raw material is due to some quality requirements. The thermal strength of the quartzite for example is of special importance, because it is connected to the gas permeability of the charge where too much fine sized material may prevent gas flow. The carbon quality is important for the environmental performance of the process, because the coal and coke contains normally sulphur and some other unwanted elements. If for instance carbon contains mercury or other vaporous elements, they will evaporate in the process and will be transferred as part of the off-gas into the environment.

9.1.2.2 Production of ferro-silicon, silicon metal and silico-calcium

Raw material is normally supplied to or closed to the plant by truck and train. Several ferro-silicon and silicon plants are located near the sea or a river where boats are mainly used for transportation of raw materials and products. The loading and unloading of raw material is done with the use of crane grips, front-end loaders or dumper trucks.

The different raw materials that are used for the Si, FeSi and SiCa-production are preferably stored on hard surfaces in order to prevent contamination. The reductants are normally stored indoors, to avoid the material from humidity caused by rain. Some of the reductants can have self-igniting characteristics. In these cases, appropriate ways of surveying have to be implemented to avoid self-combustion, e.g. charcoal or coal with a high content of volatile matter and woodchips.

Ferro-silicon, silicon metal and silicon-calcium are commonly produced in low-shaft three phase submerged electric arc furnaces. The electric arc furnaces can be of the open or semi-closed type. The furnace normally rotates e.g. once a week, in order to connect the reaction areas around each electrode tip. This homogenises the molten metal in the furnace and saves 5 to10% of electric energy. The rotation gives rise to some difficulties in obtaining good capture efficiency of the fugitive emissions at the tap-hole as the location of the tap-hole will rotate with the furnace. A typical electric arc furnace for the production of ferro-silicon is shown in the following figure.

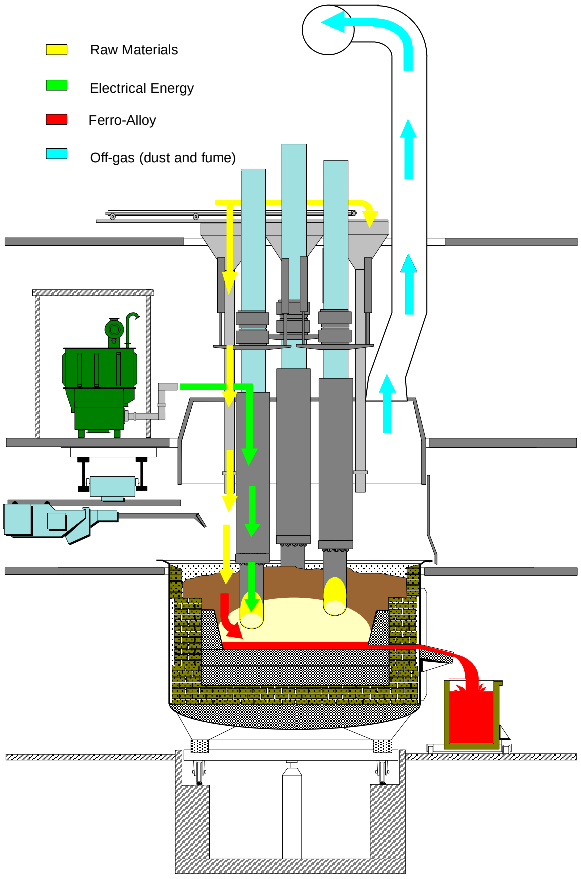


Figure 9.2: Electric arc furnace for the production of Si-metal, ferro-silicon and CaSi

The raw material is fed from storage bins above the furnace, through feeding tubes into the smelting zone around the electrodes. In small furnaces the raw material can also be feed by using of stocking cars.

The smelting of silicon metal and silicon alloys normally takes place in open or semi-closed furnaces. The open furnaces are commonly built up with moveable curtains or gates around the hoods for furnace maintenance and eventually manual feeding. The furnace hood is the upper part of the furnace. The hood has several tasks, first of all it collects the process off-gas and shields the equipment from the process heat. Secondly the hood is the site for electrode arrangements, raw material charging and cooling arrangement for the furnace. For the FeSi and CaSi production the Søderberg-technology is used. For silicon production the electrode is often pre-baked and screwed on top of the previous electrode according to the electrode consumption. In recent years an electrode has been developed utilising a combination of the Søderberg-technology and a graphite core with a stable iron electrode casing. This combined electrode allows the implementation of the Søderberg-technology in the production of silicon metal. The aim is to reduce the iron impurities caused by the electrode casing and reducing the high coasts of pre-baked graphite electrodes. The semi-closed furnace has been introduced to control the suction of air into the furnace top and thereby reducing the total gas stream from the furnace.

This increases the gas temperature and requires an improved temperature control on the off gas side, but at the same time allows for an even higher energy recovery. The process off-gas containing silica fume is cleaned in a bag house using fabric filters.

The liquid metal is tapped off continuously or at regular intervals. The metal is cast from the ladle after the tapping is finished. Transportable tapping vessels can be brought to the tapping position by suitable vehicles or by overhead cranes. The metal can also be directly tapped to the casting area without using transport vessels The silicon alloy is then cast into moulds and crushed by using jaw-, rotary or roll crushers or granulated in water. A process flow diagram for the production of ferro-silicon, silicon metal and calcium silicon is presented in the next figure.

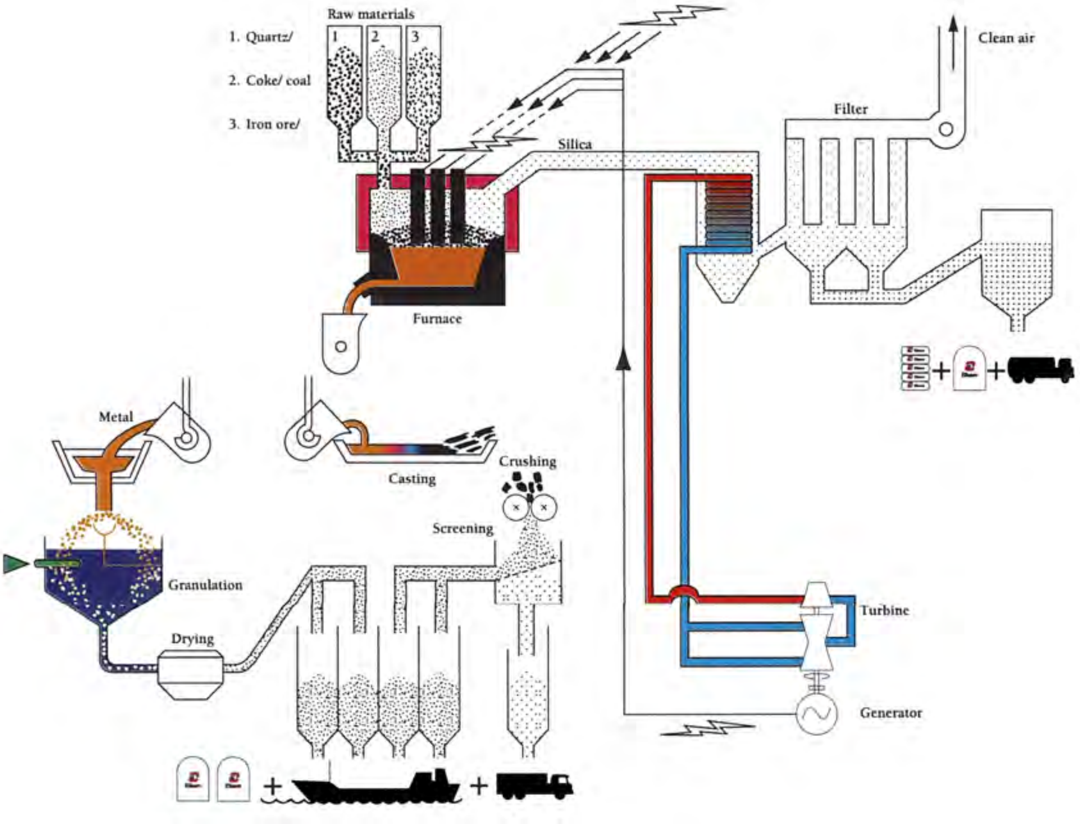


Figure 9.3: Process flow diagram for a modern production of ferro-silicon and silicon metal [tm 152, A. Schei, J.Kr. Tuset, H.Tveit 1998]

It should be noted that the production of silicon metal and ferro silicon is an almost slag free process as nearly all the impurities present in the raw material are transferred to the products, metal or micro-silica. To obtain a higher purity metal a further refining step is needed. The refining takes place by oxidising the impurities in a ladle. Injection of oxygen gas or air is done through immersed lances, porous plugs in the ladle bottom or injectors. Correcting slag can also be added to improve the refining process. The refining stage is covered with a fume collection system e.g. a fume collection hood that is connected with a bag house.

9.1.3 Ferro-manganese and manganese alloys

Ferro-manganese is another bulk ferroalloy of great importance mainly in the steel and stainless steel industry. Initially employed as a deoxidising and de-sulphurising agent, today ferro-manganese is mostly used to improve the hardness and wear resistance of steel. Ferro-manganese and other important manganese alloys can basically be classified as:

1.	**High-carbon ferro-manganese**	(HC FeMn) with max 7.5% C
2.	**Medium-carbon ferro-manganese**	(MC FeMn) with max 1.5% C
3.	**Low-carbon ferro-manganese**	(LC FeMn) with max 0.5% C
4.	**Silicomanganese**	(SiMn) with max 2.0% C
5.	**Low-carbon silico-manganese**	(LC SiMn) with max 0.05% C

9.1.3.1 Raw materials

The production of ferro-manganese and silico-manganese is based on a blend of manganese containing ores as primary raw material. In order to obtain good process efficiency the manganese ore and concentrates (with a low iron content) should be of lumpy type or as sintered material. Other raw materials that are required for the smelting process is iron ore and fluxing agents such as limestone and dolomite. Coke is used as a reducing agent and in case of HC FeMn production in a blast furnace also as an energy source. For the production of silico-manganese also rich ferro-manganese slag and quartz are needed.

9.1.3.2 Pre-treatment techniques

To use fine ores in the production of ferro-manganese an agglomeration, pelletising and sintering step is used. Beside ore fines, the burden for sinter incorporates fuels (coke fines, coal fines, gas for ignition) and fluxes like limestone and dolomite as well as recycled fines and dust. Sintering is used in order to get a more suitable size and to reduce the natural ore to an intermediate metallurgical grade raw material. The main advantages of the agglomeration and sinter process are [tm 107, Ullmanns 1996]:

- Fine ore, which has a limited application and value in conventional smelting, is agglomerated and converted to a superior product;
- Reduced gas volumes, and hence fewer furnace eruptions, result when smelting sinter;
- Furnace availability and operating loads are increased.
- Better porosity of the burden with easier penetration and elimination of the gas generated by the reduction reactions.

9.1.3.3 Production of ferro-manganese and silico-manganese

9.1.3.3.1 High-carbon ferro-manganese

High-carbon ferro-manganese (HC FeMn) can be produced by carbo-thermic reduction of lumpy or sintered manganese ore either in a blast furnace or in a three-phase submerged electric arc furnace.

The blast furnaces that are used for smelting HC FeMn are similar of those used for the production of pig iron, higher temperatures are needed for the reduction of manganese oxides. The reduction of higher manganese oxides (MnO_2, Mn_2O_3 and Mn_3O_4) takes place in the upper part of the blast furnace. The reduction process of higher manganese oxides is exothermic and contributes to maintain a relatively high temperature of the top gas. In some cases additional cooling of the furnace top is introduced to limit the temperature. Further reduction of manganese oxides requires temperatures above 1400 °C and takes place in a limited zone above the tuyeres. This reduction process is endothermic and consequently needs high coke consumption.

As a result, the production of HC FeMn in a blast furnace is related to a high generation rate of CO. The quantity of CO produced is much higher than that necessary to heat the blast in the hot stoves. The excess gas is commonly used to produce electric energy.

The CO containing off-gas has to be de-dusted before it can be used to heat the hot stoves or burned to produce steam of the electricity generation. For the off-gas de-dusting a variety of different techniques are available, e.g. electrostatic precipitators, scrubbers, washing towers or bag filter. In order to prevent the hot stoves from damage of the refractory material and to minimise the dust emissions the de-dusting system is designed to work below 10 mg/Nm^3 of dust. These techniques are described in detail in section 2. The production of HC FeMn in a blast furnace is shown in the next figure.

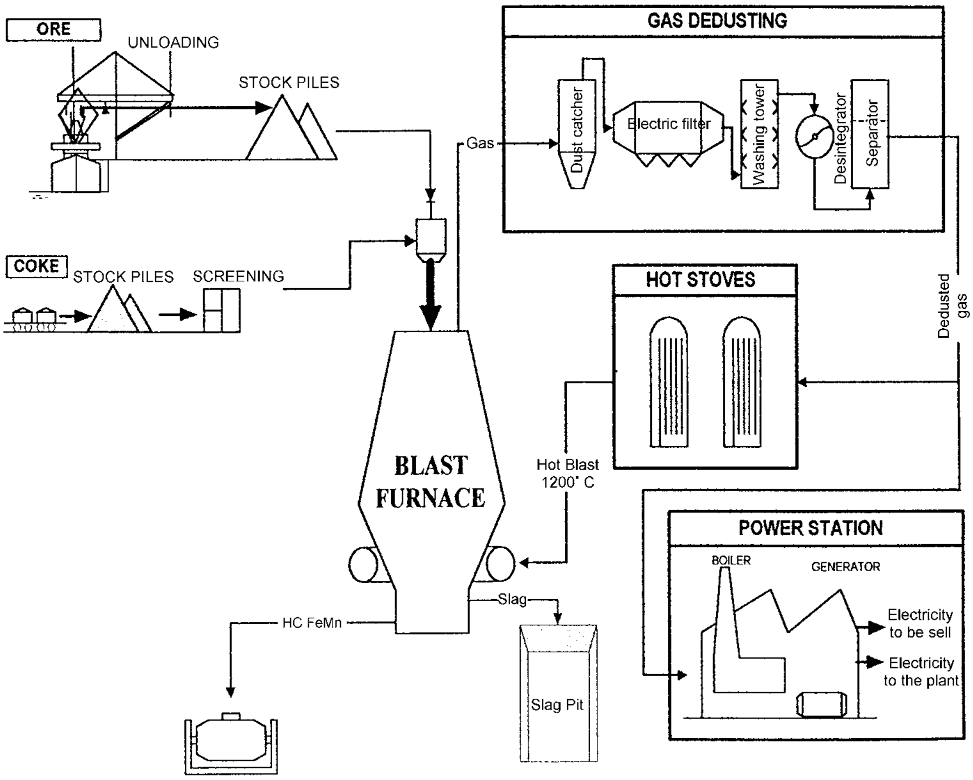


Figure 9.4: Production of HC FeMn in a blast furnace

Because of the high coke consumption in a blast furnace the majority of producers use electric arc furnaces to produce HC FeMn. The advantage of the electric arc furnace is due to the fact that the energy for smelting the burden is supplied by electric current. Carbon in form of coke and coal is only needed as a reducing agent. The consumption of coal or coke is consequently much lower than the amount of coke that is used in a blast furnace.

The commonly used electric arc furnaces are of the closed, semi-closed and open type, which has no or only limited consequences on the furnace itself but affects the gas composition, flow-rate, recovery and de-dusting system. The diameter of the furnace varies from 2 to 20 m. Smaller furnaces which are still under operation have the advantage to be more flexible, because they can switch more easily between different products.

The raw material is fed to the smelting process by gravity from storage bins above the furnace. The feeding tubes are placed around the electrodes in order to ensure an even distribution of raw material to the furnace.

The electric arc furnace for the production of HC FeMn needs to be adapted compared to the furnaces that are normally used to produce ferro-alloys. According to the high vapour pressure of ferro-manganese the smelting process needs a careful temperature control because the charge should not be overheated. The vapour pressure together with a relatively low resistivity of the ferro-manganese burden results in a low current density of the electrodes. As a consequence the furnace needs to be operated at low voltage which requires a larger diameter of the electrodes for the high current that is need for the process.

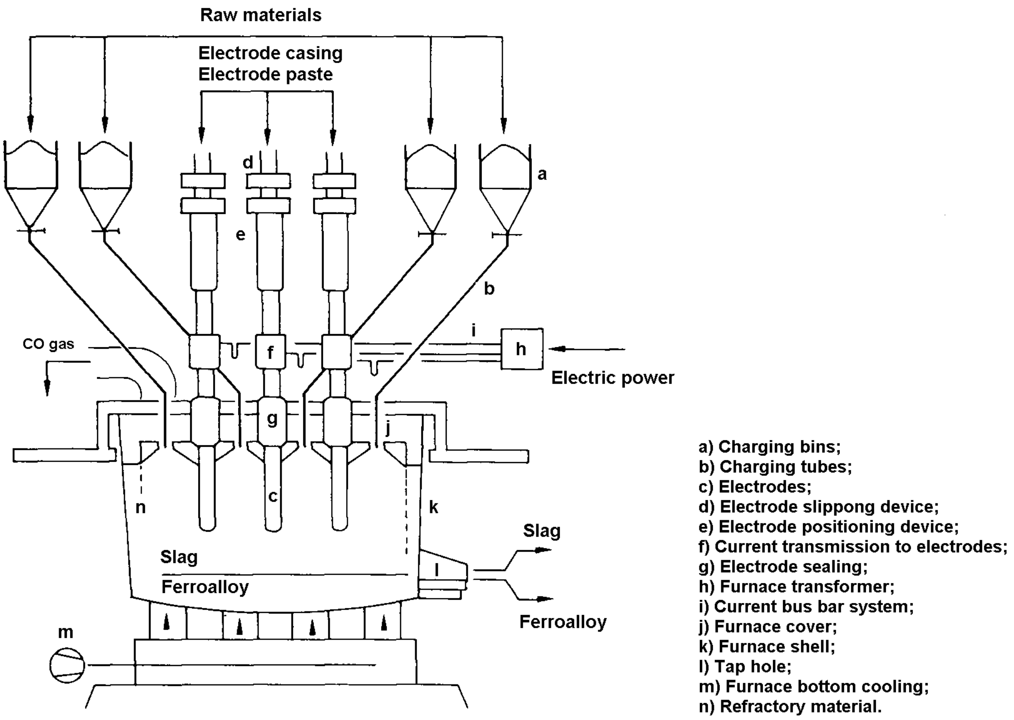


Figure 9.5: Closed electric arc ferro-manganese furnace operating Søderberg electrodes [tm 107, Ullmanns 1996]

Electric arc furnaces for the production of ferro-manganese are operated only with self-baking Søderberg electrodes. Because of the large diameter, the use of pre-backed electrodes is uneconomic compared with the Søderberg electrodes.

The Søderberg electrodes consists of a mild steel or stainless steel casing which is stiffened with internal fines and is filled with a carbonaceous paste, consisting of a solid aggregate, usually calcined anthracite, and a binder of coal tap pitch. The tar becomes plastic when hot and fills the entire volume of the casing. On further heating of the electrode by the current and furnace heat, the paste is baked and becomes solid [tm 107, Ullmanns 1996]. A typical closed electric arc furnace for the production of ferro-manganese operating Søderberg electrodes is shown above.

The molten metal and the slag can be tapped off continuously or in regular intervals. The metal is cast into moulds lined with crushed ferro-manganese. A casting machine can also be used for casting the liquid metal. The solidified metal in then crushed and screened for the specific needs of the customers. Slag is normally obtained as rich slag (with about 30% Mn) and used further for the production of silicomanganese

According to the lower coke consumption of the electric furnace the off-gas contains less CO than the off-gas from the blast furnace. However there are some facilities where the CO rich off-gas is used to produce electricity. The CO rich gas can also be utilised for other industrial uses, for instance as a raw material for chemical synthesis, which depends on the local conditions.

9.1.3.3.2 Medium-carbon ferro-manganese

For the production of Medium carbon ferro-manganese (MC FeMn) two different routes can be used: - the silico-thermic reduction of manganese ore and: - the de-carburisation of HC FeMn in the oxygen blown converter. The most important process that is used by most of the producers is the refining process of HC FeMn.

For the de-carburisation of HC FeMn, oxygen is blown into the molten metal, which is tapped off from the furnace. The oxygen blown into the melt oxidises part of the manganese and increases the bath temperature from about 1350 to 1550 ºC. With increasing temperatures the carbon present in the HC FeMn also tends to be oxidised and again raises the temperature from 1550 up to 1750 ºC. The oxidisation of carbon consequently reduces the carbon content of the ferro-manganese. For the production of MC FeMn the de-carburisation process ends when a corresponding carbon content of about 1.3% is reached. The high temperature also leads to the vaporisation of ferro-manganese that leaves the process as fume. The fume can be collected by using hoods and sent back to the HC FeMn smelter.

In contrast to the refining process that uses HC FeMn as a raw material, the silico-thermic production needs manganese ore and lime or a high-grade slag and silico-manganese. The reduction itself is performed in a three-phase electric arc furnace, with electrodes made of graphite. At the end of the cycle, the molten alloy and the slag are cast and separated. The slag is recycled after cooling and crushing as raw material to the silico-manganese production plant. The fumes of the furnaces will be de-dusted in a fabric filter. With the silico-thermic reduction the production of MC FeMn containing 1% of C is possible.

The main advantages of the refining process are the lower operating and capital investment coasts. The advantage of the silico-thermic process is to produce Low-carbon ferro-manganese in the same process.

9.1.3.3.3 Low-carbon ferro-manganese

Low-carbon ferro-manganese (LC FeMn), which contains less than 0.75% C is usually produced by a silico-thermic process. The production of LC FeMn by de-carburisation of HC FeMn has recently also performed. As a raw material a rich slag is suitable because of the low level of impurities. Also the presence of already reduced manganese oxides in the rich slag is favourable for the process. The production of LC FeMn takes place in an electric arc furnace very similar to that used for MC FeMn, produced by a silico-thermic process. the slag obtained is used for silico-manganese production as raw material.

9.1.3.3.4 Silico-manganese

Silico-manganese is required as an alloying element in the steel industry as well as a raw material to produce MC and LC FeMn. The production of silico-manganese is based on manganese ore or sinter and quartz as raw material. Instead of manganese ore, a rich ferro-manganese slag like that produced as rich-slag in a HC, MC and LC FeMn production may be used as a manganese source. Silico-manganese is today only produced in submerged electric arc furnaces, which can be of a closed semi-closed or open type. The furnaces are the same or very similar to those used for HC ferro-manganese production and often a furnace is operated with alternate campaigns of each alloy. According to the composition of the feed mix silico-manganese with a silicon content from 15 to 35% can be produced. For a proper furnace operating and effective silicon reduction it is necessary to penetrate the electrodes deeper in the burden in order to reach the high temperature needed for the process.

9.1.4 Ferro-nickel

9.1.4.1 Raw materials

Ferro-nickel (FeNi) as well as ferro-chrome is the major alloying agent in the production of stainless steel. Laterite ore is the main raw material. Laterite ore is characterised by a relatively low nickel content (1.2 – 3%) and a high moisture content (up to 45%) together with chemically bound water in the form of hydroxide [tm 107, Ullmanns 1996]. Besides laterite ore, coke or coal is the second raw material that is needed in the ferro-nickel production. Coke or coal is used as a reducing agent because the ferro-nickel production takes place by a carbo-thermic process. FeNi can also be produced from secondary raw materials, such as spent catalysts and sludge from the galvanising industry.

9.1.4.2 Production of ferro-nickel from primary raw material

The production of ferro-nickel from primary raw material is carried our exclusively by the rotary kiln-electric furnace process. As mentioned before the raw material carries a significant amount of water, therefore the first step of the process is a drying operation. Drying normally takes place in a directly fired rotary dryer where the moisture content can be reduced from about 45 to 15%. Further drying below 15% should be avoided in order to keep the dust generation in the subsequent calcining and smelting process as low as possible.

The next process step is homogenisation where the different ores are mixed with coal and pelletised dust, which is recycled from the main process. The dry feed mix is then fed to a rotary kiln. The rotary kiln is used to de-hydrate the ore by calcination and to pre-reduce the nickel and iron oxide. The process takes place at about 900 – 1000 ºC. The calcining and pre-reducing process results in a furnace feed which contains about 40% of the nickel as a metal and the iron content in form of iron(II)-oxides.

The hot pre-reduced calcine can be introduced directly to the smelting furnace or by insulated containers. The containers may be used for two reasons, first to conserve the heat and second to add coke or coal required for complete reduction before they are discharged into the electric furnace, where or melting and final reduction occurs [tm 113, M. T. Antony and D. S. Flett 1997].

Ferro-nickel smelting today only takes place in electric arc furnaces. In the electric furnace the reductive smelting operation occurs by the combined action of carbon electrodes and added solid carbonaceous reductant. The slag melting temperature in the ferro-nickel smelting process is strongly dependent on the FeO-content. The operation mode of the furnace therefore changes if the slag melting temperature is above or below the melting temperature of the metal. If the melting temperature of the slag is higher than the melting point of the metal the furnace can easily be operated with a covered bath. In this case the electrode tips are not immersed in the slag and the final reduction of the nickel and iron oxides takes mostly place in the hot charge which covers the slag layer. If the melting temperature of the slag is below the melting temperature of the metal the furnace is more difficult to operate. In order to reach the melting temperature of the metal the electrodes should penetrate deep in to the slag layer. The highest bath temperature will then be around the electrode tips where smelting takes place in the slag-metals interface. These operating conditions result in a high generation rate of CO-gases, which requires an open bath surface around the electrodes.

To reduce a high content of nickel oxides commonly the burden contains an excess proportion of carbon. These also increase the amount of iron that will be reduced and the final carbon content of the crude ferro-nickel. To reduce the iron and carbon content a further refining step is necessary. To avoid further refining several process improvements had been made. For instance in the “Ugine Ferro-nickel Process” no reductant is added. The electric furnace produces a molten ore, which is reduced to ferro-nickel by using ferro-silicon in a further ladle furnace. In the “Falcondo Ferro-nickel Process” a shaft furnace is used instead of a rotary kiln. In the shaft furnace a briquetted ore is reduced with a reducing gas (low sulphur naphta). The subsequent electric furnace is then only used to melt the metal and to separate it from the slag.

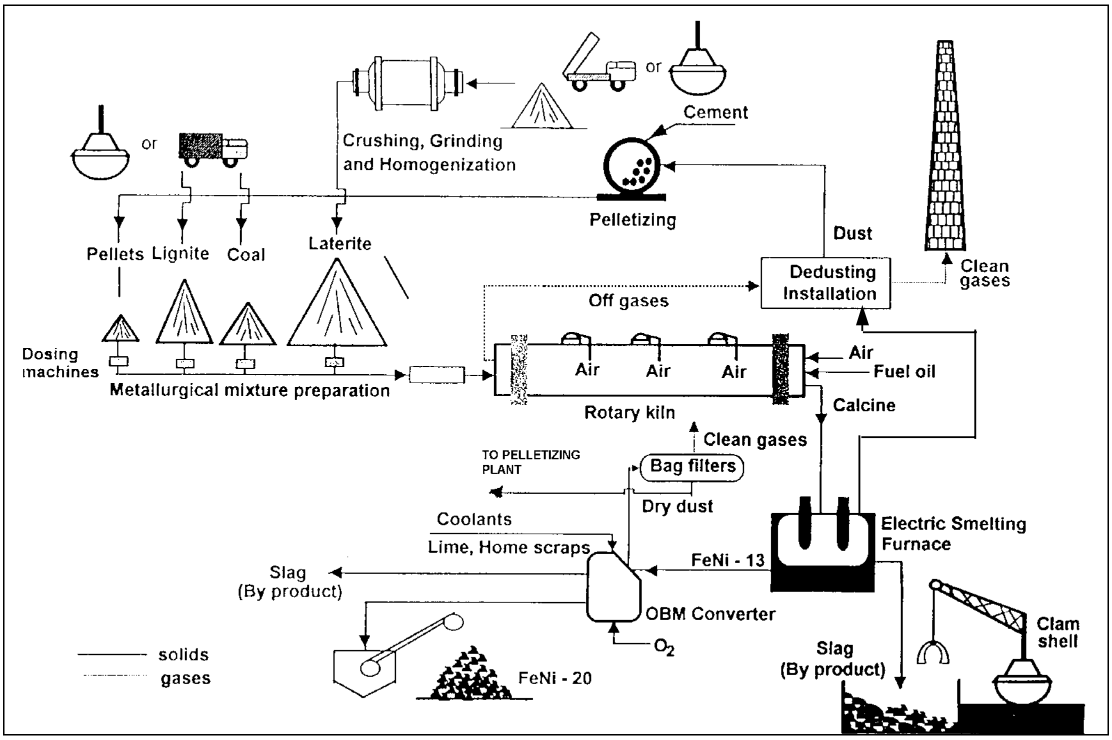


Figure 9.6: Rotary kiln-electric arc furnace process for the ferro-nickel production

Ferro-nickel produced by the conventional process needs further refining. Besides the reduction of iron and carbon the impurities like sulphur, silicon and phosphorus should be removed. For ferro-nickel refining a variety of equipment is available e.g. shaking reaction ladle, induction furnace, electric arc furnace and oxygen blown converters. The purified ferro-nickel is cast into ingots or granulated under water.

The dust containing off-gas from the rotary kiln, the electric arc smelting furnace and the refining step is treated by an appropriate abatement system. The dust content can be pelletised and recycled to the raw material blending station. A flow sheet of a ferro-nickel production is presented in the above figure.

9.1.4.3 Production of ferro-nickel from secondary raw material

FeNi can also be produced from nickel containing residues used as secondary raw material. These residues, mostly spent catalysts from the grease production, are burned in a rotary kiln in order to concentrate the Ni-content as Ni-oxide in the flue dust. The flue dust containing off gas is cleaned in a membrane bag filter, where the collected dust is used as the raw material for the smelting process. The production of FeNi then takes place in a submerged electric arc furnace. The molten alloy is tapped, granulated in water and packed in drums or big-bags for supply.

9.1.5 Ferro-vanadium

The addition of ferro-vanadium to a steel melt increases the tensile strength and the high temperature strength of carbon steel even if small amounts are added. Vanadium alloyed steel is therefore used for high speed cutting tools.
Ferro-vanadium (FeV) can be produced by a carbo-thermic or a metallo-thermic reduction of vanadium oxides assisted by the presence of iron. Because carbon is used in a carbo-thermic reduction the final carbon content of the produced alloy is high. The production of ferro-vanadium by using carbon as a reducing agent is therefore only possible if there are no requirements of a low carbon content. Currently, ferro-vanadium is usually be produced by an alumino-thermic reduction.

When necessary, grinding, sizing and drying can be carried out prior to charging the mix to the smelting process. The alumino-thermic reduction of vanadium oxide is a self-sustaining process that can be carried out in a refractory lined crucible. The reaction vessels used for this process can be of the following type.

- Refractory lined crucible using a non-reusable lining.
- Refractory lined ring placed onto a pit containing sand.
- Electric furnace where additional energy can be supplied either to increase the heat of reaction or to enable slag-refining operations to be carried out. The electric arc furnace is also used, because the FeV-fines generated by FeV crushing can be remelted.

The smelting operation takes place in a batch-process, where the whole charge is transferred to the reaction vessel and ignited. After ignition the combustion time for a common batch size of about 1 t of ferro-vanadium takes only a few minutes. Due to the short reaction time the content of vanadium oxides in the slag and the aluminium content in the metal may not reach equilibrium. The production in an electric furnace has therefore the advantage of keeping the charge in a molten state until the reaction is completely finished. The fumes from the process are exhausted and cleaned by using fabric-filters or wet scrubbers.

Depending upon the process type, the slag and metal can be allowed to cool down in the crucible, or slag and metal can be tapped in ladles or in beds to allow separation of slag and metal and to provoke rapid cooling. Tapping of the crucible requires extraction hoods and extraction rates sufficient to evacuate the fumes and the dust escaping during the tapping. The slag from the alumino-thermic process can be used for further crucible linings or crushed and sized to be used in other industries. The metal block can be air-cooled or water-cooled which facilitates further crushing. All crushing and sieving have dedicated dust extraction units, from which the dust is returned to the production process at the most appropriate point to ensure a continuous recycling of recovered products.

9.1.6 Molybdenite roasting and the production of ferro molybdenum

9.1.6.1 Molybdenite roasting

Technical grade molybdenum trioxide (MoO_3) is the main raw material in the production of ferro-molybdenum as well as the starting compound for a number of other molybdenum containing products such as ammonium dimolybdate, sodium molybdate and molybdenum metal [tm 107, Ullmanns 1996]. Roasting as it is shown schematically below performs the conversion of concentrated molybdenite (molybdenum sulphide ore) into technical grade molybdenum trioxide for the metallurgical or chemical industry.

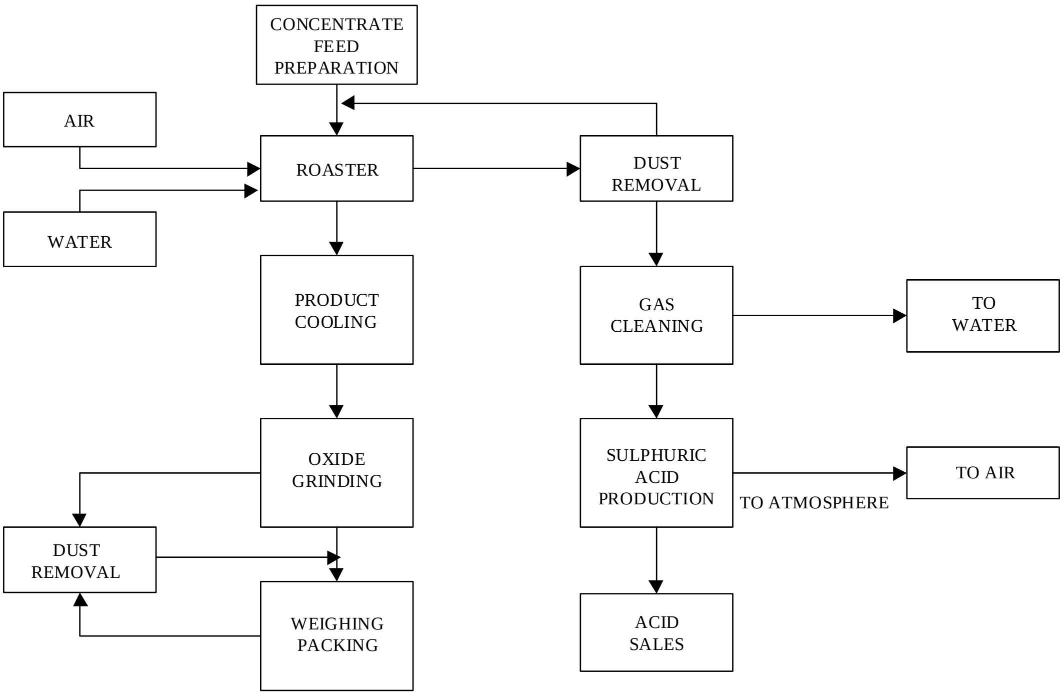


Figure 9.7: Molybdenite roasting flow sheet

The process of roasting molybdenite ore takes place in a multiple heard furnace of the Nichols Herreschoff or Lurgi design. The Nichols Herreschoff type furnace is described in detail in section 2. The multiple hearth furnaces consist of a number of vertically arranged hearts. In the upper part of the furnace additional energy is added in form of natural gas in order to burn off flotation oils and evaporate water.

The roasting process itself is exothermic and doesn't need additional energy unless the heat losses associated with the centre axle column cooling air, radiation from the shell of the roaster and the discharge of hot oxide from the roaster are significant. By means of induced draft fans, the roaster operates at a negative pressure relative to the atmospheric pressure. This serves to control the inflow of ambient air for oxidation and cooling and prevents any emissions of sulphur dioxide to the environment. Airflow, transportation rate and sometimes water spray injection control the reaction rates and temperatures. The molybdenum oxide produced is discharged from the roaster and then cooled, ground to a fine powder, sampled and analysed prior weighing and packing.

The off-gas from the process contains large amounts of sulphur dioxide and dust (up to 15% of the concentrate feed). The dust content can be removed from the gas stream by using high temperature electrostatic precipitators and recycled to the concentrate feed entering the roaster. The sulphur dioxide is normally converted into sulphuric acid in an adjacent sulphuric acid plant. The conversion of sulphur dioxide into sulphuric acid is described in detail in section 2. In addition to the generation of dust and sulphur dioxide rare earth metals such as rhenium and selenium that enter the furnace with the raw material leaves the process as vaporised metal oxides. These elements can be removed from the gas stream by wet scrubbing with a subsequent treatment plant for the scrubbing liquor. Selenium and rhenium are then recovered from the ion exchangers used in the wastewater treatment plant by special companies.

In toll conversion of molybdenum concentrates batches of raw material can have high differences in Mo-content (46% - 58%) and in other components. The roasting of batches with different grades influences the treatment of the off-gases,

9.1.6.2 Production of ferro-molybdenum

Ferro-molybdenum can be produced either by the carbo-thermic or metallo-thermic reduction of molybdenum trioxide. According to practical reasons like the smelting equipment used for the process and the reduced manufacturing costs the metallo-thermic production of ferro-molybdenum is much more important than the carbo-thermic reduction. However the carbo-thermic reduction will briefly be described to provide a complete overview of the ferro-molybdenum production.

9.1.6.2.1 Raw materials

The production of ferro-molybdenum is based on technical grade molybdenum trioxide (MoO_3) as a raw material. Besides the main raw material, molybdenum trioxide, iron oxide or mill-scale iron scrap, steel punchings or turnings are needed to produce ferro-molybdenum. Lime and fluorspar are commonly used as fluxing agents and charcoal, silicon (ferro-silicon) or aluminium, depending on the production route, are needed as a reductant.

9.1.6.2.2 Carbo-thermic production of ferro-molybdenum

For the carbo-thermic reduction an electric arc furnace of the single or three-phase type may be used. Compared with the three-phase electric arc furnace the single-phase system has the advantage of generating a higher energy density within the furnace. This is due to the fact that the furnace is equipped with a bottom carbon electrode. The process takes place as a batch process that normally is started by re-melting of processed slag from a previous smelting operation. The molybdenum trioxide is than added to the process as briquettes. The slag can be tapped off the furnace and the metal stripped off while it is still hot and then cooled with water. The disadvantage of the carbo-thermic process is the fact that the slag contains relatively high amounts of molybdenum. The slag therefore needs to be remelted in a separate process in which a high-carbon intermediate alloy is produced that can be used as a recycling material to start the main process.

9.1.6.2.3 Metallo-thermic production of ferro-molybdenum

As mentioned before, today the metallo-thermic reduction is the most common process that is used for the production of ferro-molybdenum. Due to the higher Gibbs free energy of aluminium compared with silicon, ferro-silicon is the preferred reducing agent in order to assure safe process conditions. However, to obtain the required heat balance for the reaction, it is necessary to use a small amount of aluminium.

The metallo-thermic process requires dry raw material for the process. Mill-scale that arrives wet is stored in a covered bunker prior to screening and drying in order to prevent fugitive losses. Steel scrap that also arrives in bulk is off loaded and packed into containers prior to be stored. Smooth efficient smelting reactions require a blend of suitably sized raw material, this is of particular importance with respect to the oxides and the reducing agents. Fluorspar is sometimes added to improve the slag and metal separation. To get the right sized raw material it is necessary to grind and screen ferro-silicon. All the pre-treatment operations like grinding, screening transferring and blending should be carried out by using dust control measures.

The smelting operation can be done in a number of ways, the most common are [tm, 128 EuroAlliage 1998]:

1. The use of long pits containing sand where refractory lined steel cylinders are placed to form crucibles that contain the metallo-thermic reaction. The reaction itself can be carried out in different ways. The so-called top fired reaction takes place when the whole charge is

placed in the crucible and then ignited from the top. Alternatively only a part of the charge can be placed in the crucible and ignited, the remainder of the charge can then be added as the reaction proceeds (fed reactions).

2. The use of refractory lined crucibles that are placed inside a chamber that can be enclosed. As in the previous description the reaction can then be carried out by placing all of the charge in the crucible and igniting it, or by adding only a part of the charge, initiating the reaction and then progressively adding the rest of the charge as the reaction proceeds.

The dust and fumes generated by the process must be extracted, recovered and recycled in order to assure overall molybdenum yield of 97 – 99%. The collected dust and fume is exhausted to a reverse air jet cleaning bag-house. The filter bags may be manufactured from special fabrics sometimes applied with additional coating to withstand high temperatures. The bag-house dust can then be fed directly back to the main smelting process. Good housekeeping is also necessary to recycle all splashings, floor sweepings etc. in order to get an efficient overall molybdenum yield.

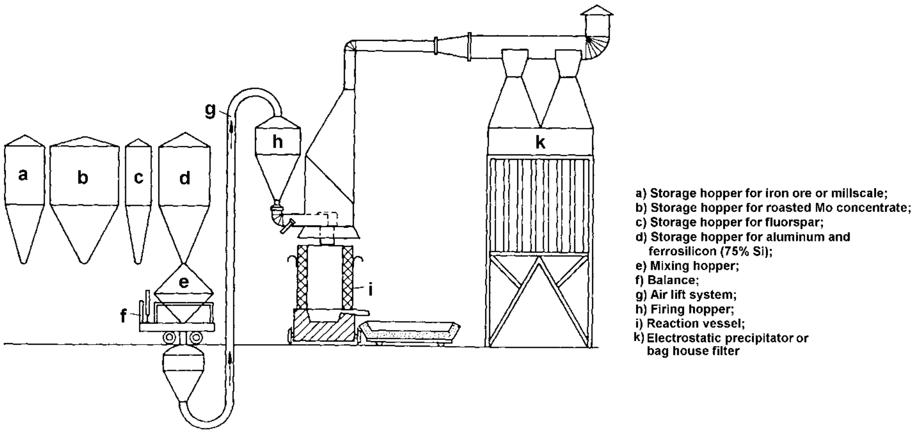


Figure 9.8: Metallo-thermic firming arrangement
[tm 107, Ullmanns 1996]

The smelting process produces an alloy block (mass) that weighs between 2.5 – 3 tonnes. After the slag is separated the hot metal block has to be cooled. This can either be achieved by natural cooling in air or by quenching in water. The cooled metal block is than broken into pieces that can be fed into an integrated crushing and screening plant to produce the wide range of product sizes used world-wide.

A process flow sheet that demonstrates the principle steps of the metallo-thermic ferro-molybdenum production is presented in the next figure.

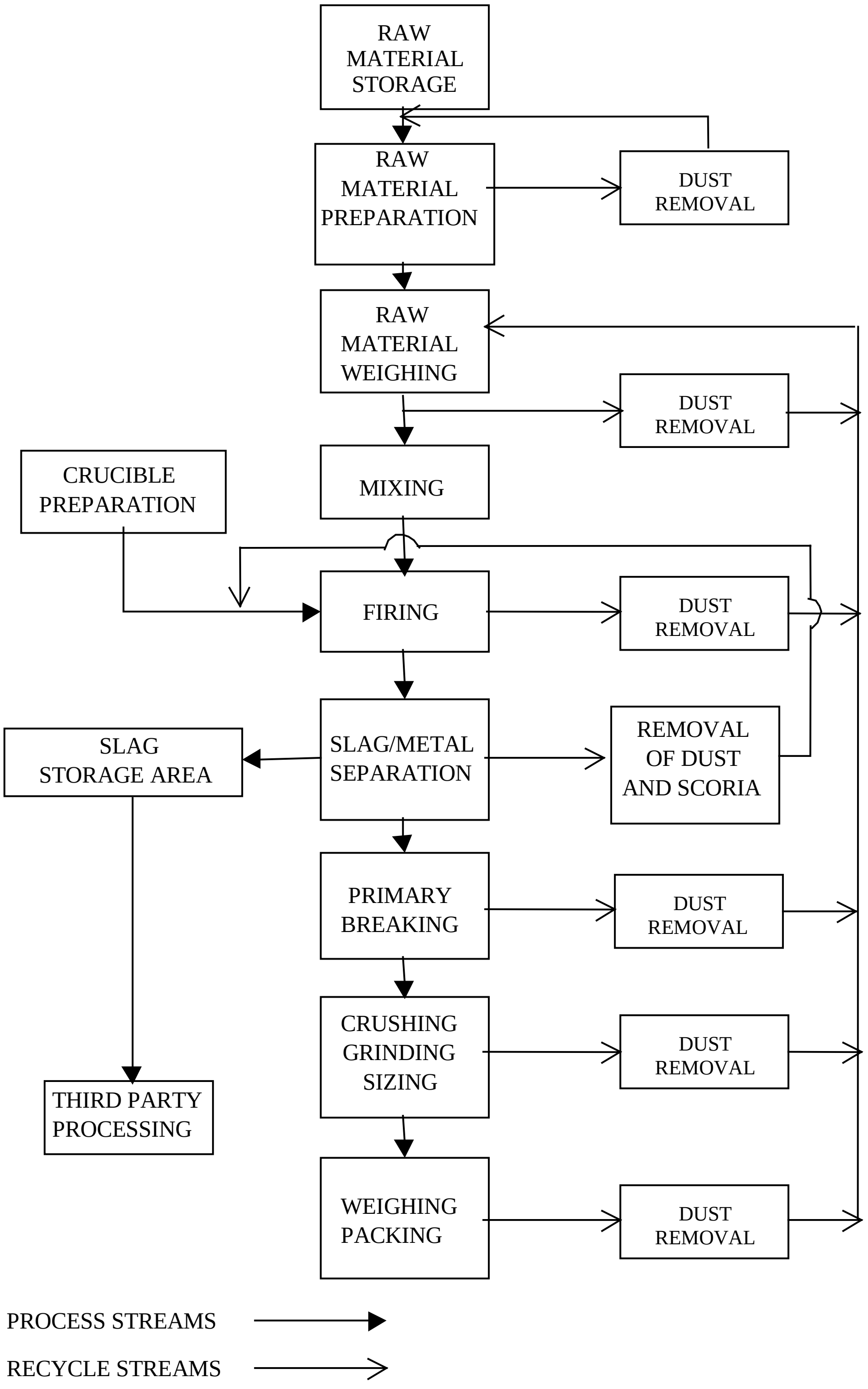


Figure 9.9: Production of ferro-molybdenum by a metallo-thermic reduction

9.1.7 Ferro-tungsten

Ferro-tungsten as well as Tungsten Melting Base (TMB) which is made from secondary raw material is mainly used to improve the properties of steel. Tungsten as an alloying element forms stable carbides and therefore increases the hot strength and wear resistance of steel. Such steel (high-speed steel) is needed to produce high speed cutting tools that can be used up to temperatures of about 600 ºC. Besides this tungsten will increase a number of other properties like the hardness, yield strength and the ultimate tensile strength [tm 107, Ullmanns 1996].

9.1.7.1 Production of ferro-tungsten and tungsten melting base

9.1.7.1.1 Ferro-tungsten

Ferro-tungsten can be produced from different raw materials containing tungsten oxides, e.g. wolframite, scheelite and hübnerite. The reduction of these minerals can be done either by carbo- or metallo-thermic reduction as well as by a combination of both.

The carbo-thermic process that is known as the solid block melting process takes place in an electric arc furnace. Due to the high melting temperature of ferro-tungsten the produced alloy can not be tapped off from the furnace. After the smelting bas been started the metal accumulates in the bottom of the furnace. When the amount of metal has reached the desired weight the furnace is switched off. The metal ingot can then be recovered from the furnace after the refractory lining has been removed. The metal is than crushed and screened. If several furnaces are used in parallel the production can than take place as a quasi-continuous process. The off-gases from the furnace are treated by a gas purification system in order to minimise the environmental impact and to recover the amount of tungsten trioxide in the flue dust.

A combination of the carbo- and metallo-thermic process using both carbon and ferro-silicon as a reducing agent are used to produce a ferroalloy with high tungsten content. The process is carried out in three successive stages in an electric arc furnace. In the first stage, a tungsten trioxide slag is produced that is furthering reduced with ferro-silicon in the following stage. The third and final stage is needed to increase the tungsten content by refining the low-tungsten metal from the second stage by adding tungsten concentrates.

The metallo-thermic process is less valid from an economic viewpoint because the process requires very pure and therefore expensive raw material. In order to keep the process self-sustaining a mixture of silicon and aluminium is normally used as a reducing agent. The metal can be recovered from the furnace vessel after cooling and removing of the furnace linings. According to the economic disadvantages the metallo-thermic production of ferro-tungsten is today only suitable if there are special customer requirements.

9.1.7.1.1.1 Tungsten Melting Base (TMB)

Tungsten Melting Base (TMB) is a tungsten alloy that is produced from secondary raw material. The main sources are different kinds of tungsten metal scrap. The TMB production is only a re-melting and alloying process, which can take place in an electric arc furnace. The fact that more and more tungsten scrap is available on the market increases the importance of the re-melting process that requires less energy as the primary smelting process.

9.1.8 Ferro-titanium

Ferro-titanium can be produced either from primary and secondary raw material and is used for a variety of different purposes. As an alloying element it increases yield strength and reduces the cracking tendency. In the production of stainless steel with a high chrome and nickel content, ferro-titanium is used to bond the sulphur [tm 107, Ullmanns 1996].

For the production of ferro-titanium the primary raw material titanium oxide containing minerals such as ilmenite are used. The reduction occurs commonly by the metallo-thermic process because the carbo-thermic reduction produces an alloy that contains too much carbon and is therefore not interesting as an alloying element in the steel industry. The production takes place as a batch process in a refractory lined crucible or in an electric furnace depending on the process variation.

In recent years the availability of titanium scrap on the market increased and therefore the production of ferro-titanium from secondary raw material is more important. The production of ferro-titanium is achieved by melting ferrous scrap and titanium in an electric induction-melting furnace. The alloying process is a slag free process.

Ferrous units are purchased to a specification in the form of mild steel solids. Titanium scrap is delivered to site in container trucks. The feedstock includes lump scrap metal castings, wrought products and turnings (swarf) from machining processes. Upon receipt, materials are checked to ensure that are not contaminated with radioactive materials. Large lumps of scrap are reduced in size by oxy-flame cutting. Swarf is chipped using a swarf pulveriser and then fed through a centrifuge to remove oil and moisture.

The titanium swarf is degreased in a rotary dryer, where the oil bearing gases are led through a cyclone to remove dust and carry over. These gases then pass though an afterburner. Combustion gases/fumes are either recirculated through the dryer or are ducted to a second cyclone. After passing through the cyclone, sorbent (sodium bicarbonate) is introduced to neutralise the gas stream. Finally the gas passes through a ceramic filter before being discharged to the atmosphere via a stack.

Furnace charges are calculated based on the analysis of the raw materials. The materials are weighed into pans and fed into an electric induction melting furnace. A chute system is used to feed in materials during the melting operation. When melting is complete, the molten metal is tapped into an ingot mould and a stream sample is taken for analysis. After cooling, the ingot is transferred to other operations such as breaking, crushing and grinding to achieve the required product size. The next figure presents a flow-diagram for the production of ferro-titanium.

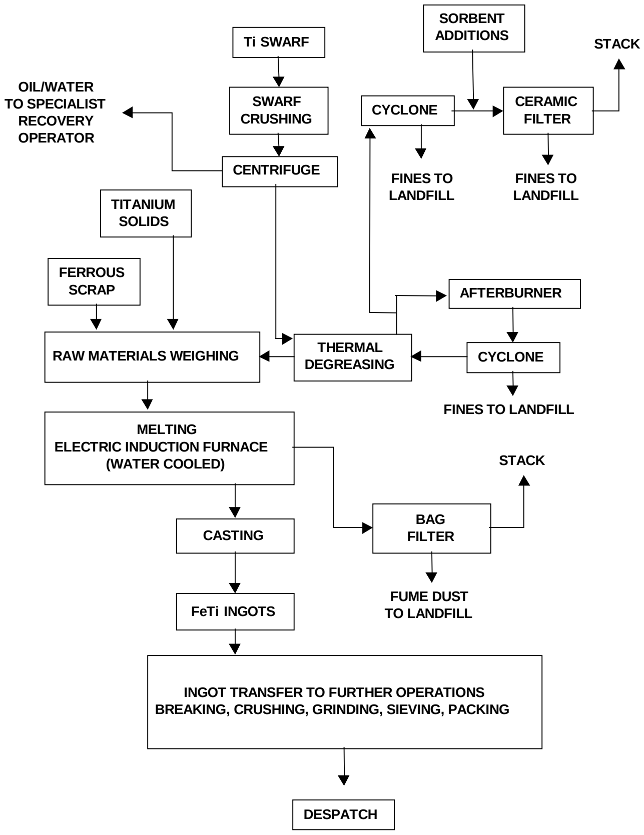


Figure 9.10: Flow diagram of the ferro-titanium production

9.1.9 Ferro-boron

Ferro-boron is mainly used as an additive in steel making to increase the hardenability, creep resistance and hot workability because boron alloyed steel is oxidation resistant up to 900 ºC. The raw material to produce ferro-boron are boric oxides and boric acid. Carbon (charcoal), aluminium or magnesium are used as a reducing agent. The production can even be done by the carbo-thermic or metallo-thermic reduction.

The raw materials arrive in a variety of packed forms, for example, drums, flexible intermediate bulk containers, pallets, stillages and polyethylene wrapped bales. The materials are weighed out into enclosed bins at a specially designed weigh station. The bulk bags are discharged from a framework incorporating a sealing membrane, which prevents fugitive emissions. A local exhaust ventilation system vented to a filter unit further the removal of any dust.

The carbo-thermic reduction takes place in single or three-phase submerged electric arc furnaces depending on the process specification. There exist some variations of the carbo-thermic process. One reduces boric oxides and iron oxides simultaneously with charcoal in a submerged electric arc furnace, where another process is based on boric acid iron powder and charcoal in a Héroult-type electric arc furnace. The following flow-sheet shows the process for ferro-boron and boron –alloy production.

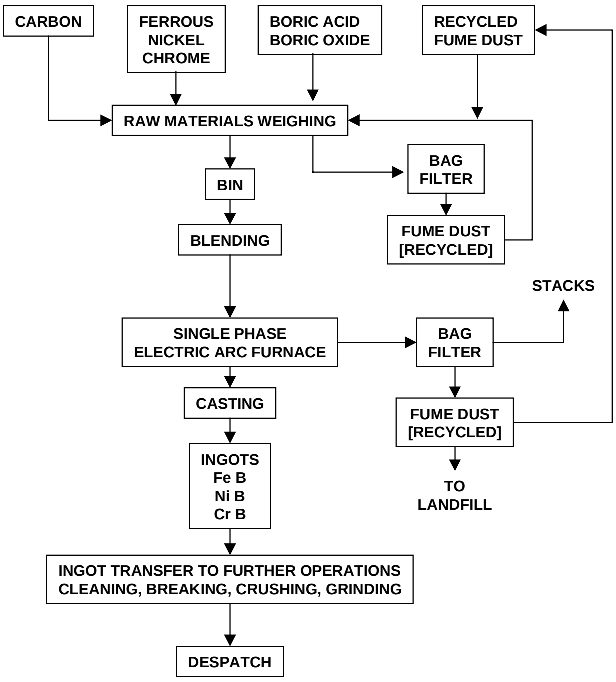


Figure 9.11: Process for ferro-boron and boron –alloy production

The metallo-thermic process uses aluminium together with a small portion of magnesium as a reducing agent. This reaction is highly exothermic and needs only a few minutes to take place in a refractory lined crucible. The reaction can be ignited as a whole charge or as a starting mix. After the reaction is finished the metal-alloy that builds the bottom of the furnace can be removed mechanically. It can than be crushed and screened in order to produce the desired particle size.

9.1.10 Ferro-niobium

Ferro-niobium as an alloying agent improves the corrosion resistance and weld-ability of steel and prevents especially stainless chrome-nickel steel of inter-crystalline corrosion. The raw materials to produce ferro-niobium are niobium containing ore and concentrates and iron oxide. The reduction occurs as an alumino-thermic process. The reaction normally takes place in a refractory lined crucible, where the whole charge can be ignited or just a part of it that then serves as a starting mixture.

9.1.11 Production of ferro-alloys from secondary raw material

Due to the large amount of available secondary raw materials, especially metal oxides from the production of stainless steel, the recovery of ferro-alloys, mainly ferro-chrome has become an important part of the ferro-alloy industry. The development of the various processes followed the increasing need of the stainless steel manufacturers to treat their waste products in order to reclaim the valuable metal content and to limit or prevent dumping of waste.

The total waste treatment market of these kind of residues from the stainless steel industry in Europe is estimated to be approx. 150000 tonnes per year corresponding to approx. 75000 tonnes of alloys. Two third of this market are presently processed respectively converted into metal. The market is strongly related to the development of the stainless steel industry and is showing positive trends for the coming years.

9.1.11.1 Raw material and raw material preparation

The typical raw materials for the production of secondary ferro alloys are the following residues generated mainly within the production of stainless steel:

- Electric arc furnace (EAF) filter dust
- Converter filter dust
- All kind of scale fines
- Shot blasting dust
- Grinding dust

The chemical and the physical characteristics of these raw materials vary extremely. However they might be described as follows:

Element	Content
Cr_2O_3	10 - 25%
NiO	2 - 15%
MoO_3	0 - 5%
Fe_2O_3	30 - 65%
CaO	1 - 30%
Al_2O_3	0.5 - 4%
SiO_2	1 - 15%
MgO	1 - 5%
ZnO	1 - 20%
PbO	0.2 - 1%
CdO	0.001 - 0.05%
CuO	0.1 - 3%
S	0.2 - 0.5%
Cl	0.1 - 1%
F	0 - 3%
Hg	0 - 15 ppm

Table 9.2: Typical amounts of metal oxides in secondary raw material

The aggregate composition of the residues is mostly oxidised with a smaller, variable fraction metallic, mostly from surface treatment operations such as grinding, shot blasting etc.. The grain size of the raw material is typically between 1.0 - 3 - 0 µm. Agglomerations and compacted raw materials are usually found in the deliveries.

The moisture content in the raw material might vary between 0 - 35% due to different gas cleaning or other separation steps installed at the steel mills. This requires to a certain extent a flexible handling and conveying equipment as well as drying equipment.

Owing to the various sources and qualities of residues, the economic viability of the activity requires a minimum content of alloying elements: Ni, Cr and if it can be valued, Mo. Residues from the manufacture of austenitic (18 - 8 or more) stainless steel offer an appropriate content of typically > 3% Ni, > 12% Cr, while a large proportion of residues from ferritic stainless steel production (17% Cr) are still dumped for processing cost reasons.

The product range of the single steelworks mainly influences the composition of the waste products, by the technology employed and by the raw materials fed. Two major issues in this relation are e.g. the amount of lime in the filter dust and its zinc content. The lime content is mainly influenced by the different operations in the steel plant itself and the quality of the lime. The quality of the lime i.e. its proportion of fines influences the total quantity of lime present in the filter-dust. The zinc content in the filter dust and other heavy metals e.g. Pb, Cd, Hg is mainly dependent on the quality of the scrap feed for the electric arc furnace. If there is a high portion of scrap feed containing galvanized scrap, the entire zinc content is collected in the filter dust.

Dioxins may be present in the furnace filter dust. The presence and the quantity of dioxins is dependent on the quality of the scrap feed in the stainless steel melt shops and the manner how the off gas is treated there. Plastic impurities (chlorine compounds) are supporting the formation of dioxins in the filter dust.

The quantity of raw materiel necessary to produce the ferro alloy is also varying considerably because of differing metal contents in the feed. Typically the reclamation produces 400 - 600 kg per metal per tonne of dry raw material feed

9.1.11.2 Preprocessing

Due to the presence of various undesired coarse elements in the raw material e.g. filtermasks, scrap pieces, refractories it is necessary to screen the raw materials. The raw material can be delivered in big bags or in bulk. The big bags are emptied in an enclosure that is equipped with separate dedusting equipment. The dry raw material is then conveyed to a vibrating screen where foreign elements are removed on a screen > 10 mm. After this step the material is conveyed with a bucket conveyor to a silo group which is used as a buffer silo prior to the mixing step.

In case of using the submerged arc furnace the free lime contained in the raw materials is neutralised with water in a specific mixer prior to agglomeration by briquetting. After several days of curing under cover, the briquettes are mixed with other charge ingredients and feed to the furnace.

9.1.11.2.1 Mixing and drying (Plasmadust process only)

After screening, the slag forming agents are analysed in the raw materials in order to determine how much sand or lime has to be added to balance the basicity of the slag. The necessary amount of slag formers are added - predominantly silica sand - together with a approx. 1 - 10% of water in a high turbulent batch mixer in order to obtain enough free flowing micro pellets. The consumption of silica sand is dependent on the raw material respectively its basicity, however typically in the range 0 - 100 kg/tonne of dry raw material.

The aim of drying the material is to obtain a homogeneous dry feed that can be sent pneumatically to the furnace building. The indirect rotating dryer used for this purpose is heated with CO rich process gas. The dryer is equipped with a combined gas and oil burner. After drying the material leaves the dryer with less than 1000 ºC. The material is screened again before it is conveyed to an intermediate bunker.

A filter unit is used where the mercury emissions are monitored continuously on-line. Before entering the dryer a small amount of Na_2S is added to the material if necessary to form stable mercury compounds in order to prevent evaporation of mercury.

9.1.11.3 Submerged arc furnace process

The recovery process that uses a submerged electric arc furnace is very similar to the production of ferro-chrome in an electric arc furnace. One installation in the U.S. employs a rotary hearth furnace for the pre-reduction, followed by melting in a submerged arc furnace.

The furnace off gas is dry filtered in a conventional bag filter. The gas is diluted by the ambient air in the open top furnace where the combustion of CO is complete. Typical composition is 90% air (18 to 20% excess O_2), *7%* CO_2, and 3%H_2O

Off-gas cleaning is done in a two-stage bag house. After cooling below 200 ºC, furnace dust is separated in the first stage and collected for recycling or further processing. In the second stage, absorbent granules (activated carbon or lignite coke) is injected. Volatile metals notably mercury and to a lesser extent cadmium and lead is chemisorbed on the surface of the carbon. The absorbent also traps chlorine compounds including dioxin. This second stage operates below 130 ºC. The same bag filter collects the fumes from the tapping process.

A limited amount of water is injected and vaporised in the off gases for temperature control. Process and cooling water are close circuited, the net consumption being released as steam in the furnace flue gases and by evaporative coolers.

Therefore, the process does not produce liquid effluents. About 60% of the water consumption is insured by the collection of rainwater falling on the industrial site (ground and buildings).

The liquid slag is separated from the metal by gravity. The use of multiple cascades affords virtually complete separation. The low basicity of slag (0.7 to 0.8) insures the formation of stable silicates, which are non-leaching. Prior to shipment, chemical composition and leaching tests are performed to qualify each production lot. The slag is used in various construction applications after the appropriate down sizing.

The alloy is cast in iron moulds. The pigs weight 2 to 4 tonnes each. The free flowing slag is collected in an open pit where is solidifies. After the solidification of the metal, the ingots are broken in a few large pieces with a hydraulic hammer in order to facilitate shipment and remelting. Because of its nickel content, the metal is relatively tough (not brittle) contrary to most ferro-alloys. It requires no further processing and is apt to bulk transport by truck or rail cars.

9.1.11.4 Plasmadust process

After the pre-processing steps secondary raw material as it is also used for the submerged arc process is pneumatically transported by means of a closed vacuum system from the raw material preparation building to the furnace building.

Smelting takes place in a shaft furnace comprising a 12 m high water cooled shell with an inner diameter of approx. 2.5 m. The furnace is equipped with for example three plasma generators providing for an installed plasma heating effect of 18 MW. The shaft is filled with lumpy coke, which acts as a reductant. The plasma generators symmetrically placed around the furnace’s lower part supply the energy required for the endothermic reactions. The plasma gas recirculated process gas - is led to the furnace through water cooled copper tuyeres. The material feed is injected through tuyeres and mixed with the plasma gas (approx. 4000 - 5000 ºC) in the raceway where the reaction take place.

Coke is charged from the top of the furnace in regular intervals. The coke column acts as reductant and filter for the gas being led out of the furnace. Due to the equal heat distribution in the furnace and its height a high yield can be achieved in terms of the reduction of the valuable elements Ni, Cr, Mo, Fe and a comparatively low carry over into the gas-cleaning step. Before tapping is reached, raw material feed is injected in the shaft. In regular intervals the furnace is tapped by drilling a hole at the bottom of the furnace similar to the procedure on blast furnaces. The hot metal is cast at a temperature of approx. 1400 ºC into casting beds lined with refractory material, to pigs of 3 - 4 tonnes each. This corresponds to 40 - 60% metal yield. The alloy is enriched with carbon (4 - 6%) and can be crushed to pieces of approx. 500 - 800 kg, according to the requirements of the end users in the various steel mills.

The gas cleaning system is equipped with a 3-step venturi scrubber combined with a wet electric precipitator (WEP) that is located after the third step of the venturi system. The WEP cleans further the process gas. After these filtering steps the off-gas is further cleaned from mercury in a selenium filter. Here, mercury vapour is bound to mercury selenide. The clean off-gas is either used for heating the dryer, supplied to a district heating system or burned in a flame.. About 50% of this energy for the district heating system is produced by direct heat exchange of cooling water from the furnace, the other 50% are produced in a hot water boiler. About 50% of the process gas is re-circulated into the plasma generators through a compressor and used as heat transfer gas. Since a short time also the mercury emissions in the gas stream after the flare are measured continuously on-line.

The slag is separated from the metal by gravity and skimming the slag from the metal. The inert slag flows into a pit where it is regularly dug out and crushed at the same time. Then, the slag is separated externally from metal pieces. By experience, the basicity is approx. 1.0 (CaO, SiO_2)

so that this kind of slag product can be sold as a non leaching material useful for road construction.. Long term large scale leaching tests have been made, in which slag from the production was exposed to rain water during 1.5 years. They have proven the slag to be a suitable material for road construction purposes due to its very low leachability of metals and characteristics similar to those of natural mineral rocks.

9.2 Present Emission and Consumption Levels

The manufacturing of ferro-alloys is in general an energy consuming process, because the smelting takes place at high temperatures. The ferro-alloy production is therefore related to a relatively high consumption of raw materials such as ore, concentrates and fluxes as well as reductants and fuels like coke or coal and electrical energy. The environmental impact on air, water and land can be classified as follows.

- **Consumption of raw material and energy**
  - Raw material and energy consumption

- **Emissions to air**
  - Dust and fume emissions
  - Other emissions to air (SO_2, NOx, CO-gas CO_2, poly-cyclic aromatic hydrocarbon (PAH), VOCs, dioxins and heavy metals.
  - Emissions of noise and vibrations

- **Solid residues, wastes and by-products**
  - Dust, fume and sludge
  - Slag

- **Wastewater emissions**
  - Wastewater from wet scrubbing systems
  - Wastewater from slag and metal granulation
  - Blow down from cooling water cycles

- **Energy recovery**
  - Energy recovery in terms of the utilisation of the CO- rich off gas from closed furnaces.
  - Energy recovery from the waste heat of semi closed furnaces

9.2.1 Consumption of raw material and energy

The available data of the consumption of raw material and energy for the production of ferro-alloys are presented in terms of specific input factors based on a tonne of produced product in the following tables. Although raw materials and energy consumption depend on the quality of the ores used.

To avoid false differences between process alternatives it is important to present only the gross energy consumption. The energy sources going into the production process consist of electrical energy and latent chemical energy in the carbonaceous material. One kg of carbon has a potential gross energy content on conversion to CO_2 of approximately 8.8 kWh, or approximately 7.7 kWh/kg coke. If these figures are used, the gross consumption of energy for the production of bulk ferro-alloys can be calculated as shown in the next tables. The emitted gross amount of CO_2 will be directly proportional to the amount of coke consumed in the process.

Raw material	HC FeCr				MC FeCr	LC FeCr
Chromite kg/t	2400 – 3000 (N 1)	2300 – 2400 (N 2)	n.a.	n.a.	n.a.	1600
Reductant kg/t	550 – 700 (N 1)	500 – 550 (N 2)	600 (N 3)	n.a	n.a.	675 (FeSiCr)
Fluxes kg/t	100 – 400 (N 1)	200 – 300 (N 2)	n.a.	n.a.	n.a.	1100
Others kg/t	Electrode 8 –25 Remelts 0 -300	Electrode 7 - 10	n.a.	n.a.	n.a	Sand < 100 kg Si < 40 kg Electrode 10 kg Boric acid 3k
Electrical energy kWh/t	3800 – 4500 (N 1)	3100 – 3500 (N 2)	2600 – 3100 (N 3)	4500 (N 4)	n.a	3400 (N 5)
Potential energy by using coke kWh/t	4235 – 5390 (N 1)	3850 – 4235 (N 2)	4620 (N 3)	n.a.	n.a	n.r.
Total energy input kWh/t	8035 – 9890 (N 1)	6950 – 7735 (N 2)	7220 – 7720 (N 3)	n.a	n.a.	3400

Notes:

(N 1)	Consumption data of a conventional open submerged arc furnace, lumpy and fine ore without agglomeration, pre-heating and/or pre-reduction processes.
(N 2)	Consumption data by using preheated pellets as raw material and no remelts.
(N 3)	Consumption by using pre-reduced pellets as raw material. In this case the energy consumption is dependent on the grade of metallisation
(N 4)	DC furnace without pre-reduction process
(N 5)	The presented energy consumption refers to the conversion of FeSiCr to LCFeCr. If the production of the intermediate product – FeSiCr – is included, the electrical energy is 8050 – 9500, potential energy by using coke 5750 – 6400 and the total energy input 13800 – 15900 kWh/t LCFeCr.

The above-mentioned electricity and reductant consumption's are for the whole production process. The electrical energy consumption is about 95% of the total consumption. The main part of the remaining 5% is electrical energy needed for the off-gas treatment.

n.a. = data not available n.r. = not relevant

Table 9.3: Gross consumption of raw material and energy by producing ferro-chrome

The energy consumption used for sintering chromite ore depends on the type of sinter furnace that is used and on the characteristics of the different chromite concentrates. Coke breeze consumption will generally be in the range of 60 - 90 kg/t of sinter. With sinter consumption between 2 and 2.5 tonnes per tonne of ferro-chrome, this equals to 120 – 225 kg of breeze per tonne of ferro-chrome. The external energy consumption of a steel belt sinter furnace ranges between 200 – 400 kWh/t pellets. The energy comes from coke breeze and CO-gas from smelting. The coke breeze consumption is 20 - 40 kg/t of pellets and the proportion of CO as external energy is about 20 – 40%. The external energy for coke drying in a shaft furnace is about 200 kWh/tonne of coke equalling to 100 kWh/t of FeCr.

The consumption of Søderberg electrode paste ranges between 7 – 20 kg/ t of FeCr, the lowest consumption is achieved when using pre-heated or pre-reduced and agglomerated charge.

Water is used in the production of ferro-chrome both as process water and cooling water. Process water is used for scrubbing and slag granulation. If the process water treatment is in a closed circuit 5- 15 m^3 water/t of ferrochrome is normally used. For cooling purposes also 5 – 15 m^3 water/t of ferro-chrome is used.

Oxidised steel mill waste, dust and scale are recovered using processes adopted from high carbon ferro-chrome production. The energy consumption for the metallurgical reduction is shown in the following table for typical contents of recoverable metals. Two types of furnaces are in use, conventional submerged arc furnaces and DC plasma shaft furnaces.

	Conventional submerged electric arc furnace	Plamadust process
Residues kg/t	1650 – 2500	1650 – 2500
Reductant kg/t	400 – 500	400 – 500
Electricity kWh/t	3000 –3400	2800 – 3800
Metal contents% (input)		
Ni		
Cr	3 – 15	3 – 15
Mo	15 – 25	15 – 25
C	1 – 5	1 – 5
Si	4 – 6	4 – 6
Iron	0.5 – 8	0.1 – 1
	Balance	Balance
Water m^3/t	1.0 – 1.5	2.8 – 3.2
Alloy recovery (output)		
Cr	> 80%	90 – 95%
Ni	> 90%	90 – 98%
Mo	> 90%	90 – 98%
Fe	> 90%	90 – 98%

Table 9.4: Consumption data for the recovery of ferro-alloys from steel mill residues as specific input factors based on one tonne of recovered metal

The consumption of energy and raw material for the production of ferro-silicon and silicon metal is presented in terms of specific input factors as an example in the following table, because due to plant and product specific reasons also other raw material combinations are common. The amount of electrical energy that is given in the table is due for a commonly used open or semi-closed submerged electric arc furnace without energy recovery.

	Ferro-silicon (75% Si)	Silicon-metal	CaSi
Quartzite kg/t	1800	2600	1500
Reductant kg/t	850	1150 - 1500	925
Electrode kg/t	50	100 (N 2)	120
Iron ore pellets kg/t	350	n.r.	n.r.
Limestone kg/t	n.r.	n.r.	900
Woodchips kg/t	0 - 400	1000 - 2000	n.r.
Electrical energy kWh/t	8500	10800 – 12000 (N 1)	9500
Potential energy assuming coke or coal is used kWh/t	6545 (coke/coal)	10120 – 13200 (coal)	7122 (coke)
Total energy input kWh/t	15045	20920 - 25200	16622

Notes: n.a. = data not available n.r. = not relevant

(N 1) The ideal energy consumption for the production of silicon metal is 10100 kWh/t (heat of reaction = 8 kWh/t, heat loss with the metal = 0.9 kWh/t and heat loss in the off-gas = 1.2 kWh/t).

(N 2) Some silicon producers are using a combined Søderberg/graphite electrode. The aim is to use the Søderberg technology, but reduce the iron impurities caused by the electrode casing

Table 9.5: Consumption of raw material and energy by producing ferro-silicon, silicon and CaSi as **specific input factors**

Recent development work has resulted in a new electrode type utilising a combination of the Søderberg-technology and a graphite core, to allow the system for the production of silicon-metal. The aim is to reduce the iron impurities caused by the electrode casing.

The specific input factors for the production of the different sorts of ferro-manganese as well as for silico-manganese and the sinter process of manganese ores and concentrates are given in the table below.

Source	Sinter	HC FeMn		MC, LC FeMn (silico-thermic)	SiMn (standard and LC SiMn)	Notes
		BF	EAF			
Ore kg/t	1000 - 1300	2000	1900 – 2100	1600 – 2000	500 – 1700	(N 1)
Coke kg/t	100	1100 – 1450	410 – 450	200 – 300	400 – 600	
Coal kg/t	100	n.r.	n.r.	n.r.	n.r.	
Gas m^3/t	150 – 200		n.r.		n r.	
Electrode kg/t	n.r	n.r	8 - 20	6 - 8	20 – 30	
Water m^3/t	12 – 18	cooling water	1.5–40 (N3) cooling water	cooling water	1.5 – 40 (N 3) cooling water	(N 2)
Others kg/t	n.r.	n.r.	n.r.	Fluxes 800 – 1000 SiMn 700 - 1000	FeMn slag 400 – 2500	
Electricity kWh/t	n.r	n.r.	2200 – 3000	1600 – 2000	3800 – 6000	
Potential energy by using coke kWh/t		8470 - 11165	3157 - 3465	1540 - 2310	3080 – 4620	
Total energy input kWh/t		8470 - 11165	5357 - 6465	3140 – 4310	6880 - 10620	

Notes:

(N 1) The consumption of raw materials normally contains recycled materials such as dusts and sludge's from the abatement system

(N 2) The consumption of water is dependant of the water processing equipment and varies from 20 to 40 m^3/t in open circuits and from 1.5 to 5 m^3/t in closed circuits

(N 3) Water consumption is associated to wet dedusting

BF = Blast Furnace EAF = Electric Arc Furnace n.a. =data not available n.r. = not relevant

Table 9.6: Consumption data for the production of manganese ore sinter, ferro-manganese and silico-manganese as specific input factors

The available information about the consumption of raw material and energy for the production of various special ferro-alloys are presented in the following table.

	FeNi alloys	**FeV**	**FeMo (N 3)**	**FeTi**	**FeB**
Metal oxides kg/t	n.a	1100 - 2000 (N 1)	n.a (N 3)	n.a.	n.a.
Electric energy kWh/t	1500	2200 - 2800	160 – 405	770	6000 – 11000
Gas m^3/t	120	n.r.	148 – 155 MJ/t	55	75
Water m^3/t	6.9	(N 2)	n.r.	n.m.	0.3
Quicklime kg/t	n.a	n.r	20 – 180	n.r.	n.r.
Fluorspar kg/t	n.r.	n.r.	0 – 30	n.r.	n.r.
Aluminium kg/t		800 - 1000	36 – 70	n.r.	n.r.
Metallic iron kg/t	n.a	100 - 150	23 – 210	(N 4)	n.a
Millscale kg/t	n.r.	n.r.	250 – 550	n.r.	n.a
Others kg/t	n.a	n.a	620 – 700 (FeSi)		n.a

Notes:

(N 1) The data presented contains the amount of V_2O_3 and V_2O_5
(N 2) The Consumption of water is very site specific and therefor not representative
(N 3) The consumption data for the production of FeMo are based on one tonne of molybdenum.
(N 4) The amount of metallic iron depends upon the alloy being made e.g. 70% FeTi contains 700 kg of Ti 300 kg of iron per t of alloy; whereas 40% FeTi contains 400 kg Ti and 600 kg iron per t of alloy.

n.a = data not available n.r = not relevant in this production process n.m. = not measured

Table 9.7: Consumption data for the production of special ferro-alloy as specific input factors

The process of roasting molybdenite concentrates is an autothermal process since the oxidation reaction is ignited. External energy in form of electricity will therefore only be needed for the mechanical operation of the multiple hearth furnaces. Natural gas is used to dry the concentrates and to ignite any flotation oil and elevate the temperature to the point where the exothermic reactions are ignited.

9.2.2 Emissions

9.2.2.1 Emissions to air

9.2.2.1.1 Dust and fume emissions

According to the raw material that is needed and the unit operations used, e. g. crushing, drying, sintering, smelting tapping and product handling the most important source of environmental input are dust and fume emissions. The following figure shows the potential emission points for dust and fume emissions from a ferroalloy producing plant.

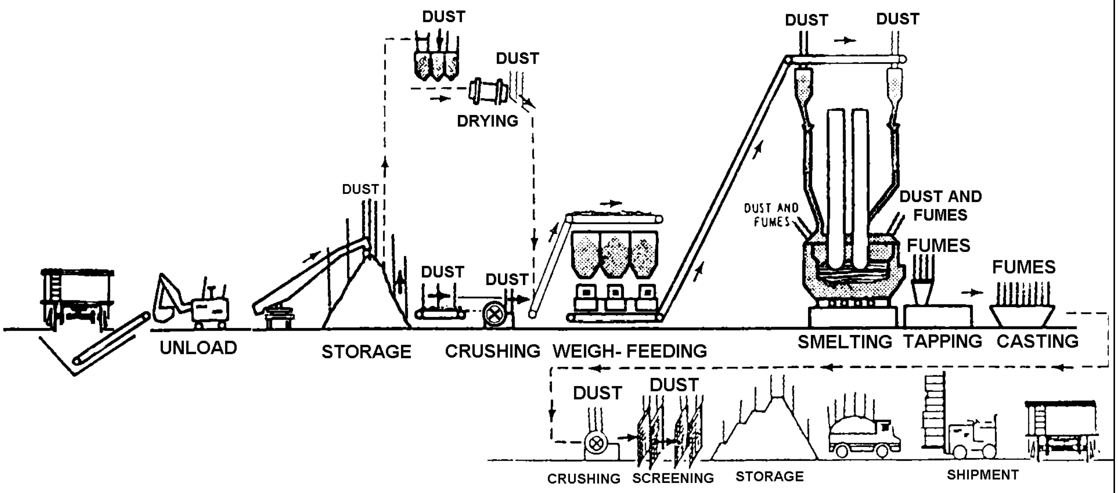


Figure 9.12: Ferroalloy production flow diagram showing potential points of air emissions [tm 35, ECE 1995]

Unloading and storage of raw material can generate dust when the material falls from one conveyor to another. Dust can also be produced if the conveyor is running to fast (i.e. more than 3.5 m/s). If a front–end loader is used dusting is seen during the transport distance.

The dust that is produced by the smelting process is collected by hoods or in case of a closed furnace by the furnace sealing directly and transferred to an abatement plant and de-dusted (e g. by a fabric filter or a wet scrubber). Scrubbing is used for closed furnaces.

Tapping off-gas consist of dust and fumes from oxygen lancing, dust from drilling, fumes from vaporised slugs if a tapping gun is used and fumes from all exposed metal and slag surfaces. These fumes that arises from tapping will mainly be oxides of the metals involved in the smelting process.

The following tables present the available emission data for the emission of dust by producing varies ferro-alloys.

Source	**HC FeCr**		**MC FeCr**		**LC FeCr**	
	kg/t	**mg/Nm^3**	**kg/t**	**mg/Nm^3**	**kg/t**	**mg/Nm^3**
Raw material handling	0.01 0.02	f (N 2)	n.a	f (N 2)		f (N 2)
Drying	0.002 (Coke)	1 - 50	n.a	n.a	0.082 (Ore)	5
Crushing	0.002		n.a	n.a	0.003	3
Pelletising/sintering	0.01 - 0.02 /t pellets	1 - 15	n.r.	n.r.	n.r.	n.r.
Sintering	0.2 – 0.5	1 – 30 (N 4)	n.r.	n.r.	n.r.	n.r.
Dosing station	0.01 - 0.02	1 – 30 (N 4)	n.a	n.a	0.024	5
Pre-heating	0.001 - 0.005	1 – 15 (N 4)	n.r.	n.r.	n.r.	n.r.
Smelting furnace	0.02 - 0.1 (N 1)	1 – 100 (N 4,5,6)	n.a	n.a	0.101	8
Tapping	(N 3)	5 – 12 (N 4)	n.a	n.a	(N 7)	(N 7)
Casting	(N 3)	5 – 12 (N 3)	n.a	n.a	0.2 – 0.4 (N 4)	3 - 15 (N 4)
Slag handling	n.m.	n.m.	n.a	n.a	0.04	10 -15
Product handling (crushing screening storage etc.)	0.02 - 0.05	r	n.a	n.a	n.a	n.a

Notes:

(N 1)` The Cr(VI) content of the furnace dust is between 5 – 100 ppm in the closed and between 1000 – 7000 ppm in the open furnace

(N 2) The amount of material loss caused by handling and storage of raw material is estimated to be less than 2%.

(N 3) Sampling of the ventilation air leaving the furnace building including tapping and casting area over long periods of time can give an indication of the average values. These show average dust concentrations between 5 and 12 mg/Nm^3 and total dust emissions amounting to 0.2 -– 0.6 kg/tonne of produced alloy.

(N 4) The present dust emissions are dependent on the furnace type and the used off-gas abatement technique. For instance bag house filters are achieving in many cases already less then 5 mg/Nm^3. Dust emissions from a sinter furnace by using a cascade wet scrubber are reported to be below 4 mg/Nm^3.

(N 5) This illustrated the range between good and pour performers.

(N 6) The furnace gas from a closed furnace is used as fuel after wet scrubbing The gas is flared only if a customer is temporarily not available.

(N 7) Included in source “smelting furnace”

n.a. = data not available n.r. = not relevant n.m. = not measured f = fugitive dust emissions
r = dust is recycled back into the process

Table: 9.8 Dust emissions by producing ferro-chrome based on one tonne of produced alloy

Source	**FeSi**		**Si-metal and calcium-silicon**	
	kg/t	**mg/Nm^3**	**kg/t**	**mg/Nm^3**
Raw material handling	f (N 2)	f (N 2)	f (N 2)	f (N 2)
Drying of Woodchips	n.m.	n.m.	n.m.	n.m.
Crushing	n.m.	n.m.	n.m.	n.m.
Weighing dosing station	f	f	f	f
Smelting	0.1 - 2	1 - 20 (N 1)	0.1 – 1.5	1 - 20 (N 1)
Tapping	(N 3, 4)	(N 3) 5–12 (N 4)	(N 3, 4)	(N 3) 5–12 (N 4)
Casting	(N 4)	5 – 12 (N 4)	(N 4)	5 –12 f (N 4)
Refining	(N 3)	(N 3)	(N 3)	(N 3)
Product crushing	0.3 – 0.5	r	0.3 – 0.5	r.

Notes:

(N 1) Using a bag-house filter some plants are achieving dust emissions below 5 mg/Nm^3, corresponding to a cleaning grade of above 99.5%. The silica fume is collected in the filter as a by-product (Micro Silica).

(N 2) The amount of material loss caused by handling and storage of raw material is estimated to be less than 0.2%.

(N 3) If the fume and dust from the tapping area is collected and cleaned in the bag-house the dust emissions are in the same range than the concentration of dust emissions from the smelting furnace.

(N 4) Sampling of the ventilation air leaving the furnace building including tapping and casting area over long periods of time can give an indication of the average values. These show average dust concentrations between 5 and 12 mg/Nm^3 and total dust emissions amounting to 0.2 -– 0.6 kg/tonne of produced alloy

n.a. =data not available n.r. = not relevant n.m. = not measured f = fugitive dust emissions
r = dust is recycled back into the process

Table 9.9: Dust emissions by producing ferro-silicon and silicon-metal based on one tonne of produced alloys

Source	HC FeMn				MC and LC FeMn		Silico-manganese	
	BF		EAF		kg/t	mg/Nm^3	kg/t	mg/Nm^3
	kg/t	mg/Nm^3	kg/t	mg/Nm^3				
Raw material handling	f	f	f	f	f	f	f	f
Weighing dosing station	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Smelting	n.a.	1 - 10	0.1 - 0.4	5 - 60 (N 3)	n.a.	< 25	0.1 - 0.4	5–60 (N 1) (N 3) 1 - 30(N 2)
Tapping	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Casting	n.a.	n.a. n.a.	0.05 - 0.1	n.a.	0.05 - 0.1	n.a.	n.a.	n.a.
Refining	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Product crushing	0.1 - 0.3	r	0.1 - 0.3	r	0.1 - 0.3	r	n.a.	r
Waste heat boiler	n.a.	1 - 10	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
Electricity production	n.a.	1 - 10	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.

Notes:

(N 1)	Dust emissions from an closed sealed furnace with an venturi scrubber
(N 2)	Dust emissions from an open furnace
(N 3)	If the de-dusting of the off-gases from a closed sealed furnace takes place in a cascaded wet scrubber dust emissions below 10 - 20 mg/Nm^3 are achieved. Some plants that are operating semi-closed furnaces using bag houses for de-dusting are achieving dust emissions below 5 mg/Nm^3

BF = Blast Furnace EAF = Electric Arc Furnace
n.a. = data not available n.r. = not relevant f = fugitive dust emissions
r = dust is recycled back into the process.

Table 9.10: Dust emissions by producing ferro-manganese and silico-manganese based on one tonne of produced alloy

	Fe Ni	FeV	FeMo	FeTi	FeB	Molybdenite roasting
Source	**mg/Nm^3**	**mg/Nm^3**	**mg/Nm^3**	**mg/Nm^3**	**mg/Nm^3**	**mg/Nm^3**
Raw material handling	1 – 15	< 5	0.5 - 2	1 – 15	1 – 15	1 – 15
Raw material drying	1 – 15	n.r.	4 - 17	1 – 15	1 - 10	n.r.
Crushing		n.r.	1 - 5			n.r.
Pelletising		n.r.	n.r.			n.r
Sintering/ Roasting	< 1 (N 2)	n.r.	n.a.			1 – 15
Dosing		n.r..	1			n.m.
Pre-heating		n.r.	n.r.			n.r.
Smelting	1 - 15	< 5	1 - 30	1 – 15	1 - 10	n.r.
Tipping/Tapping	n.a.		5 - 15 (N 1)	n.a.	n.a.	n.r.
Casting				n.a.	n.a.	n.r.
Slag handling	n.a.	n.a.	n.a.	n.a.	n.a.	n.r.
Product crushing	1 - 15	< 5	0.5 - 5	n.a.	n.a.	n.m.

Notes:

(N 1) Emissions are estimated from the roof exhaust fans

(N 2) Data is due for the production of secondary FeNi where a modern membrane bag filter is used. The presented figure gives the amount of Ni-oxide as part of the emitted dust from the rotary kiln.

n.a. = data not available n.r. = not relevant n.m = not measured f = fugitive dust emissions r = dust is recycled back into the process

Table 9.11: Dust emissions to air (after abatement) by producing ferro-alloys

9.2.2.1.2 Other emissions to air

The most important pollutants from the production of ferro-alloys beside dust are SO_2, NOx, CO-gas CO_2, HF, poly cyclic aromatic hydrocarbon (PAH), volatile organic compounds (VOCs) and heavy metals (trace metals). The formation of dioxins in the combustion zone and in the cooling part of the off-gas treatment system (de-novo synthesis) may be possible. The emissions can escape the process either as stack emissions or as fugitive emissions depending on the age of the plant and the used technology. Stack emissions are normally monitored continuously or periodically and reported by on-site staff or off-site consultants to the competent authorities.

In the carbo-thermic process only the fixed carbon content is used as a reductant, that means the content what is left when volatile matters ashes and moisture are deducted. The volatile matter consists mainly of hydrocarbons, do not take part in the reaction but leaves the furnace together with the CO when the furnace is closed or burns near the surface in a semi-closed or open furnace. In both cases the energy content in the volatile matters is utilised.

The sulphur content in metallurgical coke varies between 0.4 and 1.0%. 60 – 85% of the sulphur remains in the slag and about 5% escapes the furnace as $SO_{2.}$ The production of silicon alloys requires different reducing agents like coal, coke, petrol-coke and charcoal. This material contains different amounts of sulphur, typical variations are between 0.5-and 3%. In the silicon alloy production, which is almost slag free, nearly all sulphur escapes the furnace as SO_2 or as bounded sulphur to the micro-silica. By using a reducing agent or a mixture of different carbon sources, which contains in total a high sulphur content of about 2 - 3%, higher SO_2 emissions may occur.

The off-gas generated by roasting molybdenite concentrates contains large amounts of SO_2 that is normally cleaned in a desulphurisation plant producing sulphuric acid. Detailed information on desulphurisation plants is given in Chapter 2 of this document. The tail-gas from the desulphurisation plant of a molybdenite roaster contains SO_2 since the conversion for SO_2 into SO_3 will hardly be 100%. The off-gas contains also a certain amount of sulphuric acid mist as well as some SO_3.

Heavy metals are carried into the process as trace elements in the raw material. The metals with boiling points below the process temperature will escape as gases in form of metal vapour, which partly condenses and oxidises to form part of the dust from the smelting furnace. Even after tapping and especially during refining the temperature of the molten metal and slag are high enough to allow vaporisation of components both from the metal and from the slag. The fumes arising from this evaporation evolves the whole time, from start of tapping until casting is finished. Even after the ladle is emptied, some fumes may evolve from the metal scull. During tapping most of the fumes are collected and cleaned, trough the tapping fume collection.

Depending of the type of ore that is used, mercury may be emitted to air. One plant producing SiMn has been reported to have high mercury-emissions due to a high mercury content in the raw material. Other producers of FeMn and /or SiMn may use the same raw material with a higher mercury content. Therefore control of mercury-input in the furnace and control of subsequent mercury-output of the processes is advisable, if such raw materials are used. In this case the raw material needs a pre-treatment to remove the mercury otherwise the mercury has to be removed from the furnace off-gas by using a mercury-removal step.

In the production of FeMo, fluorspar may be used to improve slag and metal separation. Fluorspar is a calcium fluoride ore that is used as a flux and lowers the melting point and the viscosity of the slag resulting in an enhanced fluidity of the slag. Additionally, when mixed with lime, it reduces the phosphorus and sulphur content of the metal. Lower melting points favour the metal-slag separation, since the slag remains a longer time liquid during the cooling. This effect together with the reduced viscosity makes it possible for small dispersed droplets to sink, coagulate in the metal phase at the bottom. However, the use of fluorspar as a fluxing agent results in emissions of fluorides within the range of 150 to-260 mg/Nm^3. According to the bio-toxic nature of fluoride the use of fluorspar should be minimised as far as possible.

Table 9.12 below presents some figures of recently measured emissions to air by producing bulk ferro-alloys.

	FeCr				FeSi		Si-metal		FeMn						Silico-manganese	
	HC FeCr		MC and LC FeCr						HC FeMn				MC and LC FeMn			
									BF		EAF					
	kg/t	mg/Nm^3	kg/t	mg/Nm^3	kg/t	mg/Nm^3	kg/t	mg/Nm^3	kg/t	mg/Nm^3	kg/t	mg/Nm^3	kg/t	mg/Nm^3	kg/t	mg/Nm^3
SO_2	0.2 - 3.0	n.a.	n.r.	n.r.	20 (N 7)	230.	12 - 18	100 - 160	1 - 1.5	n.a.	0.002 - 0.1	n.a.	n. a.	n.a.	0.002 - 0.1	n.a.
CO	n.m.	n.m.	n.m.	n.m.	traces	traces	n.m.	n.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
CO_2	1200 – 2000 (N 1)	n.a.	110 (N 3)	n.a.	4240- (N 4)	55 g/Nm^3	6500 (N 4)	55 g/Nm^3.	4000 - 4500	n.a.	1200 - 1500	n.a.	1560 - 2340 (N 5)	n.a.	1100 - 1800	n.a.
NOx	0.5 - 1.5	n.a.	n.m.	n.m.	15	170	10 - 13	80 - 110.	1	n.a.	n. a.	n.a.	n.a.	n.a.	n. a.	n.a.
HF	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
PCDD/F	0.2 g/a (N 2)	n.a.	n.m.	n.m.	5µg/t (N 8)	n.a.	3µg/t (N 8)	n.a.	n. a.	n.a.	n.a.	n.a.	n.a.		n. a.	
Heavy metals	Cr (in the dust) 1 - 15% CrVI 0.1 - 0.3% (N 6)	n.a.	Cr < 0.01 Cr^{6+} < 0.002	n.a.	n.a.	0.78 µgHg/Nm^3 (N 8)	n.a.	0.131 µgHg/Nm^3 (N 8)	Hg (n.a.)	n.a.	Hg (n.a.)	n.a.	n.a.	n.a.	Hg (0 - 0.002)	n.a.
PAH	n.m.	n.m.	n.a.	n.a.	0.0015 (N 8)	0.02	0.003 (N 8)	0.02	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
VOC	n.m.	n.m.	n.a.	n.a.	0.045 (N 8)	0.9	0.13 (N 8)	0.9	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Cyanides	0.02 - 0.05	n.a.	n.a.	n.m.	n.m.	n.m.	n.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Notes

(N 1) The emissions of CO_2 include total emissions from the pre-treatment smelting and post furnace processes. The external use of the CO-gas from the smelting furnace reduces the local emissions from the FeCr plant only

(N-2) The yearly amount of dioxin emissions is only due for a sinter furnace. Dioxins from one sinter furnace have been measured to 1.5-4 g/a This data is however limited and needs further investigation.

(N 3) The emissions are due to 80 kg/t for natural gas fired of dryer, ladle heating etc. and 30 kg/t form the electrode pastes that is consumed.

(N-4) This CO_2 data contains the amount of fossil as well as the amount of biological CO_2.

(N 5) This CO_2 data is due for the silico-thermic production of LC FeMn. The CO_2 emissions by producing MC FeMn from HC FeMn are about 100-500 kg/t of alloy.

(N 6) The amount of Cr VI in the dust is emitted from a semi closed furnace; cyanides = 0.2 - 0.05 from a closed furnace.

(N 7) The high value correspond to a production of high purity FeSi. in which a great quantity of petrol coke is used

(N 8) Results from comprehensive 24 h surveys of air emissions from the production of FeSi 75 and high purity Si-metal. In this case it should be noted, that the data are based on relatively short measuring periods at two specific plants, and should not be taken as general for the industry. More measurements are planed within the industry.

: n.a. = data not available n.r. = not relevant n. m. = not measured

Table 9.12: Emissions to air (after abatement) by producing bulk ferro-alloys

The major emissions to air by producing primary ferro-nickel are listed in the table shown below.

Operation	Emissions to air									
	Dust/Fume			Gases						
	Total	Ni	Others	SO_2	CO_2	CO	NO_X	H_2S	$Ni(CO)_4$	others
Ore crushing	HL	LL	-	-	-	-	-	-	-	-
Drying	HL	HL	-	LL	ML	LL		-	-	-
Roasting	HL	HL	-	HL	ML	LL	LL	-	-	-
Reductive calcination	HL	LL	-	LL	ML	LL	LL	-	-	-
Smelting	HL	LL	-	-	ML	ML	LL	-	-	-
Converting	HL	ML	SiO_2	-	ML	LL	LL	-	-	-
Pouring	HL	LL	-	-	-	-	-	-	-	-

VL Very low level LL Low level - Absent
ML Medium level HL High level

Table 9.13: Emissions to air from Ferro-nickel
[tm 109, UNEP 1993]

Emission concentration figures for the production of ferro-alloys recovered from steel mill residues in a submerged electric arc furnace are presented below.

Pollutants	Concentrations (gas and particles) mg/Nm^3
Dust	2 - 5
$S0_2$	< 100
CN	0.002 - 0.006
HC	< 50
F	0.1 - 1.5
Cd	< 0.001
Cd +Hg + Ti	< 0.1
As	< 0.003
Se	< 0.002
Te	< 0.002
Zn	0.02 - 0.05
Pb	< 0.005
CO_2	1.2 – 1.5 t/t of alloy

Table 9.14: Emission concentration figures by producing secondary ferro-alloys

9.2.2.2 Emissions of noise and vibrations

The heavy machinery such as crushers and large fans used in the ferro-alloy production can give rise to emissions of noise and vibration. Also the mechanical scull releasing from the ladles may be a source of noise.

9.2.2.3 Emission to water

For the production of ferro-alloys the emissions to water are very dependent on the process for instance the abatement system and the type of wastewater treatment used. There exist a variety of different water collection and wastewater treatment systems in the ferro-alloy industry. Some plants use a central wastewater treatment plant in which water from different production processes as well as surface run-off water will be cleaned together. Other facilities are using a separate treatment system for rainwater and special treatment processes for the different process wastewater streams. The main water pollutants are suspended solids and metal compounds. The wastewater is treated in order to remove dissolved metals and solids and is recycled or reused as much as possible in the process. The possible wastewater streams are:

- Surface run-off and drainage water
- Waste water from wet scrubbers
- Waste water from slag and metal granulation
- Cooling water

The contaminated water is normally led to a thickener or a settling pond to settle out the suspended solids. Precipitation steps are often used to remove metal compounds from the water. In special cases for instance by cleaning scrubbing water from a molybdenite roasting furnace ion exchangers are used to remove metal compounds such as selenium and rhenium from the scrubbing water.

The particles mostly consist of very fine particles, it may therefore be necessary to add flocculent to assist settling in thickeners. After the treatment in a thickener or a settling pond the suspended solids are usually below 20 mg/litre, which allows reuse in scrubbers as cooling water or as process water for other purposes.

By the production of FeCr in a closed furnace typical emissions to water, based on one tonne of produced FeCr, will be for suspended solids in the range of 5 – 10 g with a total Cr-quantity of 10 - 20 mg and a PAH quantity of 0.3 – 1g. The process water treatment includes in this case a lamella thickener, vacuum filters, a sand and carbon filter. If a thickener, slag granulation and settling ponds are used emissions of suspended solids will correspondingly be 75 – 150g with a total amount of Cr at about 5g, zinc 3 – 7g and cyanide in the range of 1 – 3g/tonne of FeCr. For the production of LC FeCr is has been reported that the amount of Cr discharged in the wastewater is less then 0.3 g/tonne of product. PAH emissions to water after abatement for the production of FeMn have been reported to be in the range of 0.05 – 0.2 g/t FeMn.

The scrubber system's contaminated wastewater from an alloy recovery plant is cleaned in a separate wastewater treatment plant in which may also rainwater from the site is cleaned. The partly oxidised particles contained in the water are concentrated in a thickener and in a later step separated from free water in two filter presses. The resulting filter cake with 20 - 25% moisture consists of the following main constituents:

ZnO	30 - 40%
SiO_2	10 - 15%
CaO	5 - 15%
FeO	5 - 7%
PbO	3-5%
Hg	0.001%

The amount of dry cake generated is 200-400 kg/tonne of alloy.

This filter cake is shipped in regular intervals for zinc and lead recycling either to ISP (Imperial Smelting Process) or Waeltz process.

Due to the necessity to control the salt concentration in the wastewater, the bleed off from the scrubber system's circulating water, approx. 0.5 - 2 m^3/tonne off recovered ferro-alloys is cleaned in several steps.

- Cyanide removal
- Reduction of Cr_6+ to Cr_3+
- Precipitation of metal hydroxides at high pH together with oxidisation of cyanides
- Precipitation of fluoride and cleaning the water from particles in a sand filter

The wastewater treatment results in emissions to water, which are presented blow.

	As	Cr	Ni	Zn	Cu	Cd	Pb	Hg	F	N	CN
g/t	0.002	0.02 - 0.06	0.03 - 0.08	0.06 - 0.16	0.03 - 0.08	0.006 - 0.03	0.006 - 0.03	0 - 0.005	9.0 - 28.0	12 - 64	0 - 0.08

Table 9.15: Emissions to water by recovering ferro-alloys from steel mill residues by using the plasmadust process with a wet scrubber as the used abatement technique

Data reported for a wastewater treatment plant for a molybdenite roaster is presented in the following table.

H_2SO_4 kg	**HF kg**	**Mo mg**	**Bi mg**	**Pb mg**	**Cu mg**	**Zn mg**	**Sn mg**	**COD mg**	**Re mg**	**As` mg**	**Se mg**
32.9	0.3	25.9	0.03	0.29	0.05	1.72	0.03	0.42	7.10	0.26	0.29
Notes: Elements based on 1 tonne Mo produced as molybdenum trioxide											

Table 9.16: Emissions to water by roasting molybdenite

9.2.2.4 By-products, process residues and wastes

The production of ferro-alloys is related to the generation of a number of by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). The most important process specific residues are filter dusts, sludge from wet scrubbers, slag form the smelting process, used furnace linings and packaging material like drums or big-bags. These residues are partly sold as by-products, recycled to the process or in cases of wastes without economic utility transported to a deposit or a landfill. The amount of slag and filter dust or sludge generated per tonne of produced ferro-alloy and their possibilities of valorisation are shown in the next tables.

Ferro-alloy		Slag/t of alloy	Analytical composition	Recycling, reuse and discharge
FeCr	**HC FeCr**	1.0 - .17 t/t	Mainly mixture of spinel. MgO, Al_20_3, forsterite, 2MgO , SiO_2 and Cr_2O_3 (3 – 15%)The slag is chemically very stable	• Crushed lump and granulated slag are used as building material and road construction materials • Slag can be used also as a sand blasting grid, and for the production of refractory castables
	MC FeCr	n.a.	n.a.	
	LC FeCr	1 t/t	CaO 44 - 45% SiO_2 23–33% MgO 9 - 13% Al_20_3 5 - 9% Cr_2O_3 2.5 - 6.5% FeO 0.6 - 1.2%	• The slag will be landfill
Alloy recovery from steel mill residues		0.4 - 1.2 t/t	CaO 25 - 40% SiO_2 35 - 50% MgO 3 - 15% Al_20_3 12 - 18% Cr_2O_3 < 3% Fe_2O_3 < 2%	• The low basicity of slag (0.7 to 0.8) insures the formation of stable silicates, which are non-leachable. The slag is used in various construction applications.
Silicon-metal FeSi		20 – 30 kg/t	Si or FeSi 20 - 30% SiO_2 5 – 20% SiC 20 –40% CaO 25 – 40% Al_2O_3 3 – 35%	• The production of silicon metal and FeSi is almost a slag free process (small amounts of quartz are transformed into slag, < 1%). The slag will go to a landfill. • During refining of silicon-metal and FeSi, some small amounts of refining slag is produced The slag will go to landfill.
Calcium-silicon		0.4 – 0.6 t/t	SiO_2 10 – 20% SiC 15 –25% CaO 50 – 60% Al_2O_3 5 – 10% CaC_2 3 – 8%	• All the slag is recycled to the furnace
FeMn	**HC FeMn**	Blast furnace 0.4 - 0.8 t/t	n.a.	• Standard exhausted slag (low content of MnO) from a blast furnace is used as a construction material • Rich slag from a blast furnace (high content of MnO) is sold as raw material for the production of silico-manganese
		Electric arc furnace 0.4 –0.8 t/t	n.a.	• Standard exhausted slag (low content of MnO) is used as a construction material • Rich slag (high content of MnO) is sold as raw material for the production of silico-manganese
	MC FeMn	1.6 - 1.9 t/t	n.a.	• The slag is used as raw material in the production of silico-manganese
	LC FeMn	1.6 - 1.9 t/t	n.a.	• The slag is used as raw material in the production of silico-manganese
SiMn		0.9 - 2.2 t/t	n.a.	• Slag is used as a construction material
FeNi		n.a.	n.a.	
FeV		2.6 - 3 t/t	n.a.	• Slag is sold as secondary raw material to the process industry e.g. for the production of refractories.
FeMo		1.5 - 2 t/t (N 1)	n.a.	• Depending on the composition the slag is sold for further processing or deposited in a landfill
FeW, FeTi, FeB		n.a.	n.a.	
FeNb		1.9 t/t	n.a.	
Notes: (N 1) Slag/tonne of alloy for Fe Mo includes the weight of sand that is attached to the slag.				

Table 9.17: Generation, recycling, reuse and discharge of ferro-alloy slag

Ferro-alloy		Dust or sludge/t of alloy	Recycling, reuse and discharge
FeCr	**HC FeCr**	20 - 80 kg/t (N 1)	• The dust from the furnace will be landfill • The dust from crushing and screening is remelted in the furnace, or in used in the stainless steel production • The dust from the raw material transport systems, coke drying, agglomeration and dosing station can be recycled back into the processes • Sludge from wet scrubber will contain PAH and heavy metals and need to be discharged on a hazardous waste landfill • About 8 - 10 kg/t of coarser dust with high chromium content that is collected in a waste heat-boiler alter a semi-closed furnace can easily recirculated to the furnace after agglomeration
	MC FeCr	n.a.	
	LC FeCr	70 kg/t	• The dust is recycled back to the smelting furnace
Alloy recovery from steel mill residues		100 - 500 kg/t.	• The furnace dust is high in ZnO (20 - 60%) and PbO (2 - 6%). It is pelletised and recycled by the Zn industry (I.F. smelter, or by using the Waelz process as an intermediate concentration step. • Sludge from wet scrubber will contain PAH and heavy metals and need to be discharged on a hazardous waste landfill
FeSi		200 - 300 kg/t	• Silica fume (micro silica) is collected in the bag filter and sold as a by-product. Micro silica is used as a cement additive, which increase the strength of the concrete and led to a very smooth surface that prevents the concrete from water infiltration.
Silicon-metal		300 - 400 kg/t	
FeMn	**HC FeMn**	Blast furnace 100 - 300 kg/t	• The coarse part of the dust that is relatively rich in manganese is agglomerated and recycled to the furnace or used as raw material for the production of silico-manganese in an electric arc furnace. • The fine dust can sometimes be valued in other industries or is discharged to a landfill • Sludge from wet scrubber will contain PAH and heavy metals and need to be discharged on a hazardous waste landfill
		EAF 30 - 50 kg/t	• Dust and sludge is recycled, valued in other industries or discharged to a landfill • Sludge from wet scrubber will contain PAH and heavy metals and need to be discharged on a hazardous waste landfill
	MC FeMn	EAF 30 - 50 kg/t	• Dust and sludge is recycled, valued in other industries or discharged to a landfill
	LC FeMn	EAF 30 - 50 kg/t	• Dust and sludge is recycled, valued in other industries or discharged to a landfill
SiMn		30 - 50 kg/t	• Dust and sludge is recycled, valued in other industries or discharged to a landfill • Sludge from wet scrubber will contain PAH and heavy metals and need to be discharged on a hazardous waste landfill
FeNi		n.a.	
FeV		n.a.	• Dust is recycled to the smelting process or partly be discharged to a landfill
Molybdenite roasting		n.a.	• The off-gas leaving the roaster contains dust up to 15% of the concentrate feed. • Most of the dust and sludge from the off-gas cleaning is recycled to the concentrate feed.
FeMo		n.a.	• Dust is recycled to the smelting process or partly be discharged to special waste disposal
FeW, FeTi, FeB, FeNb		n.a.	• Dust from the furnace is discharged to a landfill except for some FeNb

Notes:

(N 1) The composition of the dust or sludge varies depending on the used smelting furnace and the raw materials.

(N 2) In dust from a semi-closed ferro-chrome furnace a Cr VI content of 0.1 0.3% has been detected

Table 9.18: Generation, recycling, reuse and discharge of dust and sludge from the air abatement system

9.2.3 Energy recovery

The production of ferro-alloys is a high energy consuming process, because high temperatures are needed for the reduction of metal oxides and smelting. Factors affecting the energy consumption are among other things the quality of raw material and their pre-treatment before smelting, the utilisation of reaction energies and the heat content of the processes. The energy used in the process can be supplied as electrical energy or fossil fuel in form of coal, coke charcoal or sometimes natural gas. The supplied energy either in a blast furnace or in an electric arc furnace is transformed into chemical energy formed by the reduction process as well as off gas energy (CO rich gas) and heat.
The off-gas energy is mainly represented as process heat in case of a semi-closed furnace or by the content of CO, CH_4 and H_2 when a closed furnace is used. The process-gases are produced in the smelting process if carbon is used as a reducing agent. The CO can be utilised as a secondary fuel and transferred by means of pipelines within the plant area like any other fuel gas. It can be used by direct burning for instance in the sinter-furnace and for drying or pre-heating the furnace charge as well as for energy recovery in form of hot water, steam and/or electricity.

By producing HC FeMn in a blast furnace the CO rich top gas will be de-dusted and partly be used to heat up the hot stoves. The excess gas is burned in an adjacent power plant to produce superheated steam and subsequently electrical energy in a back-pressure turbine.

The energy flow diagram below shows the energy flow in a 10 MW submerged electric arc furnace for the production of silicon-metal.

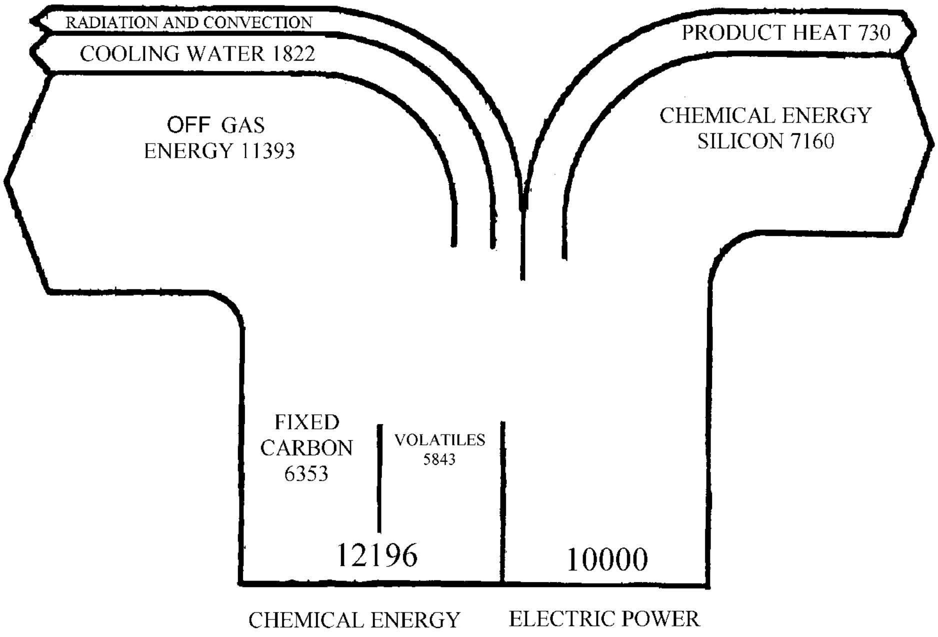


Figure 9.13: Energy flow in a 10 MW silicon furnace
[tm 152, A. Schei, J.K.Tuset, H. Tveit 1998]

If a semi-closed submerged electric arc furnace is used for the production of FeCr, FeSi, silicon-metal, SiMn or FeMn, the CO gas from the smelting process burns in air thus creating a hot off-gas. Therefore the semi-closed furnaces are sometimes equipped with a waste heat boiler as an integrated energy recovery system. The waste heat boiler generates superheated steam that can be sold to neighbouring mills or used for electricity production in a back-pressure turbine.

During the production FeCr, FeMn or SiMn in a closed electric arc furnace the off-gas contains a very high percentage of CO, which is collected without being burned above the charge surface. This CO is a high quality fuel that is favourably being used for electricity production or supplied to a neighbouring industrial plant as a secondary fuel or as a synthesis gas that serves as a raw material in chemical processes. A typical composition of a CO rich gas, formed in a closed furnace producing HC FeCr, contains of 75 – 90% CO, 2 – 15% H_2, 2 – 10% CO_2, 2 – 5% N_2 and < 5% of H_2O.

The next tables give an overview about the different possibilities of energy recovery and the use of the recovered energy.

Ferro-alloy	Number of plants	Electrical energy used [GWh/a]	Possible recovery [GWh/a]			Actual recovery [GWh/a		
			Electrical energy	Thermal energy	Total	Electrical energy	Thermal energy	Total
FeCr	1	360		140	140			
FeSi	9	4940	856	1024	1880	115	183	298
Si-metal	3	1250	163	215	378		1	1
FeMn **SiMn**	3 (N 1)	1850	80	550	630	80	216	296
Total	16	8400	1099	1929	3028	195	400	595 (N 2)

Notes: Energy recovery data of 16 Norwegian ferro-alloy plants. [tm 159, INFACON 7, 1995]

(N 1) Gas is partly used as fuel or synthetic gas
(N 2) From the reported 16 ferro-alloy plants in 1989 energy has been recovered by 8 plants

Table 9.19: Overview of energy recovery in the Norwegian ferro-alloys industry in 1989 [tm 159, INFACON 7, 1995]

Ferro-alloy	**HC FeCr**		**HC FeMn**			**SiMn**		**FeSi**	**Si**
Furnace type	**Semi-closed EAF**	**Closed EAF**	**Blast furnace**	**Semi-closed EAF**	**Closed EAF**	**Semi-closed EAF**	**Closed EAF**	**Semi-closed EAF**	**Semi-closed EAF**
Drying	■	■		■	■		■		
Ladle heating		■			■		■		
Sintering		■			■		■		
Pre-heating	■	■	■ Hot stoves		■		■		
Hot water	■	■	■	■	■	■	■	■	■
Steam	■	■	■	■	■	■	■	■	■
Electricity	■	■	■	■	■	■	■	■	■
Neighbouring mills		■			■		■		■

Remark:
Energy recovery is not always be used, because local conditions for instance local prices of energy, periods of production and the absence of possible customers should be taken into account.

Table 9.20: Energy reuse by producing bulk ferro-alloys

9.3 Techniques to Consider in the Determination of BAT

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2 “common processes” apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

9.3.1 Materials, storage and handling

The raw materials used for the production of ferro-alloys are basically ores, concentrates, reducing agents, solid fuels and additives. The main environmental impact by storage and handling of these materials are fugitive dust emissions and contamination of surface water and soil cased by wash out from rainwater.

To prevent contamination raw materials are preferably stored on hard surfaces where indoor and outdoor storage may be used, depending on the potentially dusty nature and the chemical properties of the materials. To keep the materials clean the storage area can also be divided in different storage-bays. Dry fine-grained materials should be stored and handled inside where closed silos, bins and hoppers are used to prevent fugitive emissions to the environment as well as to the workspace. Excessive dusting can also be prevented by water spraying of dry fine materials.

Closed conveyors and transfer systems are used for handling of dusty fine materials, where extraction and filtration equipment is used for dusting delivery points. The dust leaden air from the silos, closed conveyors and charging systems are cleaned by using bag filters, which may be monitored by measuring the pressure drop to control the cleaning mechanism. Some plants use crushers or agglomeration equipment to obtain the desired size of charging material. Bag filters clean the suction air of crushers and agglomeration equipment. Wet grinding, filtering and pelletising systems are as well suitable to prevent dusting. In this case the water is recycled. Crushing facilities are built in a manner that noise emissions and vibration are minimised. The collected dust is recycled to the charging system, which may need an additional agglomeration step.

9.3.2 Pre-treatment techniques

High-grade ores especially for the production of FeCr are generally not readily available as lump material. Upgrading of low grade ores, by wet grinding and upgrading by wet gravitational methods (heavy media separation, jig washing, spiral washing, wash tables etc.), to remove gangue minerals and increase for instance the Cr_2O_3 content, is therefore getting common practice worldwide. Most of these methods give a fine grained, high grade product, that must be de-watered by filtering, and must be agglomerated by briquetting, sintering or pelletising/sintering before smelting.

The reducibility of different ores is quite different.. Generally speaking for the production of FeCr, podiform ores are easily reduced, stratiform ores not as easily. For this reason, podiform ores most often will give a chromium recovery in excess of 90%, while some of the stratiform ores have below 80% recovery in conventional type production routes. This is the case with South African ores. With the DC plasma process, recovery is reportedly above 90%. This compensates for the higher consumption of electrical energy, needed to increase the process temperature to achieve faster reduction. Another way of increasing the reduction rate of stratiform ores is to increase the reaction surface. This can be achieved by grinding the ore to a very fine size and pelletising/sintering. For podiform ores, the recovery benefits of these alternative process routes will not be of the same magnitude.

Primary raw material like coke or secondary raw material such as titanium turnings and metal scrap need to be dried before using them in the process. In some cases coke drying is important to remove moisture and depending on the climate snow and ice.

EXAMPLE 9.01 DRYING OF COKE IN A SHAFT FURNACE

Description: - A shaft furnace is used for coke drying in a ferro-chrome production. The furnace uses CO rich off-gas from the smelting furnace as a fuel. For the abatement equipment a bag filter or a wet scrubber can be used as well.

Main environmental benefits: - A shaft furnace generates less dust and fines. The use of CO rich off gas as a fuel reduces the overall energy consumption of the process. The energy consumption from CO is 550 - 700 MJ

Operational data: - .Not available

Cross media effects: - The use of CO rich gas as a fuel reduces the consumption of other natural combustion fuels.

Economics: - Not available

Applicability: - For all new and existing plants which use wet quenched coke. The use of CO rich off gas is due to plants operation closed furnaces.

Reference literature: - [tm 141, Finland 1998]

Metal scrap, turnings and swarf sometimes have to be liberated from oil and cutting liquids, which may take place by drying in a rotary kiln. The following example shows a titanium swarf degreasing plant that is used in the production of secondary ferro-titanium.

EXAMPLE 9.02 DEGREASING OF TITANIUM SWARF FOR THE PRODUCTION OF FERRO-TITANIUM

Description: - The degreasing system removes oil and water from titanium turnings and swarf so that they can be safely melted in an electric induction furnace.

Swarf is degreased in a rotary dryer (installed 1993) which is designed to distribute the swarf through a flow of combustion gases recycled from an afterburner. Material is fed into the degreaser by a belt conveyor, and after degreasing is collected in hoppers prior to melting.

Ducting carries the oil-bearing gases away from the dryer and through a cyclone to remove dust and carry over. These gases then pass through the afterburner, which is heated by a gas-fired burner. The Afterburner has been designed to allow complete combustion of the oil vapour [i.e. destruction of volatile organic compounds by thermal oxidation] Combustion gases/fumes are either recirculated through the dryer or are ducted to a second cyclone. Dampers control the proportion of gas recycled. From the cyclone the gas stream enters the filtration plant (installed 1998). A sorbent material [sodium bicarbonate powder] is injected into the ducting prior to the filter unit to neutralist any acidic gases that may be present and prevent corrosion damage to the filtration plant.
Maximum temperature of gases entering the filter plant is 350 ºC. The filter is rated at approximately 7000 Nm^3/h [at 350 ºC) and contains 576 ceramic filters- The filters are tubular and manufactured from calcium silicate or alumina silicate. The cleaning cycle is fully

automated and cleaning is achieved by means of a reverse air pulse system. Particulate emissions from the stack are continuously monitored and any deviation above a pre-set level will signal an alarm. The fume plant operates with particulate emission levels below 5 mg/Nm^3.

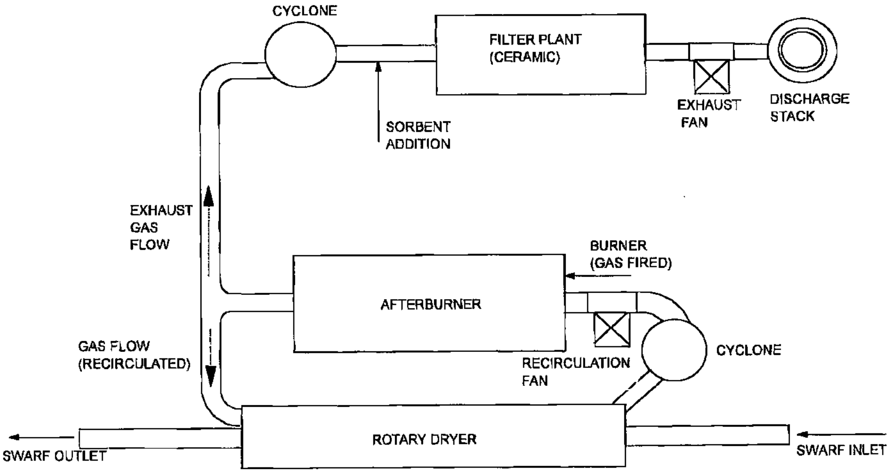


Figure 9.14: Gas cleaning system for a de-greasing plant

Main environmental benefits:

Emissions to air:
Particulate - below 5 mg/Nm^3
Volatile organic compounds [VOC's] destroyed in the afterburner VOC are well below the permit level of 20 mg/Nm^3

Emissions to water: - None

Emissions to land:
Waste fume dusts from the process are taken to a licensed landfill site. The quantity of fume dust generated will depend on the quantity and quality of swarf being processed

Operational data: The plant uses the following utilities:

Gas	the amount of gas consumed varies widely depending upon the density of the material being processed and the amount of oil and moisture contamination present. The average consumption is typically 374m^3/tonne of swarf processed.
Electricity-	the plant is not independently metered. However, it is calculated that electricity consumption is typically 180 kWh/tonne of swarf processed.
Water	None used.

Cross media effects: - The nature of the operation is such that the releases are to air, rather than to either of the other two environmental media.

For most applications the metals industry has generally standardised on a bag filter plant to control airborne emissions. -However, for this application a ceramic filter was chosen due to the high temperature of the waste gas stream. The ceramic filter would also provide good filtration with the lowest environmental impact.

Wet scrubbing systems were considered, but rejected. A wet type of arrestment such as a Venturi scrubber would result in a sludge waste that would be more difficult and costly to dispose of, and would contain a significant proportion of water. The plume from the main stack would also be wet and not so well dispersed.

Economics: **Project Costs**

The rotary dryer and afterburner was installed in 1993.	
The cost in 1998 would be in the order of	0.607 M €
Cyclone, ducting, [ceramic filter] filtration plant	
[installed in 19981	0.410 M €
Estimated overall project cost	1.017 M €

Applicability: - New and existing plants.

Reference literature: [tm 162, London and Scandinavian Metallurgical Ltd.1999]

9.3.3 Sintering

As already mentioned, a large amount of ores and concentrates are only available as fines. To use these fines some plants, especially those for the production of FeCr use sintered pellets as a raw material in the furnace. The most important reason to sinter fines is to obtain a better porosity of the burden with easier penetration and elimination of gas generated by the reduction reactions. Sintering can take place in shaft-, grate- or in steel belt sintering furnaces, where the steel belt furnace provides several economic and environmental advantages.

EXAMPLE 9.03 STEEL BELT SINTERING FURNACE

Description: - The Steel Belt Sintering Furnace is used to sinter chromite pellets in the production of FeCr. The Steel Belt Sintering Furnace is closed. The off gases from the sintering furnace and the dusting points can be cleaned by a low pressure wet scrubber or a bag filter. The operation of the process is controlled by a computerised control system.

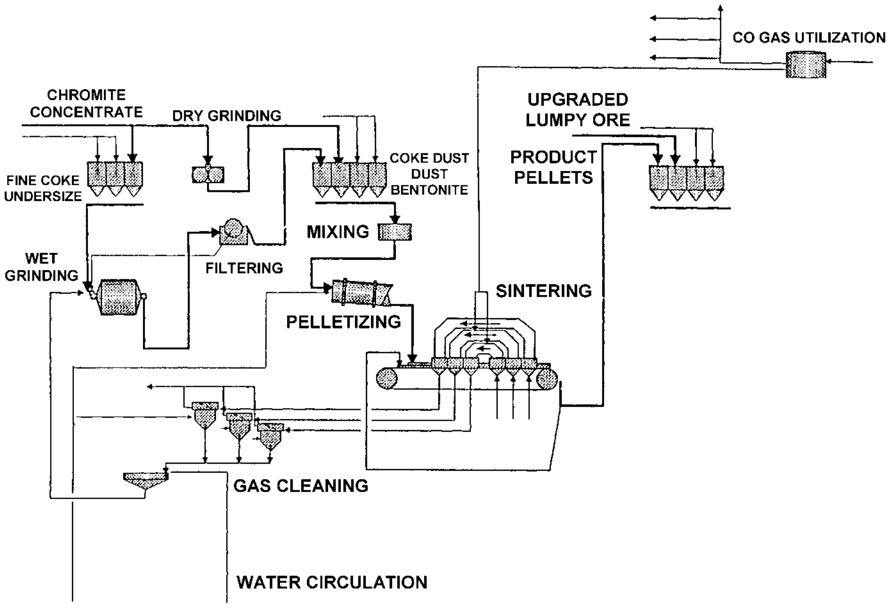


Figure 9.15: Steel belt sinter furnace

Main environmental benefits: - The external energy consumption in a steel belt sintering furnace is lower compared to a shaft and a grate furnace. As a consequence the generation of

CO_2 and SO_2 emissions are lower. The sludge from the off-gas treatment can be recycled back to the wet grinding step.

Operational data: - Energy consumption is 700 – 1400 MJ/t of pellets. CO from the smelter is used as a fuel together with coke fines.

Emission levels for dust

Wet scrubber	< 10 mg/Nm^3
Cascade wet scrubber can achieve	< 4 mg/Nm^3
Bag filter	< 5 mg/Nm^3

Cross media effects: - The use of CO gas as a fuel reduce the external energy required for the sinter process, which results in less generation of CO_2, and reduces the impact of greenhouse gases to the atmosphere if the saving of external energy resources is taken account. The wet scrubber generates a wastewater that can be recycled to the wet grinding step.

Economics: - Not available

Applicability: - To all new and existing plants where sintered pellets are used as raw material for the furnace. The use of CO as a fuel is only possible for plants using a closed furnace.

Reference literature: - [tm 141, Finland 1998]

9.3.4 Pre-reduction and pre-heating

Pre-reduction of chromite and manganese ore reduce the specific electrical energy consumption and increases the productivity of the smelting furnace. In FeCr production, chromite ore fines are pelletised with coke as a reductant and fired in a rotary kiln. A pulverised coal/CO/oil burner heats the kiln. Waste heat from the kiln is recovered in a waste-heat recovery boiler to generate steam. The exhaust gas is cleaned in a bag filter. The pre-reduced pellets are stored in a completely sealed surge hopper designed to prevent re-oxidation. The reduced material is then charged hot to the furnace, which combines pre-heating and pre-reduction. It has been reported, that the fully implemented and continuously operated pre-reduction technique in a Japanese ferro-chrome plant decreases the energy consumption down to about 2000 - 2100 kWh/t of FeCr [tm 114, EnviroSence 1995]. The weakness of a pre-reduction process is a possible accretion formation in the kiln. World wide there are only two plants using this pre-reduction process and one plant using the Krupp-Codir (CDR) pre-reducing technique.

The electricity consumption of the smelting furnace can be decreased by pre-heating the feed materials Pre-heating for instance as it is used in the production of FeCr increases at the same time the productivity of the smelting furnace.

EXAMPLE 9.04 PRE-HEATING IN A SHAFT-KILN

Description: - The shaft type furnace is used to preheat the charging material for the production of FeCr in a closed electric arc furnace. The shaft type furnace has the advantage that crushing up of charge material and dusting is lower. The utilisation of fuel energy for instance CO from the smelting furnace or natural gas is higher and maintenance work is needed less..

Main environmental benefits: - The pre-heating decreases the energy consumption By preheating the charge at 700 °C the moisture and a major part of the volatiles can be removed before the material is charged into the electric furnace Thus the formation of reduction gases in the furnace is stable

Operational data: - The electrical energy consumption of the subsequent smelting furnace is reduced by 70 - 90 kWh per 100 ºC increase in the preheating temperature for the smelting furnace.

Cross media effects: - The use of CO gas as a fuel reduces the electrical energy required for the subsequent smelting process. This results in less generation of CO_2, and reduces the impact of greenhouse gases to the atmosphere if the savings of external production of electrical energy are taken into account. The comparison of a shaft kiln has been done with a rotary kiln. Burning of CO generates CO_2.

Economics: - Not available

Applicability: - To all new and existing plants The use of CO as a fuel is only possible for plants using closed furnaces.

Reference literature: - [tm 143, EuroAlliages 1998]

9.3.5 Smelting processes

In the production of ferro-alloys the most important stage is the reduction of metal oxides and alloying with the iron present in the process. Depending on the reducing agent, different types of smelting systems (such as the electric arc furnace, the blast furnace or a reaction crucible) are used. Electric arc furnaces are normally operated submerged as a closed, semi-closed or open type. The concept of the different smelting systems are influenced by the desired flexibility in the production, the range of raw material, the possibilities of energy recovery and the environmental performance. The different techniques considered for the recovery of energy, which are very much dependent on the used smelting system but also on local conditions that means local energy prices, periods of production and the presence of potential customers, will be discussed later in this chapter.

The different furnaces used for the ferro-alloy production have been described earlier in Chapter 2 and are listed in the following table that summarises the advantages and disadvantages of the various systems.

Smelting system	Produced alloys	Gas collection and abatement	Advantages	Disadvantages
Open submerged arc furnace with three electrodes	FeCr, FeMn, SiMn, FeSi, FeNi Si-metal, alloy recovery	Hooded and cleaned in a bag filter	• Simple design • Low investment and maintenance cost • Can use almost any raw material • Easy control of the smelting process can be obtained, • Hot water production	• High electrical energy consumption (filter) • No heat recovery except hot water production • Large off-gas volumes • Need of large pollution control systems • Higher environmental impact due to the off-gas volume and the heat supplied to the ambient air.
Open submerged arc furnace with a single electrode	Special ferro-alloys FeV, FeB	Hooded and cleaned in a bag filter	• Simple design, high production flexibility Low investment and maintenance cost • Can use almost any raw material • Can remelt fines	• The open furnace with a single electrode is normally used in the production of special alloys for small quantities. The above mentioned disadvantages are therefore relatively lower.
Semi-closed submerged arc furnace	FeCr, FeMn, SiMn, FeNi FeSi, Si-metal Special ferro-alloys	Hooded and cleaned in a bag filter	• Large flexibility in raw materials • Energy recovery as electrical energy and /or steam • Hot water production • Smaller off-gas smaller filter plant • Easy control of the smelting process • Reduced environmental impact	• Relative high energy consumption • More complex system • Higher maintenance cost • Can use a limited amount of fines without agglomeration
Closed submerged arc furnace	FeCr, FeMn, Si Mn, FeNi, Special ferro-alloys	Sealed furnace with wet scrubber or a Dry wire-cloth filter	• Low environmental impact • Energy recovery in form of CO rich gas as a secondary fuel • Low off-gas volume • Fairly simple system	• Well sized lumpy or agglomerated raw materials • Off-gas consists of CO (explosive and poisonous) • Wet gas cleaning system • Wastewater and sludge need to be treated or reused
Closed submerged arc furnace with pre-heating in a rotary kiln	FeCr	Sealed furnace with a wet scrubber	• Low electrical energy consumption • Energy efficient • Low environmental impact • Increase the furnace capacity	• Need stricter amounts of well sized hard lumpy ore or concentrates that has to be agglomerated • Agglomeration or pelletising plant • Higher investment cost • Small flexibility in raw material; supply • Complex system • Wet gas cleaning system
Closed submerged arc furnace with a pre-heating shaft furnace	FeCr	Sealed furnace with a wet scrubber	• Larger flexibility's in raw material supply • Low energy consumption • Energy recovery • Low environmental impact • Increased productivity of the furnace	• Need well sized hard lumpy ore or agglomerated raw material • Wet gas cleaning system

Closed submerged arc furnace with a pre-reduction in a rotary kiln	FeCr	Sealed furnace with a wet scrubber	• Very low electrical energy consumption • Heat recovery, fully utilisation of off-gases • Higher coal consumption lower coke consumption • Increased productivity of the furnace	• Higher investment cost • Wet gas cleaning system • Very complex system • No flexibility in raw material; supply • Relatively high maintenance cost • Possibility of accretion formation
SKF Plasmachrome	FeCr	Sealed furnace	• Possibility to use any ore • Use of fines without agglomeration • Energy recovery • Use of coal instead of coke	• Higher investment cost • High energy consumption • Complex system • Lower operating time • CO in a pressurised system
ASEA DC Furnace	FeCr	Sealed furnace	• Use of fines without agglomeration • Low investment cost • Higher energy density	• Injection with unknown Difficulties • Problems with the bottom electrode when overheated • Need of prebaked electrodes
Blast furnace	HC FeMn	Closed furnace	• High production capacity • Off-gas with a high calorific value • Energy recovery, fully utilisation of off-gas energy	• Very high coke consumption • Wet scrubber • High investment cost • Complex plant
Refractory lined crucible	Special alloys, FeMo	Hooded and a bag filter	• Low investment cost • High flexibility in the production	• Higher off-gas volume • Less effective gas collection system
		Enclosed in a reaction chamber connected to a bag filter	• Low investment cost • High flexibility in the production • Effective fume collection system • Less off gas volume	• Slightly higher investment costs
Multiple heard furnace	Molybdenite roasting	Wet scrubber	• Proven technology • Sulphuric acid can be produced	

Table 9.21: Summary of advantages and disadvantages of the used smelting systems in the ferro-alloy industry.

Taking account of the above advantages and disadvantages the smelting systems to consider are:

- Open furnace for special applications and small capacities connected with a bag filter
- Semi-closed furnace connected with a bag filter
- Closed furnace systems in different applications cleaned by a wet scrubber or dry cleaning system
- Blast furnace if the waste energy will be recovered
- Reaction crucibles with an appropriate hooding system connected with a bag filter
- Reaction crucibles in a closed chamber connected with a bag filter
- Multiple heard furnace for molybdenite roasting with an dust removal and an acid recovery

The open furnace for producing bulk ferro-alloys is not a technique to be considered in the determination of BAT. The main reasons are the higher electrical energy consumption due to the higher off-gas volume to be cleaned in the filter-house. This higher off-gas volume induces, even with a high standard bag house, a larger amount of fine dust emitted to the environment. In addition the energy used to operate an open furnace can not be recovered.

9.3.6 Gas collection and abatement

The techniques for fume collection and abatement discussed in Chapter 2 of this document are techniques to consider for the production of ferro-alloys. Bag filter and wet scrubbers are normally used for de-dusting the process off-gases.

There exist a number of different bag filter designs using different kinds of filter materials, which in principal all achieve low emission values that means dust emissions below 5 mg/Nm^3. The use of the membrane filtration techniques (surface filtration) results additionally in an increasing bag life, high temperature limit (up to 260 ºC) and relatively low maintenance costs combined with dust emissions in the range of 1 - 5 mg/Nm^3. There are different suppliers in Europe who are able to provide bag filter with membrane filter bags. The membrane filter bags consist of an ultra-fine expanded PTFE membrane laminated to a backing material. The particles in the off-gas stream are captured on the bag surface. Rather than forming a cake on the inside or penetrating into the bag fabric, particles are repelled from the membrane thus forming a smaller cake. This technique is applicable for all new and existing plants and may also be used for rehabilitation of existing fabric filters[tm 144, Elkem 1998].

Bag house filters are in many cases in the ferro-alloy and metallurgical industry pressure filters with fans on the dirty fume/gas side. Recent developments led to a closed suction filter with fans on the clean-gas side. This combines the advantages of gentle bag cleaning that means longer bag life, low operating and maintenance costs and due to the closed filter a defined gas volume [tm 144, Elkem 1998].

By recovering ferro-alloys from steel mill residues the off-gas cleaning is done in a two stage bag house- In the first stage furnace dust is collected for recycling or further processing. In the second stage, absorbent granules (activated carbon or lignite coke) is injected. Volatile metals notably mercury and to a lesser extent cadmium and lead is chemi-sorbed on the surface of the carbon. Due to the highly toxic nature of mercury and cadmium emissions of this metals below 0.2 mg/Nm^3 can be achieved. The absorbent also traps chlorine compounds including dioxin. Alternatively a 3-step venturi scrubber combined with a wet electrostatic precipitator and a selenium filter may be used. The selenium filter removes mercury from the off-gas.

Wet scrubbers are techniques to consider by operating closed furnaces where the CO-rich off-gas need to be washed and de-dusted at very high temperatures. Modern wet scrubbers achieve dust emissions below 10 mg/Nm^3, with coarser dust, even achieved dust concentrations of 4 mg/Nm^3 by using a cascade scrubber to clean the off-gas from a sinter furnace have been reported [tm 200, Kantola, 1999]. Venturi scrubbers used to clean the off-gas from a closed HC

FeCr furnace achieve emissions below 50 mg/Nm^3 due to very fine dust that is produced in the furnace, but which is not emitted directly to the atmosphere. The disadvantages of the wet scrubber are normally the slightly higher dust emissions and the washing liquid and sludge that needs a further treatment. Compared with a bag-filter that is normally used for a semi-closed furnace, the wet scrubber even with the higher dust emissions do not result in an higher environmental impact due to the reduced off-gas volume from a closed furnace. One case has been reported where a closed ferro-alloy furnace is provided with a wire-cloth filter instead of a wet cleaning system. This filter recovers heat from the exhaust gases and eliminates the need of a scrubbing unit. The collected dust is pelletised and ritualised, and the cleaned gas is burned in a boiler unit [tm 202, EnviroSense, 1995].

The waste gas leaving the molybdenite roaster contains high amounts of dust that is removed by multi-cyclones in combination with a dry EP. The collected dust is recycled to the concentrate feed. The gas contains also up to 2.5% of sulphur dioxide, small amounts of unburned hydrocarbons and sulphur trioxide and some highly volatile metals. To remove these pollutants after de-dusting the gas is washed and cooled in wet scrubbers in order to produce a clean sulphur dioxide gas that can be converted to concentrated sulphuric acid. The techniques discussed in Chapter 2 should be considered in conjunction with this process. Acid produced during the process can be stored in double walled tanks placed in chemically resistant bunds or single walled tanks inside containment areas that will accommodate the total content of the storage vessel(s).

The use of hoods for tapping and casting is also a technique to consider. Tapping fume will consists of fumes from oxygen lancing, dust from drilling, fumes from the vaporised slugs if a tapping gun is used and fumes from all exposed metal and slag surfaces. These fumes will consist mainly of oxides of the metals that are involved in the smelting process. The design of the hooding system needs to take account of access for charging and other furnace operations and the way the source of process gases change during the process cycle.

EXAMPLE 9.05 HOODING SYSTEMS FOR THE COLLECTION FOR TAPPING AND CASTING FUME FROM AN ELECTRIC ARC FURNACE

Description: - The design of appropriate hooding systems to collect fume from the tapping and casting areas is very much dependent on the side specific situation of the tapping and casting arrangements. Therefore a large number of different hooding designs exist. The cleaning equipment, which today is normally used for tapping fumes, is a bag filter. This can be a separate filter, or a filter that also cleans the fumes from metal casting or the furnace off-gas. An example of a hooding system used for the collection of tapping and casting fumes is shown below.

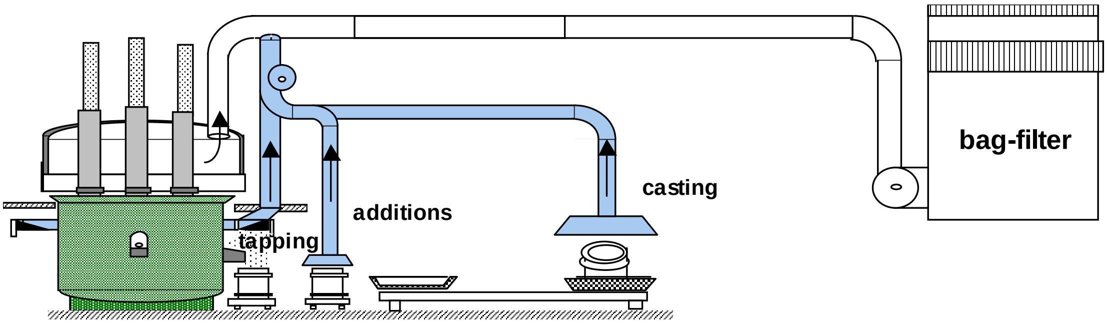


Figure 9.16: Collection of tapping and casting fume

Main environmental benefits: - Reducing the fugitive emissions from the tapping and casting area. Minimisation of the uncontrolled fumes, dust and smoke that leaves the furnace building with the ventilation air. The bag filter can achieve dust emissions blow 5mg/Nm^3

Operational data: - Sampling of the ventilation air leaving the furnace building including tapping and casting area over long periods of time can give an indication of the average values. These show average dust concentrations between 5 and 12 mg/Nm^3 and total dust emissions amounting to 0.2 - 0.6 kg/tonne of produced alloy. This amount of dust can significantly be reduced.

Cross media effects: - Reducing of fugitive emissions in a furnace building results also is better working conditions. The application of evacuation and treatment of gases requires extra energy consumption due to the use of powerful fans.

Economics: - Not available

Applicability: - To all new and existing plants.

Reference literature: - [tm 143, EuroAlliages 1998]

EXAMPLE 9.06 HOODING SYSTEM FOR THE DE-DUSTING OF TAP HOLES AND RUNNERS FROM A BLAST FURNACE PRODUCING HC FEMN

Description: - The de-dusting equipment is composed of various hoods located above the tap hole of the blast furnace, the main metal runner and the device where the liquid metal is poured in the torpedo ladle. The collected fume is cleaned in a separate bag filter. The hooding system (view from the top of the blast furnace) is shown in the following figure.

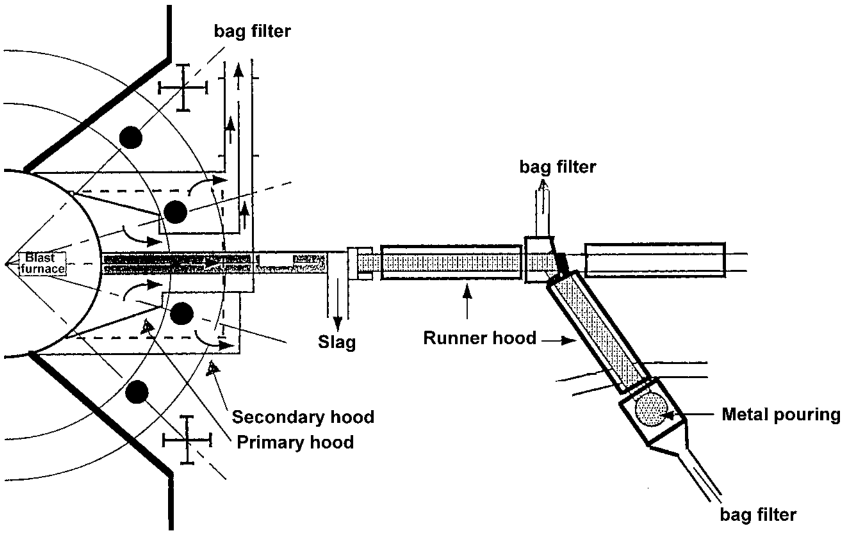


Figure 9.17: Hooding system for a blast furnace

Main environmental benefits: - Reducing the fugitive emissions from the tapping and pouring area. Minimisation of the uncontrolled fumes, dust and smoke that leaves the furnace building with the ventilation air.

Operational data: - Collection efficiency;

Main hood	96%
Hood corresponding to the pouring of metal in the ladle	86%
Runner hood	100%
Flow rate	310000 m^3/h
Measured dust emissions after abatement (bag filter)	< 5 mg/Nm^3

Cross media effects: - Reducing of fugitive emissions in a furnace building results also is better working conditions. The application of evacuation and treatment of gases requires extra energy consumption due to the use of powerful fans

Economics: - Investment cost is about 1.0 M €

Applicability: - Applicable to all new and existing blast furnaces.

Reference literature: - [tm 195, SFPO 1999]

9.3.7 Process control

The principles of process control discussed in Chapter 2 are applicable to the production processes used in this Group. Some of the furnaces and processes are capable of improvement by the adoption of many of these techniques. Computerised control systems are used for instance in the production of FeSi and Si-metal in order to follow and control the generation of silica-fume.

9.3.8 Post furnace operations

Using a pneumatic or hydraulic drill normally opens the tap hole of the smelting furnace. Oxygen lancing is also used, either as the only method or as a back up or complement to drilling. A tapping gun helps to remove blockages, but slugs containing lead and zinc should only be used if an appropriate hood is installed to remove tapping fumes. This is necessary because the lead and particularly the zinc, will to a large extent vaporise in the tap hole, and create zinc and lead fumes that otherwise would pollute the working area and subsequently participate in the ventilation air. The tap hole is closed using a mud gun.

The most frequently used technique of tapping is the cascade tapping. In this case the metal and slag is tapped together in the same vessel. The lower density slag float at the top and eventually overflows through the spout to the next ladle.

Slag granulation and water spraying of slag in a pit or teeming station will contribute to reduce emissions of fumes and dust. The used water needs a treatment in a settler to remove particles before using it again as quenching water.

The generation of very fine powder (dust) that is collected in the bag filter used for de-dusting the furnace off gases may create problems in handling, storage and transport of powders.

EXAMPLE 9.07 DENSIFICATION OF SILICA POWDER AND OTHER DUST COLLECTED IN BAG FILTERS FROM FERRO-ALLOY SMELTING FURNACES

Description: - To handle silica fume (micro silica) and other ferro-alloy filter dust a densification process involving a micro-pelletisation step has been reported. The process that forms a powder into small spheres about 0.5 - 1 mm in diameter.

Main environmental benefits: -Higher bulk density reduces the environmental impact of transportation. This means less air pollution and less noise problems from truck traffic.

Operational data: - The bulk density of raw silica dust is less than 0.2 t/Nm^3. The process of micro pelletisation increases the bulk density to 0.5 – 0.6 t/Nm^3. These reduce the transport costs by about 65% and the environmental impact of transportation.

Cross media effects: - Less truck traffic

Economics:- Not available

Applicability: - To new and existing plants where silica fume, SiMn-powder, FeCr-powder, manganese and ferro oxides need to be handled.

Reference literature: - [tm 144, Elkem 1998].

9.3.9 Water treatment

Existing treatment systems are reported to be to a high standard. Where necessary, wastewater should be treated to remove dissolved metals and solids. The techniques listed in Chapter 2 are the techniques to consider. In a number of installations cooling water and treated wastewater including rainwater is reused or recycled within the processes.

A water treatment is needed in the processes with wet scrubbers and granulation processes, because suspended solids should be removed before the water is recirculated. To reach acceptable values of harmful components, it may in some cases be necessary to polish the bleed that has to be taken from the scrubbing water cycle. This may take place by using sand filters, carbon filters or by adding suitable chemicals to precipitate harmful compounds.

9.3.10 Reduction of process residues

The processes and recycling routes that were discussed earlier as applied methods in the section on present emission and consumption levels are all measures to consider in the determination of BAT. The most important factor to reduce the environmental impact of discharging residues as waste are process-integrated measures that result in the generation of fewer residues. If the amount of process residues is minimised by using primary measures, the extended amount should be recycled or reused as much as possible. The specific feed materials will influence the final process choice. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes.

9.3.11 Techniques to reduce the overall energy consumption

As already mentioned, by presenting the total gross energy consumption in part 9.2.1 of this chapter, the production of ferro-alloys is an energy consuming process. For the slag processes producing HCFeCr or HCFeMn in closed furnaces, coke consumption for the furnace process itself lies in the range of 420 - 520 kg/tonne. Pre-reduction of the ore, can be done by using coal or other cheap carbon materials, both as an energy source and as a reductant. This will lower both the amount of coke and electric power in the reduction furnace, but might increase the total consumption of carbonaceous materials and the gross energy consumption of the process as a whole.

If all this carbon is assumed to be converted into CO, i.e. no reduction work is done by CO gas and no carbon is lost, the carbon could theoretically be recovered as CO gas. This could then be used as fuel for recovery of energy, either by burning above the top of a semi-closed furnace, or by collection from a closed furnace and later use. The quantity for instance would be between 770 and 1050 kg CO/tonne FeCr. This would be equivalent to between 2160 and 2950 kWh/tonne. In reality these figures would probably be 5 - 15% lower. The resulting amount of CO_2 produced by the furnace process alone would amount to 1200 1650 kg/tonne.

For instance in a Norwegian FeCr plant the balance for CO gas recovery and utilisation in 1998 was reported as follows:

Energy recovery and Utilisation	**Energy kWh/t**
Total recoverable energy:	2090
Total recovered energy, included internal use 190 kWh/t (sintering, coke drying, ladle heating):	1460
Flared:	630

Table 9.22: Recoverable and total recovered energy

Recoverable energy in this case is not a theoretical figure, but recovered and used CO gases internally and externally plus flared excess gas. The total energy balance for the whole plant was as follows:

Energy consumption and recovery	**Energy kWh/t**
Electrical energy:	4060
Potential energy in coke:	4430
Recovered CO gas, included internal energy use 190 kWh/t	1460
Total plant energy consumption:	7220

Table 9.23: Total energy balance for a FeCr smelter

A similar balance for other process routes can not be made due to lack of sufficiently detailed information. However, an approximate balance can be made, which includes only "fuel" or "process" energy consumption figures, i.e. electrical energy and coke and gas used as fuels, as shown in the table below. It does not include a comparison of reductant consumption and energy recovery efficiencies of CO gas.

Energy source	Conventional process (1) kWh/t	Conventional process, sintering closed furnace kWh/t	Process, closed furnace and pelletising/sintering pre-heating(3) kWh/t
Electricity	3800 - 4500	4060	3100 - 3500
Sintering	0	880 (2)	0
Pelletising/ sintering	0	0	275 - 500(3)
Pre-heating	0	0	500 - 700 (4)
Other	0- 2700 (5)	190	100 - 200
Total	3800 - 7200	5130	3975 - 4900

Notes:
(N 1) Conventional open, semi-closed or closed furnace with lump ore and/or briquettes/fines
(N 2 Energy from coke breeze used in the sintering process
(N 3) Assuming 60% of the ore is pellets
(N 4) Pre-heating to 700 °C

Table 9.24: Comparison of electrical and fuel energy consumption

This table shows that the difference in process energy consumption between production alternatives is not very big. Indeed, the "conventional" process routes may have an advantage if a considerable part of the recoverable energy can be sold externally. Most often plants do not have external energy customers. Choosing a process route that can utilise recovered heat, either for added process steps that increases efficiency and output, or for electricity generation, will then be advisable options.

An important point of the closed furnace process that uses pelletising/sintering and pre-heating is to minimise the use of fossil carbon per tonne of produced alloy, which will also minimise the specific CO_2 emission. However, the pelletising/sintering will only reduce the impact of greenhouse gases if an alternative, less energy efficient process would lead to a deficiency of CO gas.

Ore quality is also an important factor for energy consumption. Of primary importance is the content of metal oxide and the non ferrous metal/iron ratio, which should both be as high as possible. Secondarily the content of gangue minerals should be as low as possible in the ore or the ore mix (this will partly be a consequence of a high amount of metal oxide), and of a composition to minimise use of slag additives. This will lower the slag amount, and thus the proportion of the electric power necessary to melt slag.

Concerning the energy usage, the disadvantage of the smelting furnaces used without energy recovery is the high amount of energy lost as CO in the off gas and as waste heat. For instance by producing FeSi and silicon metal only about 32% of the energy consumed is chemical energy in the product, that means about 68% of the energy is lost as heat in the furnace off-gas [tm 152, A. Schei, J.K.Tuset, H. Tveit, 1998]. Energy can be recovered from the cooling cycles as hot water and from the off gas as heat which can be transferred into high pressure steam and subsequently into electrical energy or by using the CO content directly as a secondary fuel.

There are some direct plant improvements that can be done to reduce the energy consumption, such as running the process with a high metal yield, improving the furnace design to achieve lower energy loss. In addition to the direct plant improvements about 15 – 20% of the electric energy consumed by the electric arc furnace can be recovered as electricity by an energy recovery system. This percentage is considerably higher for a system that produces electricity and uses the thermal energy of the furnace cooling and the off-gas volume. This will be as well the case if the CO-gas is utilised directly as a secondary fuel in order to replace fossil fuels. The following examples show the possibilities to recover energy from the different furnace types used in the ferro-alloy industry.

EXAMPLE 9.08 ENERGY RECOVERY AND UTILISATION OF THE CO FROM A CLOSED ELECTRIC ARC FURNACE

Description: - The main part of the process is a closed electric arc furnace, which generates a CO rich off-gas (70 – 90% of CO). The off-gas is cleaned by using a wet scrubber before it can be used as a secondary fuel. One possibility is the combustion with air in an stream boiler. The steam is fed to a set of high pressure and low pressure turbines. The Energy is then recovered as electricity.

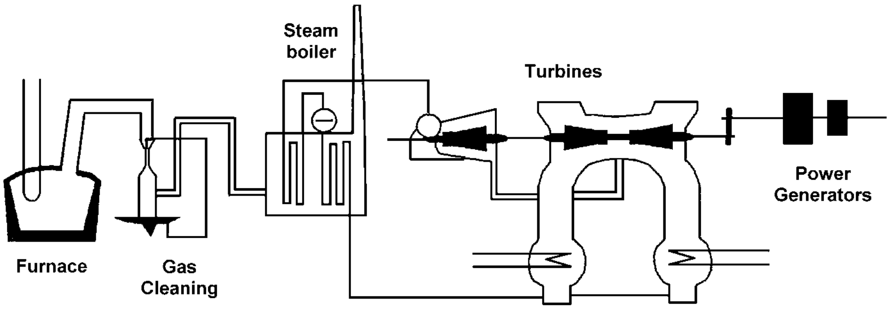


Figure 9.18: Direct use of the CO gas for the production of electrical energy

Main environmental benefits: - The recovery of electric energy from the CO gas reduces the overall energy consumption of the process, which consequently minimise the impact of global warming by emitting CO_2 from burning fossil fuel.

Operational data:

Steam produced	35 – 40 tonnes/h
Energy recovery	70 GWh/a = 13.5% of the electrical energy input

Cross media effects: - The recovered energy replaces in most cases fossil fuel like oil or coal and reduces therefore at the same time the emission of SO_2

Economics: - A cost indication is about 0.025 € per kWh (7% real interest rate and 15 years lifetime

Applicability: - To new and existing plants producing FeCr. FeMn and SiMn in closed furnaces

Reference literature:

[tm 151,Energy Recovery in the Norwegian Ferro Alloy Industry,1995]
[tm 157, 10th International Ferro-alloys conference, 1994]

Beside the production of electricity the CO gas can also be transferred by means of pipelines in the plant area and used as a secondary fuel for many purposes. The best utilities are achieved in direct burning replacing fossil fuels, e.g. heavy oil or coal. In the production of FeCr, FeMn and SiMn CO gas can be used for drying of coke and other raw materials. CO gas can as well be used as a fuel in the steel belt sintering furnace in order to reduce the primary energy consumption of the furnace. By producing FeCr, the CO gas is used to preheat the charge material, which cut the consumption of electric energy by 70–90 kWh per a 100 ºC increase in the preheating temperature. It can also be used in an adjacent stainless steel plant. [tm 141, Finland 1998]

The CO rich gas can as well be cleaned and then supplied as a synthetic gas to a neighbouring chemical plant, in which the gas serves as a raw material.

In a semi-closed furnace the CO-gas from the smelting furnace burns in the suction air thus creating a hot off gas of about 400 – 800 ºC with can also reach peaks up to 1200 ºC. The furnaces can be equipped with an integrated energy recovery system, which contains the following components:

- Exhaust hood with furnace ducting
- Waste-heat boiler
- Feed-water system
- Heat distribution system or steam turbine with generator and condenser

EXAMPLE 9.09 ENERGY RECOVERY FOR A SEMI-CLOSED ELECTRIC ARC FURNACE

Description: - The energy form hot off-gas of the furnace can be recovered in a waste heat boiler, which produces superheated steam. Relatively conventional water pipe boilers with super heater, economiser and condenser sections are used, combined with an efficient cleaning system to keep the heating surfaces clean in the heavily dust polluted flue gas.

The furnace top hood is highly exposed to the internal furnace heat, and is conventionally cooled with a water piping system covered by a ceramic lining. About 25% of the furnace heat emissions are lost to the top hood cooling water. For energy recovery the top hood may be cooled by unshielded high-pressure water piping, producing steam to the recovery boiler system. Such hood exists and contributes substantially to the energy recovery.

The steam can be used in a back pressure turbine in order to produce electricity or be sold to a neighbouring mill. The recovery system can be designed also to produce hot water, which can be used by a local heating system.

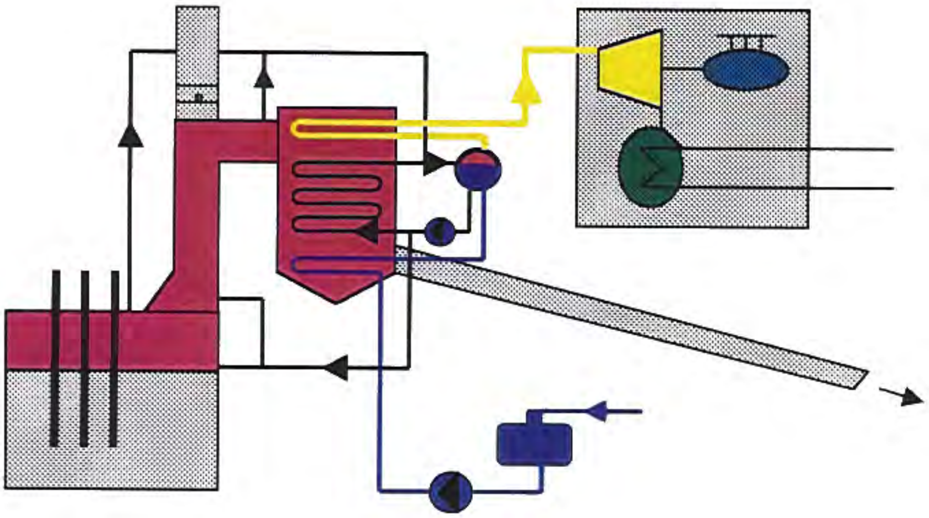


Figure 9.19: Energy recovery from a semi-closed furnace

Main environmental benefits: -The recovery of energy from the hot off gas reduces the overall energy consumption of the process, which consequently minimise the impact of global warming by emitting CO_2 from burning fossil fuel. The off-gas energy presented a large available, partly unexploited energy source that can provide new electricity without pollution and additional CO_2 emission.

Operational data: The off-gas energy can be used to produce electric power, heat energy or both. If the waste heat is utilised as electric power the recovery is up to 28 - 33% of the energy consumption. Alternately, the steam can be drained at mean pressure and be used for district heating, and the recovery will increase to approximately 80 - 90%. But then only 20% of the waste heat are recovered as electric power. The demand of district heating often varies trough the year and the most efficient solution is co-generation of electric power and heat energy to supply heat energy only when needed.

Cross media effects: - The recovered energy replaces in most cases fossil fuel like oil or coal and reduces therefore at the same time the emission of SO_2. The energy recovery produces no pollution, as the flue gas composition is not changed by the recovery. The emission of hot cooling air and water from the plant is reduced. The energy recovery creates no visual changes of the landscape

Economics: - There a two economic case studies, which have been reported. The following results should be seen as an cost indication because exact cost data is very much dependent on the specific circumstances of the plant.

First Case:
A plant with 3 furnaces and a total electric power consumption of about 117 MW has been taken into account. The furnaces are equipped with hoods of the conventional type. Net recovered electric energy will be 317.6 GWh/a, which equals 32.9% of the power consumption. Annuity depreciation for the investment of 43.1 M € over 15 years at 7% interest result in a capital cost of 4.73 M €/a. The electricity cost is approximately 0.016 - 0.017 €/kWh.

Capital cost	4.73 M €
Manning (5.5 Man-years)	0.25 M €
Total	5.76 M €

Second Case:
FeSi production with an electricity consumption of 60 MW uses a semi-closed furnace with about 750 ºC off-gas temperature. The waste heat boiler consists of 3 sections and each section has 4 economisers, 2 evaporators and 2 super heaters. The gas exits the boiler at approximately 170 ºC. The produces superheated steam is fed to a multistage turbine. The generator produces 17 MW of electric power equals to 90 GWh/a, which corresponds to 28% of the flue gas Energy and 16.5% of the electric power consumption in the furnace. The investment costs for the recovery plant has been in 1987 about 11.7 M € (20 Years annuity, 11.5% interest, electricity cost 0.02 €/kWh)

Capital cost	1.81 M €
Operation and maintenance,	0.45 M €
Manning (5.5 Man-years)	0.25 M €
Total	2.51 **M €**

Applicability: - The technology is in general applicable to both new and existing plants. Since this energy source normally presents existing installation, one of the obvious demands towards the energy recovery is that it is applicable to existing plants.

Reference literature:
[tm 186, ABB, Energy recovery in the ferro-silicon industry 1999]
[tm 187, Elkem, Energy recovery from hot gas in ferro-alloy and silicon industry 1999]
[tm 151, Energy recovery in the Norwegian ferro-alloy industry1995]
[tm 152, A. Schei, J.K. Tuset, H. Tveit, High Silicon Alloys 1998]
[tm 157, 10th International Ferro-alloys conference 1994]
[tm 199, Finkeldei, Reports from several plant visits in Sweden and Norway 1998]

EXAMPLE 9.10 ENERGY RECOVERY FROM A BLAST FURNACE OFF-GAS

Description: - The production of HC FeMn in a blast furnace results in the generation of a large amount of CO rich off-gas. This CO gas can partly be used as a secondary fuel to preheat the blast in the hot stoves. The excess gas is burned in an adjacent power plant to produce electricity.

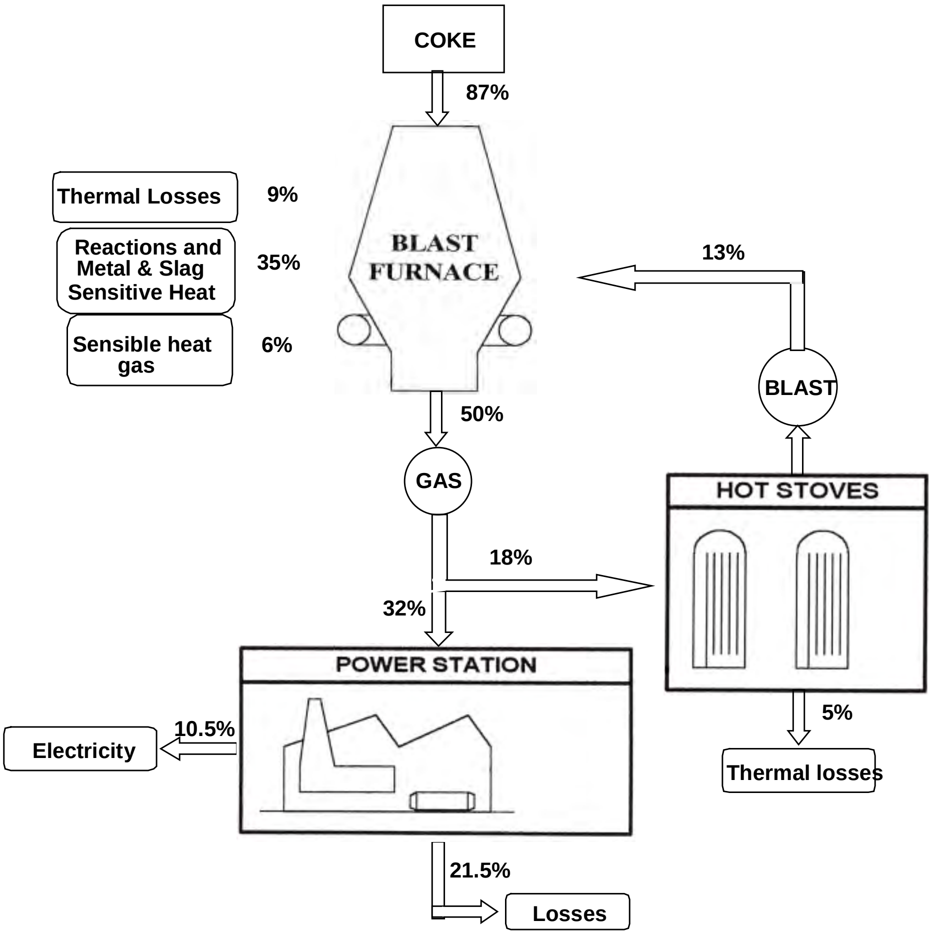


Figure 9.20: Energy recovery system for a blast furnace

Main environmental benefits: - The use of the CO gas reduces the overall power and coke consumption of the process, which consequently minimise the impact of global warming by burning fossil fuel.

Operational data:

Overall plant energy recovery (Energy is transformed into the product and recovered in the hot stoves and by electricity production)	52%
Energy recovered as electrical and thermal energy	23.5%

Cross media effects: - Blast furnace off-gas cleaning is unavoidable and thus induces generation of wastewater and a solid residue. It might be expected that preheating of the fuel media and an increase of the flue-gas temperature lead to higher NO_x emissions from the hot stoves. The application of modern burners may reduce the NO_x emissions.

Economics: - The high investment costs are saved to a large extent to the energy savings by pre-heating the blast and the income from the sold electrical energy.

Applicability: - Applicable to blast furnaces producing HC FeMn

Reference literature :
[tm 195, SFPO 1999]
[tm 199, Finkeldei, Reports from several plant visits 1998]
[BAT document on iron & steel]

For the production of FeSi and Si-metal is has been reported that a smelting furnace, which slowly rotates may contribute to the reduction of the overall energy consumption by about 10% and increase the metal yield.

The above possibilities of energy recovery are presently in operation in various systems in the ferro-alloy industry and performed satisfactory for many years. However it should be noticed that an appropriate energy recovery system means a high capital investment. Taking local conditions, such as local energy prices, periods of production and the absence of potential customers into account, the returns of investments may in several cases not be high enough to justify such investments from an economic point of view.

9.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: "How to understand and use this document". The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector; which are for the production of ferro-alloys, dust and fume, CO- and CO_2 gas, SO_2, energy recovery, wastewater, residues such as filter dust, sludge and slag;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels "associated with best available techniques" are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of "levels associated with BAT" described above is to be distinguished from the term "achievable level" used elsewhere in this document. Where a level is described as "achievable" using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous section. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this section are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

9.4.1 Materials storage and handling

The conclusion drawn for Beast Available Techniques for the materials handling and storage are shown in section 2.17 of this document are applicable to the materials in this chapter.

9.4.2 Process selection

9.4.2.1 Pre-treatment techniques

The techniques presented in Chapter 2 for pre-processing of raw materials will partly be BAT for this sector. According to the techniques to consider that are presented for pre-treatment techniques, BAT for this sector is considered as follows:

- A shaft furnace is preferably used for coke drying were the use of recovered energy or the CO rich off-gas from the smelting furnace as a secondary fuel is suitable. Bag filters are used to clean the off-gas were the associated dust emission level is 5 mg/Nm^3.
- A rotary kiln can be used for drying or degreasing of secondary raw material like turnings or metal scrap. For drying, bag filters are used to clean the off-gas were the associated emission level for dust is 5 mg/Nm^3 whilst for decreasing the optimal result of abatement is achieved by using an afterburner and subsequently a ceramic filter, which offers the possibility to recycle the hot air back to the dryer,
- For the degreasing of secondary raw material an afterburner can be used in order to destroy VOC’s. The residence time of 2 sec. and a minimum temperature of 850 ºC is suitable, however lower residence times (0.5 sec.) and may result in complete destroying of VOC’s, but this should be demonstrated at a local level. The residence time can be optimised in order to minimise the emission of VOC’s and the use of energy and subsequently the emission of CO_2 and other combustion products.
- Wet grinding, filtering and pelletising will produce an increased specific surface area of chromite and amend the reduction rate later in the smelting process. An additional effect is the reduced amount of dust generated by smelting process. By pelletising the fines, fugitive emissions are reduced and fine material that is more commonly available around the world may be used.

9.4.2.2 Sintering

The techniques presented in Chapter 2 for sintering will be part of BAT for this sector. In addition the technique to consider that is presented for sintering is considered being BAT for chromite sintering. The use of CO as a secondary fuel is suitable but it is dependent on the kind of furnace that is used. The associated emission and consumption levels are those presented in the example.

9.4.2.3 Pre-reduction and pre-heating

The technology of pre-reducing ore and concentrates is fully implemented only in two plants world-wide. As reported, there are still some problems operating this technology [tm 141, Finland, 1999]. Pre-reduction is therefore not yet recommended as a general BAT in this sector. However, for the future pre-reduction for chromite and also for manganese ore seems to be a very promising technique because this enables a substantial reduction in unit power consumption, that means a reduction of the electrical power needed in the subsequent smelting process. This may as well increase the productivity of the furnace. Pre-reduced manganese ore might play in future also an important role in reducing the high coke consumption of a HC FeMn production in a blast furnace.

Pre-heating of charge materials is suitable as far as it is possible. Combustion of CO-gas from closed smelting furnace provide heat as energy for preheating for instance the furnace charge in the FeCr-production. Pre-heating reduces the electrical energy consumption by about 70 - 90 kWh/100 ºC increase in the pre-heating temperature of the furnace. The production capacity of a furnace is increased as well by pre-heating the charge materials.

9.4.2.4 Smelting process

According to the different ferro-alloys produced and the environmental impact of the processes, which are influenced by the smelting system, the smelting furnaces presented in the next two tables are considered to be BAT for this sector.

The considered furnaces are in general all applicable to new and existing plants. However the long furnace life and the very high investment cost to build a new or replace an existing furnace should be taken into account. Therefore the best available techniques for smelting furnaces is strongly applicable only for new plants and a substantially change or replacement of a furnace. This is especially the case for replacing an open furnace by a closed furnace, because main parts of the abatement technique need to be changed as well.

The open furnace itself has not a significantly higher electrical or coke consumption, but huge amounts of cold ambient air are sucked into the furnace to burn the CO which is present in the off-gas. This consequently results in a very large volumetric flow of waste gas, which does not allow the recovery of its energy content because the temperature level is low and the flow rate large to build technically and economically efficient heat exchangers. The CO generated by the smelting process in this case is transformed into CO_2 and heat without using its energy content that is lost. Due to this the open furnace has not been considered as BAT, but can be tolerated if local conditions, for instance local prices of energy, periods of production and the absence of possible customers didn’t allow the recovery of energy from a semi-closed furnace under economic viable conditions.

For existing open furnaces retrofitting with an appropriate hood in order to change the open furnace into a semi-closed furnace is suitable and possible. By applying a nearly close hooding it is possible to limit the infiltration of air, but at the same time supply enough air to combust the CO generated in the furnace. Defining the off-gas temperature, which is about 300 – 400 ºC for an open furnace and about 600 - 800 ºC for a semi-closed furnace, can be used to make the distinction between open and semi-closed furnaces. The volumetric flow rate, which can be up to 100000 Nm^3/t of metal for an open furnace and up to 50000 Nm^3/t of metal for the semi-closed furnace can be used as an indication. Due to the increased off-gas temperature in a semi-closed furnace, the installation of an appropriate energy recovery system should than also be taken into consideration, because the major advantage of a semi-closed furnace is the possibility to recover a significant part of the process heat. The energy recovery can be done by producing steam in a waste-heat boiler and transformation into electrical energy.

For a semi-closed furnace with a nearly closed hood it should as well be noticed that the capital requirement for a collection and abatement system is proportional to the volumetric flow of gas, so that minimisation of gas volume is emphasised. This will also affect the environmental impact concerning the total amount of dust emitted. Assuming a bag filter with the same filter efficiency is used, the mass stream of dust emitted to the atmosphere will be reduced in the same way as the volumetric flow of gas will be reduced.

Smelting furnace	Ferro-alloy production	Applications		Remarks
		Abatement technique	Energy recovery	
Semi-closed electric arc furnace	HC FeCr	Bag filter	Heat energy can be recovered	
	FeSi, Si-metal	Bag filter	Heat energy can be recovered	
	HC FeMn, SiMn	Bag filter	Heat energy can be recovered	
	Other ferro-alloys produced by carbo-thermic reduction		Heat energy can be recovered	Other ferro-alloys, special ferro-alloys are normally produced only in small amounts, therefore the energy that can be recovered is low compared to bulk ferro-alloys Semi-closed furnaces can be used also for the production of FeV where fines needs to be remelted
	Alloy recovery from steel mill residues	Two stage bag filter with injection of activated carbon or a 3 step venturi scrubber an wet EP and a mercury removal by a selenium filter	Heat energy can be recovered	
Closed electric arc furnace	HC FeCr	Wet scrubber or Dry cleaning system	Energy can be recovered from CO that can be used as secondary fuel	Closed furnaces are operated in connection with different pre-treatment and peripheral techniques, such as sinter-plants, pre-heating furnaces etc. These techniques may all have a positive influence on the environmental impact, especially if CO rich off gas from the smelting furnace is used as a fuel.
	HC FeMn, SiMn	Wet scrubber or Dry cleaning system	Energy can be recovered from CO that can be used a secondary fuel	
	Other ferro-alloys produced by carbo-thermic reduction, but not FeSi and Si-metal	Wet scrubber Bag filter	Energy can be recovered from CO that can be used a secondary fuel	Special ferro-alloys are normally produced only in small amounts, therefore the energy that can be recovered is low compared to bulk ferro-alloys Due to operational problems. FeSi and Si-metal can not yet be produced in a closed furnace.

Table 9.25: Smelting furnaces considered as BAT for the production of ferro-alloys

Smelting furnace	Ferro-alloy production	Applications		Remarks
		Abatement technique	Energy recovery	
Blast furnace	HC FeMn	Dust catcher, EP and a wet scrubber or Dry cleaning system	Energy recovery using the CO-rich off gas for heating the hot stoves and electricity production	• Due to the high coke consumption the blast furnace has to be considered as BAT only if it is associated with an efficient recovery of the energy content of the CO-rich off-gas. This necessitates a high performance process control and abatement system. To reduce fugitive emissions appropriate hooding of tap holes and runners should be used. Under this conditions the blast furnace can be operated with a low environmental impact.
Refractory lined crucible enclosed in a reaction chamber	Ferro-alloys produced by metallo-thermic reduction	Bag filter	Energy recovery is not practised	• Recovery of heat energy will not be practised, because the metallo-thermic reduction takes place as a batch process, which needs only a short reaction time. • According to the bio-toxic nature of fluoride the use of fluorspar by producing FeMo should be minimised as far as possible or replaced.
Multiple hearth furnace	Roasting of molybdenite ore	Multi-clones with dry EP, wet scrubber and a de-sulphurisation plant	Energy recovery from the furnace is not practised	• The multi-clones and the dry EP serve as dust a catcher were the dust is recycled back to the furnace. • For the final de-dusting a wet scrubber is used • Desulphurisation takes place in a desulphurisation plant producing sulphuric acid. The efficiency of the de-sulphurisation plant should be in the range of 98-99% • For new plants it will be possible to achieve 99.3% conversion at a continuous basis with the single contact process.

Table 9.26: Smelting furnaces considered as BAT for the production of ferro-alloys

9.4.2.5 Process control

The techniques presented in the different sections of Chapter 2 describing possibilities to control the process by computerised systems will be part of BAT for this sector. The most important are considered being.

- Furnace operation control to optimise operating conditions. Key parameters are pressure and temperature at various points in the furnace and gas handling system, oxygen and carbon monoxide concentrations and system pressure.
- Process control using relevant methods so that it is possible to maintain operating conditions at the optimum level and to provide alarms for conditions that are outside the acceptable operating range.
- Plant operators should be trained and given instructions about the correct operating procedures and control parameters.
- Use of good maintenance practice for process plant, abatement systems and other associated processes. A system of inspection should be adopted.

9.4.2.6 Post furnace operations

The techniques presented as techniques to be considered in the determination of BAT are also techniques that are considered as BAT in this sector.

9.4.3 Gas collection and abatement

The techniques presented in Chapter 2 for off-gas collection techniques as well as air abatement techniques will be part of BAT for this sector. According to the techniques to consider that are presented for fume/gas collection and abatement, BAT for this sector is considered as follows.

- Bag filter or wet scrubbers like cascade or venturi scrubbers are suitable for de-dusting furnace off gases. A residual particulate matter concentration of less than 5 mg/Nm^3 for a bag filter and less than 10 mg/Nm^3 for a wet scrubber is the associated level.
- Dust emissions well below the associated levels may be achieved for instance with membrane bag filters if local air quality standards or the presence of harmful metal compounds requires this.
- Some metals have toxic compounds that may be emitted from the processes and so need to be reduced. For metal compounds such as nickel, vanadium, chrome, manganese etc. as part of the total dust, emissions much lower than the associated dust emissions of 5 mg/Nm^3 for a bag filter and 10 mg/Nm^3 for a wet scrubber are achievable. For nickel compounds emissions less than 1 mg/Nm^3 is the associated level.
- By recovering ferro-alloys from steel mill residues, dust and volatile metals notably mercury and to a lesser extents cadmium and lead should be reduced. Using a two-stage bag house with injection of activated carbon or lignite coke can do this. Alternatively a 3-step venturi scrubber combined with a wet electrostatic precipitator and a selenium filter can also be used.
- For harmful toxic vaporised metals like mercury, cadmium and lead as part of the off-gas, the associated emission level is below 0.2 mg/Nm^3.
- Appropriate hooding systems connected with a bag filter are preferably used for collecting and cleaning of tapping and casting fumes. Proper design and good maintenance can ensure a high capture efficiency.
- The sulphur-dioxide content in the molybdenite roasting off-gas should be removed and preferably converted to sulphuric acid. The associated conversion efficiency for a single contact plant is 98-99%. For new plants 99.3% conversion is achievable.

The following table summarises the captured emission associated with the use of best available technique and the techniques that can be used to reach these levels.

Pollutant	Emissions associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	< 5 mg/Nm^3	Fabric filter	Fabric filters are normally used for de-dusting off-gases from open and semi-closed furnaces
	< 10 mg/Nm^3	Wet scrubber	Scrubbing system are used for de-dusting off-gases from closed furnaces and the blast furnace. Venturi scrubbers used to clean the off-gas from a closed HC FeCr furnace achieve emissions below 50 mg/Nm^3 due to very fine dust that is produced in the furnace, but which is not emitted directly to the atmosphere. In this case the CO-rich off gas is used as secondary fuel.
Heavy metals		Fabric filter	High performance fabric filters (e.g. membrane fabric filters) can achieve low levels of heavy metals. The concentration of heavy metals is linked to the concentration of dust and the proportion of the metals as part of the dust.
Vaporised metal (Hg, Cd, and Pb)	< 0.2 mg/Nm^3	Two stage bag filter with injection of activated carbon or a 3 step venturi scrubber an wet EP and a mercury removal by a selenium filter	By recovering ferro-alloys from steel mill residues Hg, Cd and Pb can be emitted
CO from closed furnaces	Not directly emitted to atmosphere	Energy recovery	CO can be used in various way to recover its energy content
SO_2 from molybdenite roasting	Conversion efficiency 98 – 99%	De-sulphurisation plant (single or double contact plant)	The performance of the gas treatment plant is depending upon the individual raw material batch and the furnace loading and therefore influence the conversion efficiency With a double contact plant the conversion efficiency can be higher than 99% but due to the relatively low amount of sulphur in the roster off-gas additional sulphur needs to be burned in order to ensure reasonable conditions for the double contact plant.

Note. Collected emissions only.
Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period.
For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.

Table 9.27: Emission levels to air associated with the use of BAT

9.4.4 Wastewater

The techniques presented in Chapter 2 for effluent treatment and water reuse will be part of BAT for this sector. According to the techniques to consider that are presented for water treatment, BAT for this sector is considered as follows:

- Closed water cycles are suitable for wet scrubbers, cooling systems and granulation processes.
- The bleed form closed water cycles need to be treated to remove particulate matter and metal compounds from the water.
- Treated waste waster should be recycled and reused as much as possible
- Scrubbing liquids should also be treated and analysed before discharge.
- Containment of plant drainage systems where possible and treatment of effluents according to their content with analysis before discharge.
- In case of using the wet cleaning system in the alloy recovery process the bleed from the scrubber can be cleaned by a
  - cyanide removal,
  - reduction of Cr_6+ to Cr_3+, precipitation of metal hydroxides at high pH together with oxidation of cyanides
  - precipitation of fluoride and cleaning the water from particles in a sand filter.

9.4.5 Process residues

The techniques and recycling routs presented together with the emission levels of residues in Chapter 2 for waste minimisation will be part of BAT for this sector. In general all process steps should be analysed in order to minimise the generation of process residues and the exhaust the possibilities of recycling and reuse. According to the processes that were defined as applied techniques the following ways of recycling and reuse of slag and filter dust and sludge are considered as BAT for this sector:

Ferro-alloy		**Recycling and reuse**
FeCr	**HC FeCr**	• Crushed lump and granulated slag are used as building material and road construction material • Slag can also be used as a sand blasting grid, and for the production of refractory castables
	MC and LC FeCr	• The slag should be reused as much as possible
Alloy recovery from steel mill residues		• The low basicity of slag insures the formation of stable silicates, which are non-leachable. The slag can be used in various construction applications.
FeSi		• The production of silicon metal and FeSi is almost a slag free process (small amounts of quartz are transformed into slag, < 1%). The slag can not be recycled to the furnace • During refining of silicon-metal and FeSi, some small amounts of refining slag is produced. The slag can not be recycled to the furnace
Silicon-metal		
Calcium-silicon		• Slag can be recycled to the furnace
FeMn	**HC FeMn**	• Standard exhausted slag (low content of MnO) from a blast furnace cam be used as a construction material • Rich slag from a blast furnace (high content of MnO) can be sold as raw material for the production of silico-manganese
		• Standard exhausted slag (low content of MnO) can be used as a construction material
	MC FeMn	• The slag can used as raw material in the production of silico-manganese
	LC FeMn	• The slag can be used as raw material in the production of silico-manganese
SiMn		• Slag can used as a construction material
FeV		• Slag can be used as secondary raw material in the process industry e.g. for the production of refractories.
FeMo		• Depending on the composition the slag can partly be sold for further processing
Notes: Analysis of residual materials before transfer to other sites so that the correct disposal or recovery routes can be used Slag without any economic and technical utility need still partly to be discharged to a landfill. Depending on the composition of the slag a special slag treatment may be required before discharging it to a landfill.		

Table 9.28: Recycling and reuse of slag from the production of ferro-alloys

Ferro-alloy		Recycle and reuse
FeCr	**HC FeCr**	• The dust from crushing raw material transport and handling as well as the dust and sludge from the pre-treatment processes can be recycled. • The dust from FeCr product handling can be remelted in the furnace or used in stainless steel production.
	MC and LC FeCr	• The dust can be recycled back to the smelting furnace
Alloy recovery from steel mill residues		• The filter cake from the sludge treatment in the plasmadust process can be recycled either to the ISP (Imperial Smelting Process} or to the Waelz Kiln Process. • The furnace dust from the submerged arc furnace is high in ZnO (20-60%) and PbO (2 - 6%). It is pelletised and recycled by the Zn industry (I.F. smelter, or by using the Waelz process as an intermediate concentration step
FeSi		• Silica fume (micro silica) is collected in the bag filter as a by-product. Micro silica is used as a cement additive, which increase the strength of the concrete and led to a very smooth surface that prevents the concrete from water infiltration.
Silicon-metal **Calcium-silicon**		
FeMn	**HC FeMn**	• The coarse part of the dust that is relatively rich in manganese can be agglomerated and recycled to the furnace or used as raw material for the production of silico-manganese in an electric arc furnace. • The fine dust can sometimes partly be valued in other industries or is discharged to a landfill
	MC FeMn	• Dust and sludge can be recycled, or valued in other industries
	LC FeMn	
SiMn		• Dust and sludge can partly be recycled or valued in other industries l
FeNi		• Dust can partly be recycled to the feeding system
FeV		• Dust can partly be recycled to the smelting process. FeV fines are remelted
Molybdenite roasting		• The off-gas leaving the roaster contains dust up to 15% of the concentrate feed. • Most of the dust and sludge from the off-gas cleaning can be recycled to the concentrate feed.
FeMo		• Dust can partly be recycled to the smelting process l
Notes: Analysis of residual materials before transfer to other sites so that the correct disposal or recovery routes can be used Filter dust and sludge without any economic and technical utility need still partly to be discharged to a landfill. Care should be taken when discharging dust and sludge, because due to there hazardous nature a special treatment may be required before discharge to a landfill.		

Table 9.29: Recycle and reuse of the collected filter dust and sludge from the production of ferro-alloys

9.4.6 Energy recovery

The techniques and general principles of energy recovery presented in Chapter 2 will be part of BAT for this sector. According to the considered techniques and routes of utilisation the CO gas or to recover the heat energy from a smelting process, BAT for energy recovery in this sector is considered as follows:

Ferro-alloy	Furnace	Energy medium	Energy recovery
FeCr	Closed	CO-gas	• Production of electrical energy • Utilisation of CO as fuel in neighbouring plants • Direct burning for drying, sintering pre-heating ladle heating etc. • Use in a integrated FeCr and stainless steel plant
	Semi-closed	Heat	• Production of electrical energy • Production of high pressure steam and utilisation in the own or neighbouring plants • Production of hot water
FeSi **Si-metal**	Semi-closed	Heat	• Production of electrical energy • Production of high pressure steam and utilisation in the own or neighbouring plants • Production of hot water
FeMn **SiMn**	Closed	CO-gas	• Production of electrical energy • Utilisation of CO as a raw material in neighbouring plants • Direct burning for drying, sintering pre-heating ladle heating etc
	Semi-closed	Heat	• Production of electrical energy • Production of high pressure steam and utilisation in the own or neighbouring plants • Production of hot water
FeNi	Semi-closed	Heat	• Production of electrical energy • Production of high pressure steam and utilisation in the own or neighbouring plants • Production of hot water
FeV	Special ferro-alloys are normally produced in small amounts compared to bulk ferro-alloys. The smelting process usually takes place as a batch process in a refractory lined crucible. The metallo-thermic reaction is exothermic where the heat is used as the energy source for the process which needs in some cases only a few minutes The energy recovery from the excess process heat is difficult and doesn't justify a high investment for an energy recovery system.		
FeMo			
FeW			
FeTi			
FeB			
FeNb			
Notes: Combining the different recovery techniques can increase the overall efficiency of an energy recovery system.			

Table 9.30: BAT for energy recovery by producing ferro-alloys

The above mentioned best available techniques for energy recovery are techniques that are applicable to new plants and in case of a substantial change of an existing plant. This includes also the case where a furnace needs to be replaced.

For existing plants retrofitting of a smelting furnace with an appropriate energy recovery system is possible especially when an open furnace will be changed into a semi-closed furnace. The energy content can then be recovered by producing steam in a waste-heat boiler where the furnace hood can advantageously be integrated in the recovery system and used as superheater. The produced steam may be used in the process, in neighbouring mills but most often for the generation of electrical energy will be economically the best solution.

By building a closed furnace or replacing of an existing furnace by a closed one a cleaning and recovery system for the CO-gas is unavoidable. The CO, that otherwise needs to be flared off can be used as high quality secondary fuel for a variety of purposes or as raw material or fuel in neighbouring mills. Flaring of CO-gas is only acceptable in the case where customers inside or outside the plant are temporarily not available. The recovered CO gas can as well be used for the production of electrical energy.

The recovery of process energy reduces the consumption of natural energy resources and consequently contributes to minimise the CO_2 emissions and the effect of global warming if the total impact of the process, and the saved energy elsewhere are included into the global energy and CO_2 balance. Energy recovery is therefore a desirable option and will in future be more and more important, but it is suitable only if local conditions (e.g. local prices of energy, the presence of external energy customers, and periods of production) justify the investment. As already mentioned in the part of BAT for smelting furnaces the recovery of energy is strongly related to the used furnace type (semi-closed or closed furnace). Energy recovery should therefore also be seen in the context and the requirements of changing existing furnaces.

9.5 Emerging Technologies

The following techniques are emerging techniques, which means that this techniques are not fully implemented in the ferro-alloy industry.

- The rotary hearth furnace for pre-reducing chromite has been investigated
- Coal/oxygen or smelt-reduction processes rely upon the energy combustion of coal with oxygen or oxygen-enriched air, to provide the entire energy requirement for smelting chromite to ferro-chrome. Different companies have investigated different possibilities
- The Mintek Blobulator for granulation of ferro-chrome is still in the pilot plant stage
- Closed furnace operation for the production of ferro-silicon and silicon metal has yet not been successfully been developed.
- The fluidised bed roaster for molybdenite roasting

The fluidised bed roaster is not considered to be a viable technology for the roasting of molybdenite concentrates. Those plants that have used (or carried out development work) on roasting molybdenite concentrates using a fluidised bed have found that is does not produce a product that is sufficiently low in sulphur to meet the accepted commercial standards. In order to further reduce the sulphur level of the roasted molybdenite concentrate below the 0.10% level it is necessary to add another furnace operation such as a rotary kiln (with perhaps a grinding step between) after the fluid bed. This results in a more complex plant that will be less efficient and will result in higher operating costs.

10 PROCESSES TO PRODUCE ALKALI AND ALKALINE EARTH METALS

The group of alkali metals (lithium, sodium, potassium, rubidium, caesium and francium) is the first metal group (1 A) in the periodic table of the elements. The group of alkaline earth metals (calcium, strontium and magnesium –group 2A) has similar properties and is therefore covered by this sector.

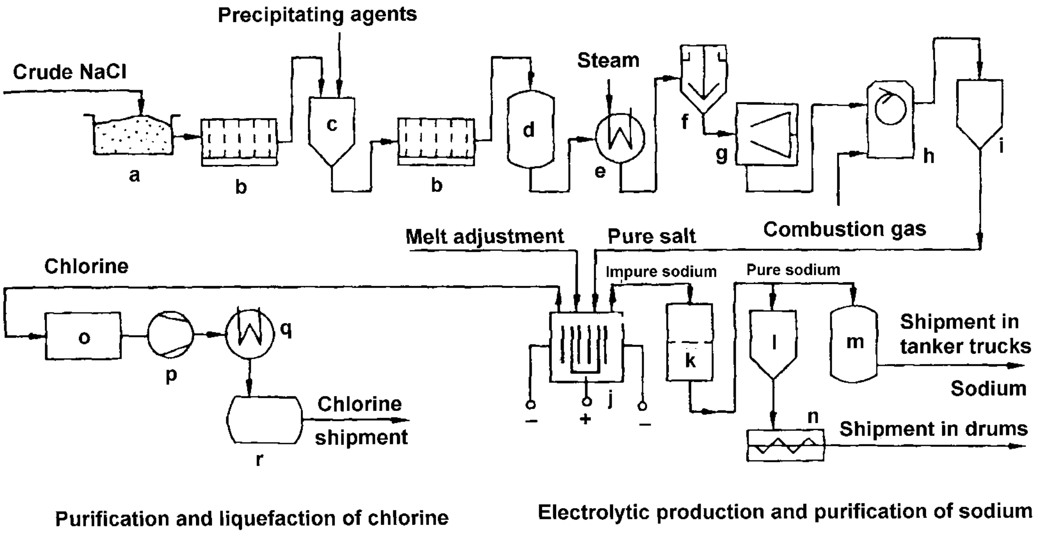
There are very few companies within the EU who produce alkali and alkaline earth metals; the processes used are therefore limited but are representative of the techniques used worldwide. There are two producers of sodium metal and one producer of lithium in the EU. Only one company produces calcium and strontium metal and there are two companies who produce magnesium metal.

10.1 Applied Processes and Techniques

10.1.1 Sodium metal

Sodium metal is produced by the electrolysis of fused sodium chloride (NaCl). Calcium and barium chlorides ($CaCl_2$ and $BaCl_2$) are added to the NaCl to form a eutectic mixture, which melts at 580 °C [tm 106, Farrell 1998].

A flowsheet of sodium metal production is presented in the next figure, where the electrolytic cell is the main part of the process.



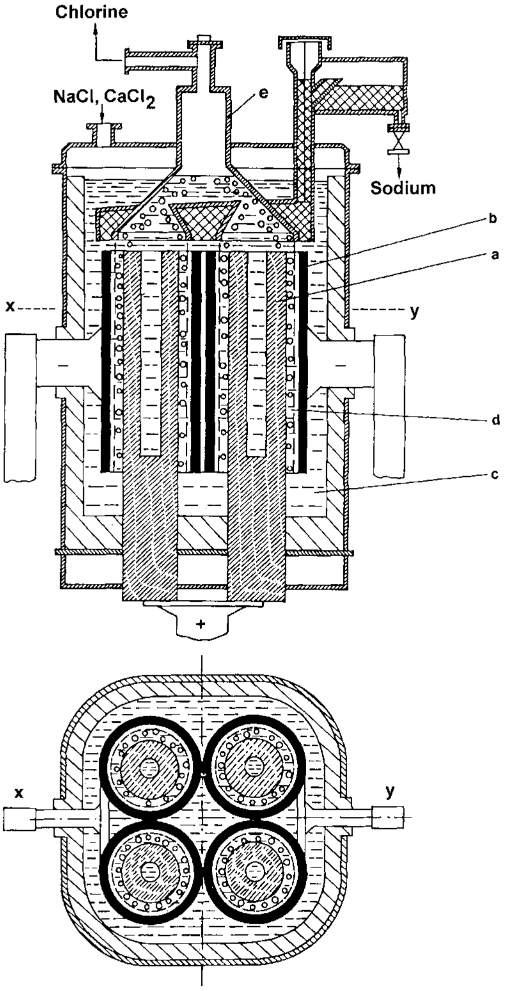
a) Dissolution vessel; b) Filter; c) Precipitation vessel; d) Vessel for pure brine; e) Evaporator; f) Thickener; g) Centrifuge; h) Rotary dryer; i) Pure salt bunker; j) Electrolysis cell; k) Sodium filter; l) Sodium storage; m) Sodium tank; n) Casting; o) Chlorine purification; p) Chlorine compressor; q) Liquefier; r) Chlorine storage vessel

Figure 10.1: Flow sheet of sodium production
[tm 107, Ullmanns 1996]

Downs Cells are used and have a special cylindrical anode and a circular concentric cathode separated from the anode by a steel mesh diaphragm. Each cell normally has 4 pairs of electrodes. Energy from electrolysis is sufficient to keep the electrolyte molten and no additional heating is needed. The cell voltage is 6.2 to 7 V and this is used to monitor and control the process. Raw materials are received as crystals and are dried in a rotary drier before use; dust is extracted and scrubbed. The sodium chloride concentration in the cell bath is held in the desired range by continuously feeding salt to the cells at the same rate as it is electrolysed to form sodium and chlorine, thus maintaining a constant cell bath level. Sodium and chlorine are collected, under the surface of the cell bath, in separate compartments of a collector assembly. The chlorine is drawn off continuously under a very slight vacuum, to a Chlorine Plant, where it is normally liquefied and passed to the liquid chlorine storage tanks. The sodium is forced, by the weight of the bath above the collector assembly, up a finned riser-pipe where it continuously overflows across a weir into receivers. These are tapped every two hours into larger, portable 24-hour receivers.

A small amount of the calcium chloride in the cells is also electrolysed, along with the sodium chloride, forming calcium and chlorine. A portion of this metallic calcium is carried out of the cells as an impurity in the sodium and separates as the metal cools. This calcium chloride in the cell bath is replaced by adding dry granular calcium chloride to the cells daily. The barium chloride is not electrolysed. Filters remove by-product calcium from the sodium and the purified sodium from the filters is transferred by vacuum to the intermediate storage tanks, and thence under gravity to final storage tanks.

Filter cake from the sodium cleaning stage is pressed to remove sodium and is then washed, dissolving it away as an alkaline effluent. This is used as a reagent to treat other site effluents. Other solid wastes arise from sediment in storage tanks, these are burnt on an open hearth and fumes are collected and scrubbed in a 2-stage water scrubber, this scrubber discharges into a 3rd stage using HCl which also treats fumes from the filter cake wash. A typical “Downs Cell” for the electrolytic production of sodium metal is shown in the next figure



a) Anode; b) Cathode; c) Molten salt; d) Diaphragm; e) Chlorine dome

Figure 10.2: The Downs Cell
[tm 107, Ullmanns 1996]

10.1.2 Lithium metal

This is produced by the electrolysis of a molten, eutectic mixture of lithium chloride (LiCl) and potassium chloride (KCl) at 450 °C [tm 106, Farrell 1998]. Lithium carbonate is received in IBC's and is converted into LiCl; the solution is concentrated and crystallised. Waste lithium hydroxide can also be converted. LiCl crystals are dried before they are drummed for manual feeding into the cells. There is some local dust extraction at handling points. KCl is not electrolysed at the voltage used (4 to 5 V) and only LiCl is added to the cells during operation.

Cells are rectangular baths each containing 5 pairs of electrodes (a cylindrical carbon anode and a concentric circular steel cathode). There is no membrane in this process and this is likely to reduce the efficiency of electrolysis, as a portion of the Lithium liberated (from the inside surface of the cathode) will react with chlorine to reform LiCl. Cells can be heated by gas burners for start up and winter use but normally sufficient heat is generated by electrolysis to keep the bath molten. Cell life is ~7 years and is prompted by wear of the weir plate.

Molten lithium is produced and accumulates at the front of the cell and is skimmed off manually using a fine mesh skimmer into a hand-held ladle. The metal is then immediately cast into small moulds (~350mm x 50mm x 50mm), no metal fume is produced but the filled moulds are immediately covered by a mineral oil to prevent oxidation. This causes an oil fume, which is extracted into a vertical lip captor and emitted untreated through a stack along with other fume extracted from the cell room that contains alkali, dust and chlorine. Lithium bar can also produced in small quantities using a hand-operated hydraulic press.

Chlorine produced by the cell room is collected by partial vacuum and is absorbed in caustic soda to produce sodium hypochlorite, which is sold. Two absorption columns are used, one on standby for emergency use.

The applied current and voltage control the process. Rectifier trips are easily handled and only cause a problem during skimming when current induced stirring of the electrolyte stops. Other problems arise from the presence of sodium as an impurity in the electrolyte as it is electrolysed and separates from Li as it cools. Na forms small “mushrooms” on the metal surface and these ignite and may cause the ingot to burn, the sodium content of the raw material is controlled to prevent this.

There are no releases to water; mother liquor from crystallisation is re-circulated.

10.1.3 Potassium metal

At the time of writing, potassium metal is produced on an industrial scale only by the reduction of potassium chloride with sodium metal. In the continuous production a fractional distillation is incorporated into a reaction column packed with molten potassium chloride. By feeding sodium into the column a vapour mixture of sodium and potassium is fractionated. Potassium metal is then obtained by distillation of the vapour mixture using air as a coolant [tm 107, Ullmanns 1996].

10.1.4 Calcium and strontium metal

Calcium and strontium metal are used for a variety of purposes. Calcium as an alloying element improves the quality of steels especially the mechanical properties like formability, drawing and machinability. Because of its strong ability to form oxides and sulphites calcium is important in the production of ultraclean steel. Calcium metal may also be used for lead de-bismuthation. Strontium metal is needed in aluminium refining as well as for the rafination of steel slag.

10.1.4.1 Calcium metal

Calcium metal can be produced by electrolysis or metallo-thermic reduction, but at present the only process used in the European Union is the high temperature vacuum reduction of calcium oxide with aluminium using the metallo-thermic process. However a short description of the electrolysis process will be given.

10.1.4.1.1 The electrolytic process

The basic electrolytic cell is a graphite-lined vessel filled with partially molten calcium chloride maintained at a temperature above the melting point of $CaCl_2$, but below the melting point of calcium metal. Calcium metal forms as a solid deposit in a water-cooled anode, This calcium contains 15-25% of entrapped salts and has to be remelted to reduce the impurity levels.

10.1.4.1.2 The metallo-thermic process

The production of calcium metal depends on a small finite equilibrium of calcium vapour in the range of 1000–1200 ºC. The calcium vapour is then transferred with a vacuum pump to a cooled region of the reactor were condensation takes place. This shifts the equilibrium at the reaction site and allows more calcium vapour to be formed.

Lime is ground in order to get a small particle size material that is then dry blended with the desired amount of aluminium. The mixture of both is then compacted into briquettes to ensure good contact of reactants. The briquettes are then heated in the furnace, which is electrically heated by resistance, up to about 1300 ºC. Due to the vacuum in the furnace a condensed block containing more than 95% of calcium metal is formed in the cooled part of the furnace. These blocks of calcium metal and calcium aluminate residue are then removed from the furnace. For some applications calcium metal needs to be reduces in size, which can be done by using special grinders adapted to the characteristics of calcium. A characteristic flow diagram of the production of calcium metal is shown below.

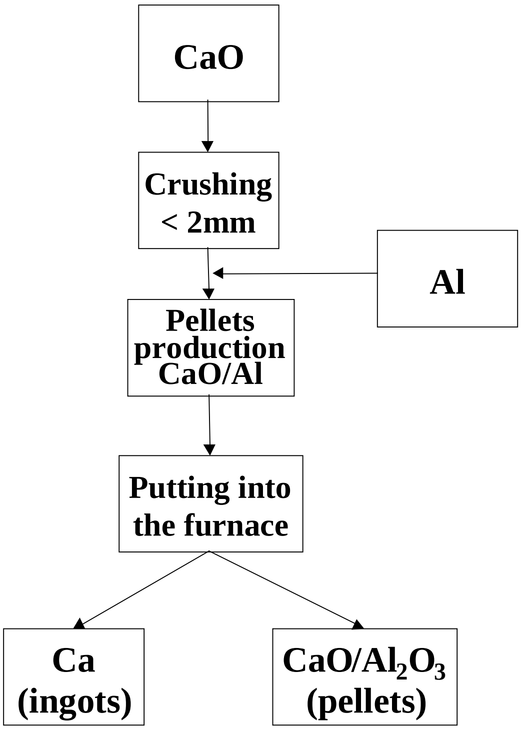


Figure 10.3: Flow diagram of the production of calcium metal

10.1.4.2 Strontium metal

Strontium metal is produced in the European Union only by thermal reduction of strontium oxide with aluminium as a reducing agent. The reaction is conducted in a similar way to the production of calcium metal in a vacuum furnace. The vaporised metal is condensed in a cooler part of the furnace. The blocks of strontium metal and strontium aluminate residue are removed from the furnace. Strontium metal then is sold as such without any additional grinding. A characteristic flow diagram of the production of strontium metal is shows below.

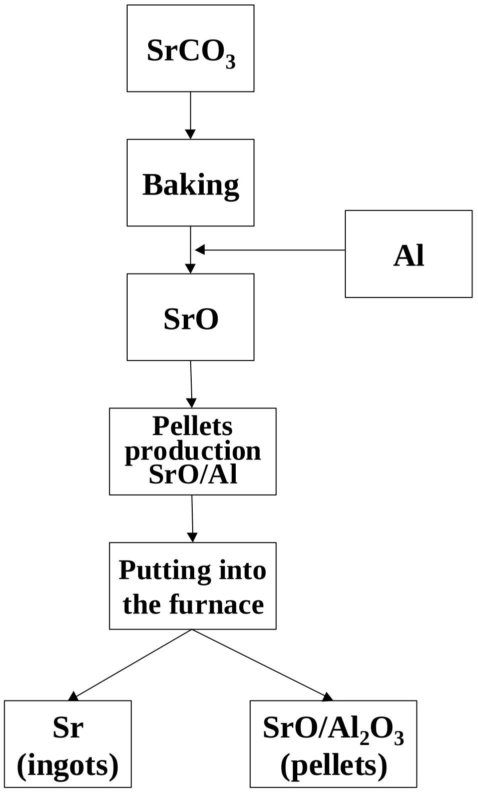


Figure 10.4: Flow diagram of the production of strontium metal

10.1.5 Magnesium metal

Magnesium metal and magnesium containing alloys have widespread use in different industrial sectors, for instance as an alloying element in aluminium as well as in automotive, telecommunication or electrical applications. Magnesium can also be used for cathodic protection of pipelines, tanks and bridges.

Magnesium can be produced either by electrolysis or a thermal reduction process. The raw materials used are dolomite, magnesite, carnalite, brines or seawater depending on the process. Magnesium will as well be recovered and produced from a variety of magnesium containing secondary raw materials.

10.1.5.1 Production of primary magnesium by thermal reduction

In the thermal reduction process calcined dolomite is reacted with ferro-silicon sometimes together with aluminium in a furnace or retort vessel. The calcination process takes place by de-carbonisation and de-hydration of dolomite limestone. For the calcination process for dolime, a rotate or vertical furnace can be used. A schematic overview of the thermal reduction process gives the next figure.

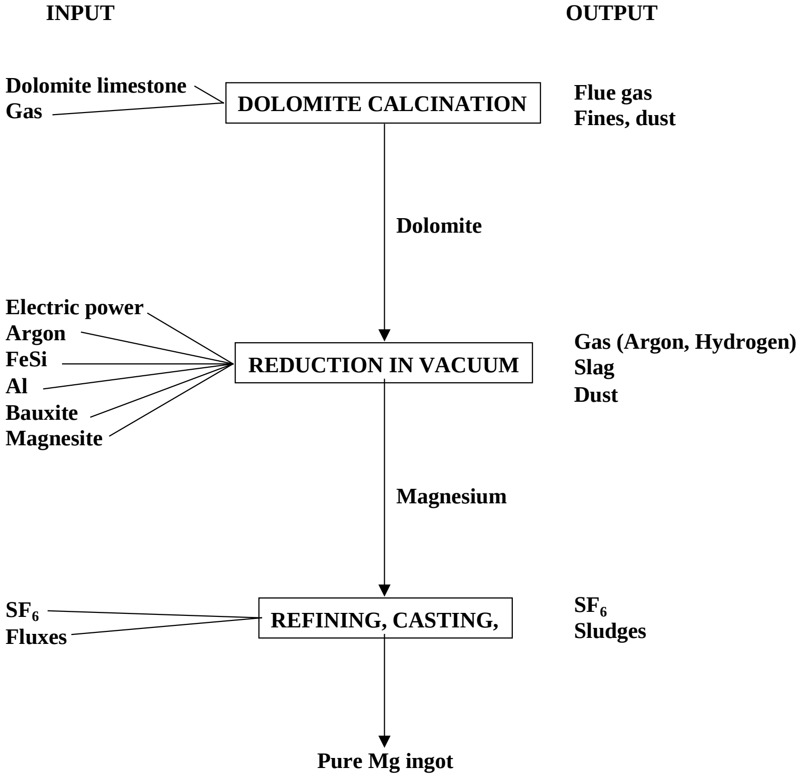


Figure 10.5: Schematic flow sheet of the thermal reduction process to produce magnesium metal

The metallo-thermic process is operated under vacuum and produces magnesium vapour, which is subsequently condensed into liquid or solid form. This operation is carried out in a furnace electrically heated by Joule effect where the liquid slag acts as a resistor between the electrode and a carbonaceous bottom lining. The reduction is carried out at 1700 ºC and 6 kPa pressure. Reductants and oxides are introduced continuously over the slag. Argon is also introduced to form an inert atmosphere. The magnesium is condensed in a condenser cooled by water (crucible). This crucible is taken apart when it is full, and then transported to the foundry to produce magnesium ingots.

10.1.5.2 Electrolytic production of primary magnesium

The electrolytic process produces magnesium by the electrolysis of magnesium chloride, which can be produced from various raw materials. In the following, the production from dolomite and seawater is described, as practised by a European producer. The dolomite, which is brought to the plant, is then calcined in a Gas-Suspension-Calciner. The feed is introduced through cyclones counter-currently to the hot exhaust gases, then calcined to dolime in a reactor fired with gas.

The dolime is slaked with seawater to produce a precipitated magnesium hydroxide. Prior to the slaking the seawater is de-carbonated by stripping with air after acidification with hydrochloric acid. The magnesium hydroxide is concentrated by reducing the water content in a thickener. The resulting magnesium hydroxide pulp is fed to a rotary kiln and calcined to a light-burnt magnesium oxide. The magnesium oxide is then mixed with carbon and pelletised.

The pellets are fed into the chlorinators, which are brick lined shaft furnaces. The chlorinators are charged from the top, and the chlorine gas that is recycled from the electrolysis stage is introduced near the bottom. The reaction in the furnace converts the magnesium oxide into magnesium chloride, which in the molten form is purified by passing over the carbon resistors

counter-currently to the incoming chorine gas. The liquid magnesium chloride is withdrawn from the furnace and transferred via closed vessels to the electrolysis stage.
Magnesium chloride is electrolysed in the electrolytic cells at 300 – 400 kA into liquid magnesium metal. The magnesium metal is withdrawn from the cells and transported in closed vessels to the cast-house where the metal is cast as pure magnesium or as magnesium alloys in ingots. To prevent the metal from oxidation by the surrounding air the use of sulphur-hexafluoride (SF_6) in the casting process can protect the metal surface.

The off-gas from the chlorination furnaces is treated in a series of wet scrubbers and wet electrostatic precipitators before finally being subjected to incineration. SO_2 gas is added to the off gas between scrubbing stages to convert Cl_2 into HCl and thereby enhance the efficiency of the scrubber.

The contaminated water streams mainly from the chlorination off-gas treatment are treated in a 2-stage water treatment plant. The first stage consists of a flocculation and solids separation, the second stage cleaning by activated carbon.

The process of magnesium production by electrolysis is shown in the following figure.

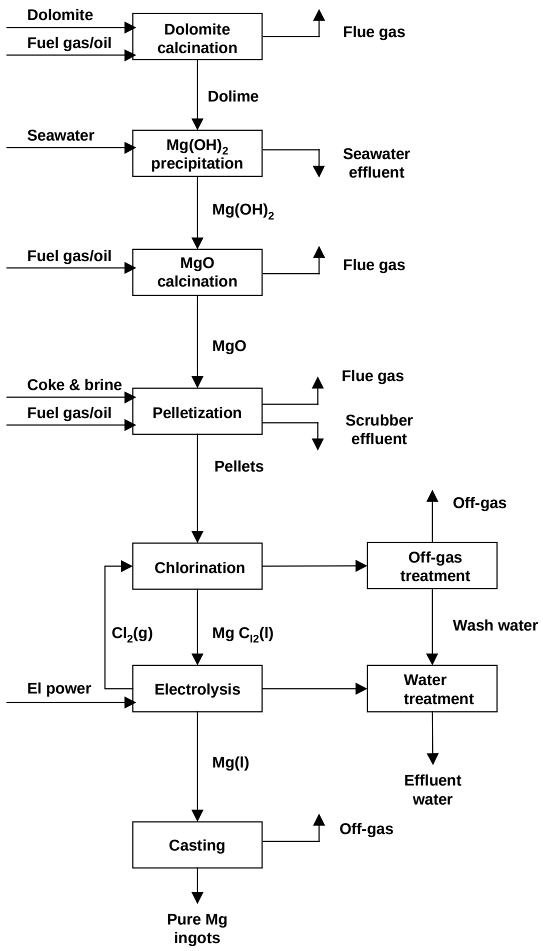


Figure 10.6: Process flow diagram of magnesium production by electrolysis

10.1.5.3 Production of magnesium from secondary raw material

Due to the increasing availability of magnesium scrap and other magnesium containing secondary raw material, the production of secondary magnesium becomes more and more important. Scrap magnesium alloys may be directly recycled in–house or sent to an external recycling facility. According to the quality, recyclable magnesium materials can be classified as follows.

Type of secondary raw material	Classification	Description
Magnesium scrap	Type 1 A	High grade clean scrap e.g. scrap castings, biscuits etc.
	Type 1 B	Clean scrap with a high surface area e.g. thin castings, flashings etc.
	Type 2	Clean scrap with steel/aluminium inserts. No copper or brass contamination. If copper or brass contaminated, the crap treated as s special case
	Type 3	Scrap castings, painted with/without inserts of steel/aluminium. No copper or brass contamination. If copper or brass contaminated, the scrap is treated as a special case
Other magnesium containing material	Type 4	Unclean metal scrap e. g. oily, wet contaminated The material may contain: • Silicon contamination e.g. tumbling, beads, sand etc. • Aluminium alloys • Copper contaminated alloys • Non magnesium sweepings
	Type 5 A	Chips, swarf machinings, which are clean, dry and uncontaminated
	Type 5 B	Chips, swarf, machinings, which are oily and/or wet
	Type 6 A	Flux free residues e.g. crucible sludge, dross etc., which should be dry and silica free (sand free)
	Type 6 B	Flux containing residues e.g. crucible sludge, dross etc., which should be dry and silica free (sand free)

Table 10.1: Definition of magnesium containing scrap and materials for recycling

A typical secondary magnesium production is shown in the next figure.

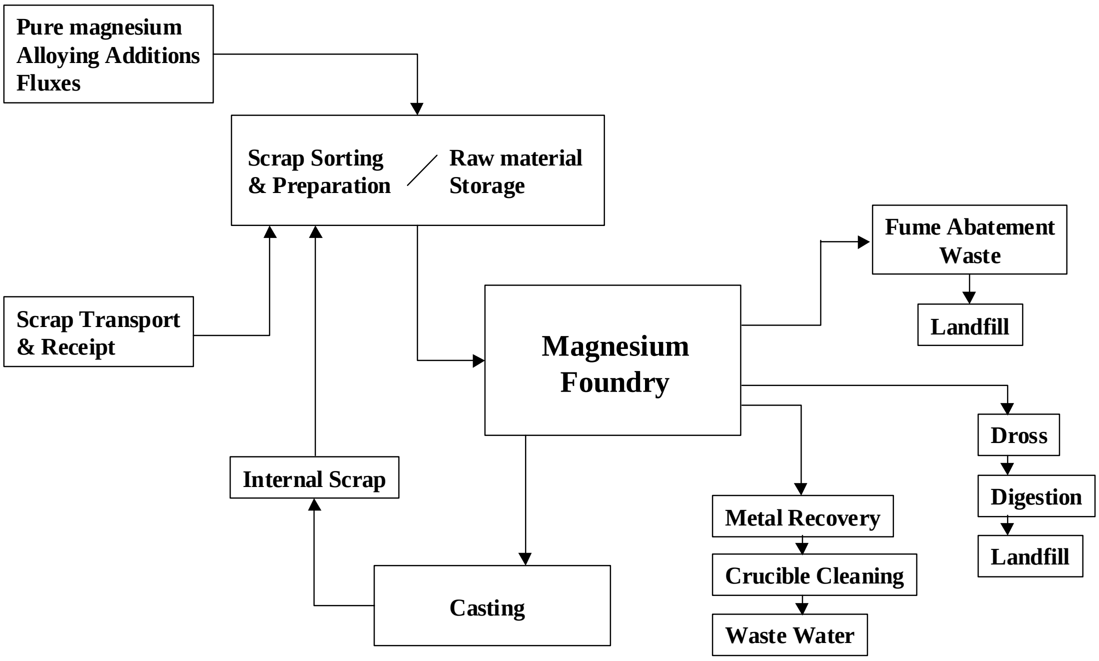


Figure 10.7: Flow sheet of a production process for secondary magnesium

The process begins with the receipt of the different secondary raw materials. After a quality control to define the type of scrap it is stored separately in order to define the most appropriate way of recycling. The sorted raw material is then send to the melting shop. Magnesium melting and alloying is carried out in indirect gas or electric furnaces. Fluxes or inert blanketing gas, sulphur hexafluoride (SF_6) may be used. The melted metal is then cast into secondary magnesium ingots of semi-finished products.

10.2 Present Emission and Consumption Levels

The production of alkali metals as well as calcium, strontium and magnesium metal causes environmental impacts to air, water and land, where the most significant releases can be classified in principle as follows.

- **Consumption of raw material and energy**
  - Raw material and energy consumption

- **Emissions to air**
  - Dust from the dolomite and the magnesium oxide calcination
  - Chlorine and HCl as part of the cell gases and the cell room ventilation
    Chlorinated hydrocarbons from the use of refrigeration and compression techniques to liquefy chlorine
  - SF_6 that is used in the casting operation to protect the molten magnesium from re-oxidation
  - Dioxins generated by the chlorination step in the electrolytic production of primary magnesium

- **Solid residues, wastes and by-products**
  - Dust, fume and sludge
  - Calcium and strontium aluminate
  -
- **Wastewater emissions**
  - Overflow water from wet scrubbing systems
  - Dioxins, because the production of magnesium in an electrolytic process generates dioxins from the chlorination step, which has to be removed from the scrubbing water.
  - Blow down from cooling water cycles

10.2.1 Consumption of raw material and energy

The required amount of energy for the production of calcium metal using the metallo-thermic process is about 20 – 25 kWh/kg of produced metal. To this direct energy is must be added the energy employed to produce the calcined CaO and electrolytically produced aluminium. The production of calcium metal by electrolysis, which is not used in Europe, requires about 33 - 55 kWh/kg of calcium metal for a current efficiency of about 60%.

The consumption of electric energy in the electrolysis of magnesium is in the range of 13 – 14 kWh/kg Mg. To this must be added the energy required for the production of magnesium chloride from the various raw materials.

10.2.2 Emissions to air

The available data of the emissions to air for the production of alkali and alkaline earth metals are presented in terms of specific emission factors that means based on a unit mass of produced product in the following sections.

Pollutant	Sodium metal		Lithium metal	
	mg/Nm^3	g/t	mg/Nm^3	g/t
Chlorine	0.1 - 1	0.05	1 - 16	18.2
HCl	n.a.	n.a.	1 - 2	103
Refrigerant R 22 (N 1)		200	n.a.	n.a.
Dust	4 - 6	120	n.a.	n.a.
Notes: (N 1) R 22 is an ODS (Ozone Depleting Substance) and targeted for phase-out. n.a. = data not available				

Table 10.2: Emission to air from the production of sodium and lithium metal

The main environmental input to the atmosphere by producing calcium and strontium metal are dust emissions. Dust may be generated by unloading and crushing the calcined lime, by mixing and compacting lime and aluminium and by grinding and screening the produced metal. Due to the baking operation that is necessary to produce strontium oxide for the production of strontium metal about 420 kg of CO_2 is generated to the atmosphere for each tonne of strontium oxide produced.

The production of magnesium metal is related to the emission of dust, SO_2, NO_X, Cl_2, HCl, dioxin and in several cases the Emission of sulphur hexafluoride (SF_6). Dust in mainly emitted from the calcination of dolime. Dioxin is generated from the chlorination furnace where magnesium oxide is converted into magnesium chloride. The emission of sulphur hexafluoride (SF_6) is due to the need to prevent the magnesium metal from re-oxidation. It should be noted that SF6 has a very high global warming potential (23900 times the effect of CO_2) and is therefore a controlled substance under the Kyoto protocol. This substance should therefore be replaced as soon possible.

Pollutant	Source and concentration mg/Nm^3	Unit mass/t of magnesium metal
Dust	From dolomite calcination 100 (N 1) From MgO calcination 16 From pellet drying 40 From chlorination off-gas treatment 3 From chlorination (vent. gas) 16	4 kg/t (representing the whole process)
SO_2	From dolomite calcination30 From MgO calcination 80 From pellet drying 30 From chlorination off-gas treatment 200 From chlorination (vent. gas) 50	7 kg/t (representing the whole process)
NO_x	From dolomite calcination 80 From MgO calcination 110 From pellet drying 50	3 kg/t (representing the whole process)
Cl_2 and HCl	From chlorination off-gas-treatment 70 From chlorination (vent. gas) 50 From electrolysis 3	4 kg/t (representing the whole process)
Dioxin	From chlorination off-gas treatment 0.8 ng/Nm^3	12 µg/t TEQ
	From chlorination (vent. gas) 0.8 ng/Nm^3	28 µg/t TEQ
	From electrolysis/chlorination (hall/ gas)	13 µg/t TEQ
CO_2	Emission from the whole process	6.3 t/t
SF_6	From the cast-house (N 2)	0.45 kg/t of cast magnesium

Notes:

(N 1) The off gas from the Gas Suspension Calciner that is used for the dolomite calcination is cleaned by using an EP

(N 2) SF_6 is used in the casting process to prevent the magnesium from re-oxidation SF_6 has a very high global warming effect (23900 times the effect of CO_2) and is therefore a controlled substance under the Kyoto protocol. This substance should therefore be replaced as soon as possible.

n.a. = data not available

Table 10.3: Emission to air by producing magnesium metal by using the chlorination-electrolytic process

Pollutant	Source	mg/Nm^3	Unit mass/t of magnesium metal
Dust	Dolomite calcining	< 100	3.5 kg/t.
CO_2		130 – 180 g/Nm^3	4.5 - 6 t/t
SO_2		0.5	0.016 kg/t
NO_x		90	3.1 kg/t
N_2O		4	0.13 kg/t
Dust	Reduction in vacuum	n.m.	0.5 kg/t (N 3)
Argon		n.m.	4.3 Nm^3/t
Hydrogen		n.m.	0.7 Nm^3/t
Dioxin	Reduction, refining and melting	0.08 ng/Nm^3	3 µg/t TEQ
SF_6	Refining and casting	n.m.	0.5 - 1 kg/t

Notes:

(N 1) SF_6 is used in the refining and casting process to prevent the magnesium from re-oxidation. SF_6 has a very high global warming effect (23900 times the effect of CO_2) and is therefore a controlled substance under the Kyoto protocol. This substance should therefore be replaced as soon as possible.

(N 2) The presented data is only bases on one single measurement

(N 3) Using a wet scrubber

n.a. = data not available n.m. = not measured

Table 10.4: Emission to air by producing magnesium metal by using the thermal reduction process

10.2.3 Typical emissions to water

For the production of alkali and alkaline metals the emissions to water are very dependent on the used process for instance the used abatement system and the type of wastewater treatment. There exist a variety of different water collection and wastewater treatments. The main water pollutants are suspended solids, metal compounds and in the case of the magnesium electrolysis also chlorinated hydrocarbons and dioxins. The production of calcium and strontium metal is not related to the generation of process specific water waters. Available information about emissions to water is presented in the following tables.

Component	Sodium metal	Lithium metal mg/l
Chlorine Total	Effluent Reused	n.a.
Suspended Solids	Effluent Reused	20 - 40

Table 10.5: Emissions to Water by producing sodium and lithium metal
[tm 106, Farrell, 1998]

Pollutant	Source	Emissions mg/Nm^{3}of water	Unit mass/t
Magnesium hydroxide	dolime slaking		21 kg/t MgO
Calcium hydroxide	dolime slaking		100 kg/t MgO
coke	pelletisation		1.6 kg/t Mg-metal
Chlorinated hydrocarbons (N 1)	water treatment	0.15	0.017 g/t Mg-metal (Total 0.053)
Dioxin	water treatment	100 ng/Nm^3	13 µg/t Mg-metal Total 33 µg/t Mg-metal (TCDD equivalents)

Notes:
(N 1) Sum of hexachlorobenzene, pentachlorbenzene and octochlorostyrene
n.a. = data not available

Table 10.6: Emission to water by producing magnesium metal using the electrolytic process

The production of secondary magnesium generates dross and crucible residues, which cannot be recycled and needs therefore be digested in water to give an inert magnesium hydroxide, with alloying elements, in the form of a hydrated sludge. Per tonne of metal about 0.5 tonnes of sludge are generated that containing approximately 50% water.

10.2.4 By-products, process residues and wastes

The production of alkali and alkaline metals is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). The most important process specific residues from the production of alkali and alkaline metals are listed below.

Metal produced	Residue	Source	Amount
Sodium	filter cake	sodium cleaning stage	n.a.
	sediment	storage tanks (N 1)	n.a.
	chlorine	produced as a by-product	1.6 t Cl/t metal
Lithium	mother liquor	crystallisation	n.a.
	used anodes	electrolytic cell	n.a.
Calcium	calcium aluminate	vacuum furnace	n.a.
	used furnace linings	vacuum furnace	n.a.
Strontium	strontium aluminate	vacuum furnace	n.a.
	used furnace linings	vacuum furnace	n.a.
Magnesium (electrolytic process)	sludge and gravel	dolime slaking	0.05 t/t MgO
	Slag	chlorination furnace	0.14 t/t metal
	dioxin containing sludge	water treatment	0.01 t/t metal
	metal containing sludge	electrolysis and cast-house	0.04 t/t metal
	dolime dust	by-product from dolomite calcination	0.28 t/t MgO
	excess electrolyte	by-product from electrolysis	0.18 t/t metal
Magnesium (thermal process)	dolomite and filter dust	dolomite and limestone screening	1 t/t metal
	Granulated slag	reduction vacuum furnace	2.5 - 3 t/t metal
	Fine dry slag		0.5 - 0.7 t/t metal
	wet slag		0.3 - 0.5 t/t metal
	slag	refining stage	0.3 t/t metal

Notes:

(N 1) Sediment from storage tanks are burnt on an open hearth and fumes are collected and scrubbed in a two-stage water scrubber discharged into a third stage using HCl, which treats also fumes from washing the filter cake

n.a. = data not available

Table 10.7: Residues by producing alkali and alkaline metals

10.3 Techniques to Consider in the Determination of BAT

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2 “common processes” apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

The raw materials handling and pre-treatment processes and the process control and abatement systems are particularly relevant. The control of electrolytic cells and furnace operating parameters and the prevention of fugitive emissions from electrolytic cells, furnaces, tapping and pouring processes are also important. Techniques used by other sectors are also applicable particularly those relating to the collection, handling and scrubbing of chlorine gas and the production of sodium hypochlorite using two scrubbers in series. These techniques are covered in the BAT Reference Document for the Chlor-Alkali Industry, which should also be referred to.

10.3.1 Materials, storage and handling

The raw materials used for the production of alkali and alkaline metals are sodium chloride, lithium and strontium carbonate etc. limestone, dolomite magnesite and reducing agents e.g. aluminium powder. The main environmental impact by storage and handling of these materials are dust emissions, which sometimes arise as fugitive dust emissions.

The raw materials are preferable stored and handled inside where closed drums, silos, bins and hoppers are used to prevent fugitive emissions to the environment as well as to the workspace. Limestone and dolomite may also the stored in stockpiles where the appropriate measures against the generation of dust should be taken.

Closed conveyors and transfer systems are used for handling of dusty fine materials, where extraction and filtration equipment is used for dusting delivery points. The dust leaden air from the silos, closed conveyors and charging systems are cleaned by using bag filters, which may be monitored by measuring the pressure drop to control the cleaning mechanism. Some plants use crushers or agglomeration and pelletisation equipment to obtain the desired size of charging material. Bag filters clean the suction air of crushers and agglomeration equipment.

10.3.2 Pre-treatment techniques

The production of magnesium metal is partly based on calcined dolomite and magnesite as a raw material. The calcination may be made in rotary or vertical furnaces. Different fuels, for instance natural gas, can heat the furnaces. A new technology used for calcining dolomite is the Gas Suspension Calcining (GSC) which is presented in the following example.

EXAMPLE 10.01 GAS SUSPENSION-CALCINING PROCESS FOR DOLOMITE AND MAGNESITE CALCINING AS A PRE-TREATMENT PROCESS BY PRODUCING MAGNESIUM METAL

Description: - The GSC process consists of several process stages. The first stage is drying the dolomite in a flash drier using the hot exit gases from the GSC plant. The dry material is than crushed in a special cone crusher. The pulverised feed is injected into the riser between tie second and the first pre-heater cyclone. On entering the riser duct, the material initially falls counter-current to the hot gas stream. After being preheated in the forth cyclone the material has reached calcining temperature and is directed to the calciner where complete calcination takes place. The calciner is basically a vertical cylinder where air, fuel and material enter at the bottom and exhaust gases carrying calcined material leave at the top. The calcined particles are carried by the gas stream to a disengaging cyclone from which the hot gases pass to the pre-heater while the product is discharged by the force of gravity to the cooler. The process is controlled by a high standard computerised instrumentation and control system.

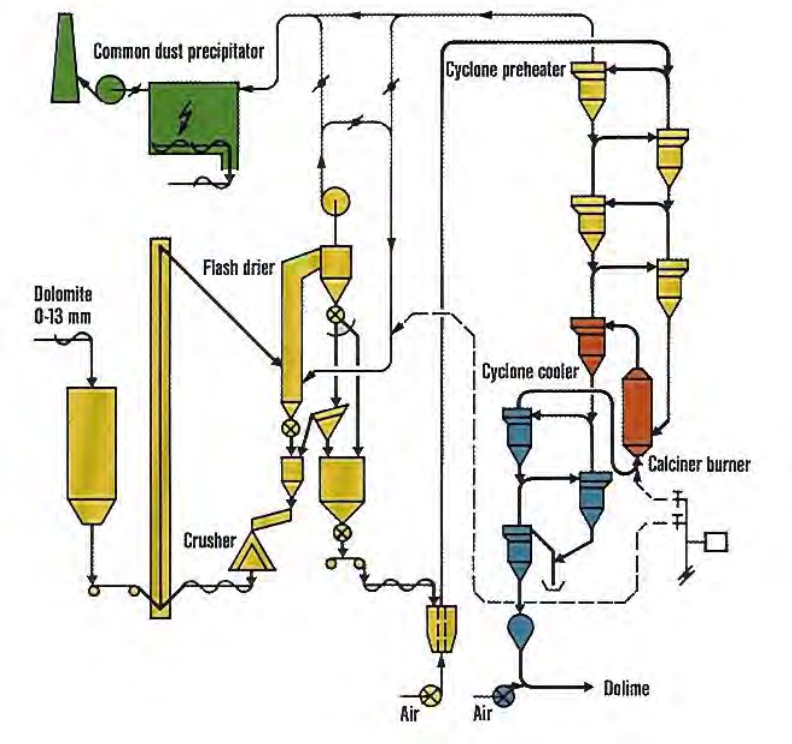


Figure 10.8: Gas Suspension calciner

Main environmental benefits: - Reduction of fuel consumption compared to other system, due to the intensive use of product and off-gas heat energy.

Operational data:

Fuel consumption	1145 kcal//kg
Power consumption	33 kWh/t product

The emission level of dust using an EP is less then 30mg/Nm^3

Cross media effects: - No cross media effects

Economics: - The GSC process has lower operating costs than other systems

Applicability: - Applicable to new and existing plants (also of other production processes where calcination takes place e.g. in the lime production).

Reference literature: [tm 150, F.L. Schmidt 1992]

10.3.3 Core processes

The most important part of the alkali and alkaline earth metal production is the electrolytic cell for the electrolytic production and the vacuum furnace used for the thermal reduction process. According the small number of producers and subsequently the small number of operated plants in the EU and world-wide, the techniques presented as applied techniques are also techniques considered in the determination of BAT.

All electrolytic magnesium is produced by electrolysis of magnesium chloride, in most cases water-free (anhydrous) chloride. Thus, there are two core steps in the process:

- The production of anhydrous magnesium chloride from raw materials, and
- The electrolysis of the magnesium chloride.

There are a number of processes for the preparation of anhydrous chloride. The following example gives the description of a recently be developed and successfully implemented "Dehydration process"

EXAMPLE 10.02 PRIMARY MAGNESIUM PRODUCTION USING THE DEHYDRATION PROCESS

General description: The $MgCl_2$ brine dehydration process developed by Norsk Hydro has been implemented in the Norsk Hydro Canada plant started up in 1989. The process is described in the following and illustrated in the enclosed block diagram.

The $MgCl_2$ brine dehydration plant: The plant produces $MgC1_2$ brine by dissolving magnesite rock in hydrochloric acid (HCl). After purification to remove dissolved impurities as iron and aluminium, the brine is subjected to evaporation and particulation to create a granular material ("prilis") suitable for fluidised bed drying techniques. The prills are subsequently dried in two stages, first by hot air and then by HCl gas, to produce an essentially anhydrous $MgCl_2$ product.

Electrolysis and HCl synthesis: The high-amperage electrolysis cells of Hydro design are operated at around 400 kA. They are fed on a continuous basis with anhydrous $MgCl_2$ prills from the dehydration plant. Liquid Mg metal is withdrawn from the cells intermittently and transported in closed vessels to the casthouse.

The chlorine gas formed in the electrolysis process is recycled by reaction with hydrogen to produce the hydrochloric acid used in the magnesite dissolving stage. Energy is recovered from this HCl synthesis stage in the form of steam generated.

Refining, alloying and casting: In the casthouse, the magnesium metal is refined, alloyed and cast into ingot products.

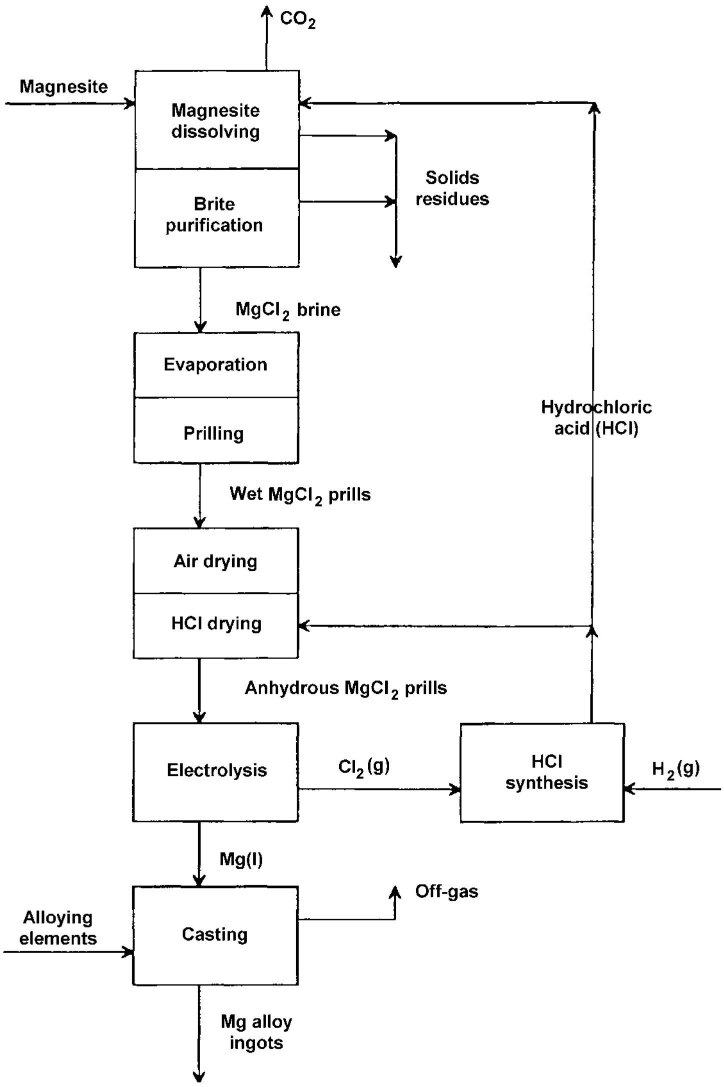


Figure 10.9: Block diagram for the dehydration process for primary magnesium production

Environmental performance: The following typical environmental performance data have been achieved:

Air emissions:

Dust	0.4	kg/t Mg
SO_2	< 0.2	"
NOx	2	..."
Cl_2 + HCl	< 1	..."
SF_6	0.5	..."
Dioxins[1]	< 1 0	µg/t Mg

Water emissions:

Chlorinated Hydrocarbons[2]	< 0.01	g/t Mg
Dioxins[1]	< 0.1	µg/t Mg

[1] Sum of PCDDs and PCDFs expressed as TCDD-equivalents.

[2] Sum of hexa- and penta-chlorobenzene and octachlorostyrene.

Applicability: New plants

10.3.4 Gas collection and abatement

The techniques for fume collection and abatement discussed in Chapter 2 of this document are techniques to consider for the production of alkali and alkaline metals. Bag filter and wet scrubbers, also multi-stage scrubbers are normally used for the off-gas cleaning. The ventilation air from a cell-room where sodium metal is produced can be extracted by using a two-stage venturi-scrubber and a packed tower using caustic soda to remove chlorine.

As can be shown in the next example, the off-gas from the chlorination furnace in a magnesium production is cleaned in a series of wet scrubbers and wet electrostatic precipitators before being finally subjected to incineration in an afterburner. The chlorine gas formed by the magnesium electrolysis is cleaned in a bag filter in order to remove entrained salts before recycled back to the chlorination stage.

EXAMPLE 10.03 TREATMENT OF OFF-GASES CONTAINING DIOXINS AND CHLORINATED HYDROCARBONS

Description:

General description: - Off-gases from the chlorination furnaces in the magnesium plant contain Cl_2 and HCl, and also dioxins and chlorinated hydrocarbons (CHC’s). The off-gases are treated in a series of wet scrubbers to remove the Cl_2 and HCl, and then wet electrostatic precipitators to remove aerosols from the gas, before finally being subjected to incineration. SO_2 gas is added to the off-gases between scrubbing stages to convert Cl_2 to HCl and thereby enhance the efficiency of the scrubbing. Water from the off-gas treatment is transferred to a water treatment plant.

The incineration plant: - The off-gases after scrubbing still contain unacceptable amounts of dioxins and CHC’s. They are therefore subjected to a final incineration treatment, where volatile organic compounds including dioxins and CHC’s are destroyed.

The incineration plant has 5 vertical chambers filled with ceramic stoneware for heat exchange, being switched by flow control valves to achieve effective heat recuperation. In-coming gas is led through chambers in "inlet" model and heated to reaction temperature before entering the horizontal combustion chamber on top of the chambers. In the combustion chamber the CO content of the gas (approx. 1 - 2%) is burned together with fuel gas supplied through three gas burners to keep the temperature in the combustion chamber above 800 ºC.

The treated gas is then led through chambers in "outlet" mode to recover its heat content for heating in-coming gas after switching of chambers. Treated gas is then vented to the stack.

Main environmental benefits: Significant reduction of chlorinated-hydrocarbons and dioxins. Recovery of the heat energy that is generated in the combustion chamber of the incineration plant.

Destruction efficiencies achieved:

Chlorinated hydrocarbons	99.9% (total efficiency)
Dioxins	99.9% (total efficiency)
CO	100%

Outlet concentrations:

Chlorinated hydrocarbons	0.01 mg/Nm^3
Dioxins	0.8 ng/Nm^3

Chlorinated hydrocarbons as sum of hexa- and penta-chlorobenzene and octachlorostyrene.
Dioxins as sum of PCDDs and PCDFs expressed as TCDD equivalents.

Operational data for the incineration plant:

Volumetric capacity:	70000 Nm^3/h
Combustion chamber temperature:	Above 800 ºC
Residence time in combustion chamber:	Minimum 2 seconds

Energy consumption (external):

Fuel gas	30000 GJ/a

Cross media effects:- In the scrubbers the dioxins and chlorinated hydrocarbons are transferred from the air to the water side, therefore an additional water-treatment is needed.

Economics: - Not available

Applicability: - To all new and existing plants

Reference literature: [tm 203, Hydro Magnesium,1999]

10.3.5 Process control

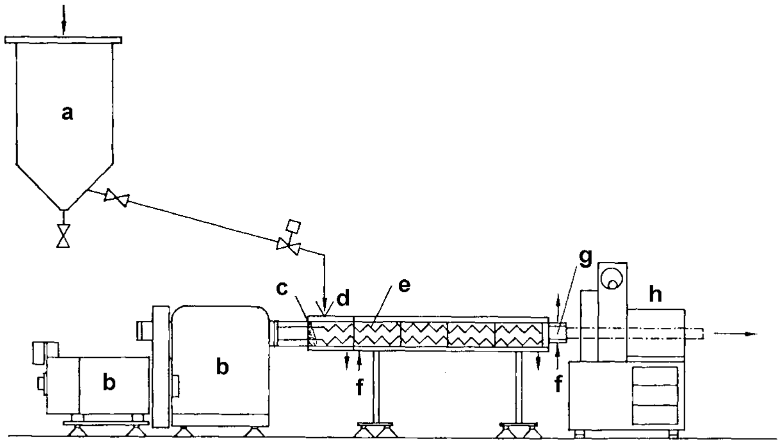
The principles of process control discussed in Chapter 2 are applicable to the production processes used in this Group. Computerised control techniques can be used for most of the process stages and different production routes.

10.3.6 Post furnace operations

Alkali and alkaline metals are often sold in ingots, which is the case for magnesium or in shaped pieces of different sizes. Metal ingots are made by casting the liquid metal into moulds where the metal need to be prevented from re-oxidation. Alkali metals such as sodium is also pressed is metal billets.

EXAMPLE 10.04 EXTRUSION PLANT FOR THE PRODUCTION OF SODIUM METAL BILLETS

Description: - The metal is feed into a twin screw extruder, which is cooled in a way that the temperature falls slightly below the melting point just before the extrusion die. The sodium metal billets produced can be cut by automatic cutting device under a protective gas.



a) Sodium storage tank, heated; b) Drive; c) Sealing layer of sodium; d) Feeding nozzle;
e) Twin-screw extruder; f) Heating and cooling jacket; g) Extrusion die; h) Cutting machine

Figure 10.10: Schematic of an extrusion plant for the production of alkali-metal billets

Main environmental benefits: - The formation of impurities by reaction with air and atmospheric moisture is avoided

Operational data: - Not available

Cross media effects: - No reaction with air and atmospheric moisture

Economics: - Not available

Applicability: - All new and existing plants

Reference literature: - [tm 107, Ullmanns, 1996]

10.3.7 Water treatment

This is a site-specific issue, existing treatment systems are reported to be to a high standard. All wastewater should be treated to remove dissolved metals and solids as well as dioxins and chlorinated hydrocarbons. The removal of dioxins and chlorinated hydrocarbons from scrubbing water is necessary. Therefore the following example is presenting an example of a wastewater treatment plant that reduces dioxins and chlorinated hydrocarbons from scrubbing water.

EXAMPLE 10.05 TREATMENT OF WASTEWATER CONTAINING DIOXINS AND CHLORINATED HYDROCARBONS

Description: - Contaminated wastewater streams from various parts of the magnesium plant, including water from the chlorination off-gas treatment, are treated in a wastewater treatment plant to reduce the contents of dioxins and chlorinated hydrocarbons by more than 99%.

The water treatment plant: - The wastewater treatment plant that is shown in the next figure is based on three different unit operations

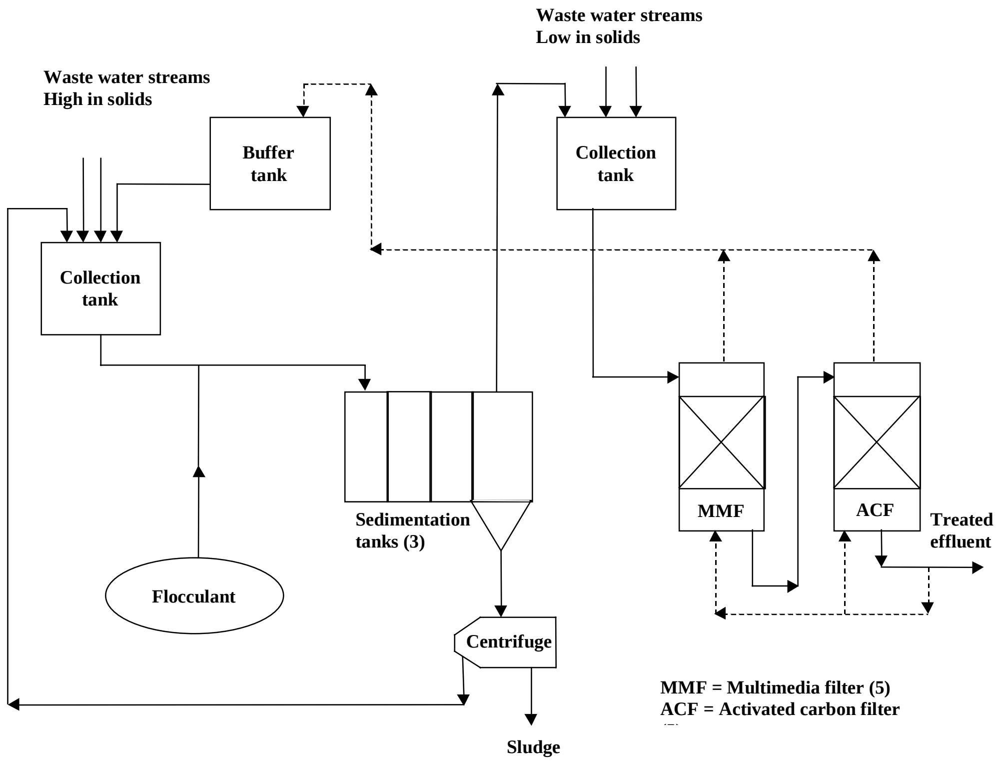


Figure 10.11: Treatment plant for cleaning dioxin and chlorinated hydrocarbon contaminated wastewater

Wastewater streams with high concentrations of solid particles are collected and the solids separated by use of flocculation and sedimentation. The sludge from the sedimentation units is de-watered in a centrifuge to a water content of approx. 50%. The solids from the water treatment, containing dioxins and chlorinated hydrocarbons, are incinerated off-site.

The larger volume of wastewater streams with low solid particle concentrations are treated in multimedia filters (sand filters), removing particles down to 1 um. Solids are periodically washed back to the sedimentation units.

The last step in the treatment process is polishing on activated carbon. Small particles and the water-soluble part of dioxins and chlorinated hydrocarbons are adsorbed on activated carbon. The carbon is replaced periodically, and used carbon is incinerated off-site.

The wastewater treatment plant is an integrated part of the chlorination plant. The plant is operated from a central control room with no extra operators needed. Periodical work is related to sludge handling, maintenance and replacement of the activated carbon.

Main environmental benefits:

Efficiencies achieved:

Chlorinated hydrocarbons	99.5% or better
Dioxins	99.5% or better

Water outlet concentrations:

Chlorinated hydrocarbons	0.15 mg/Nm^3 of water
Dioxins	100 ng/m^3 of water

Chlorinated hydrocarbons as the sum of hexa- and penta-chlorobenzene and octachlorostyrene. Dioxins as the sum of PCDDs and PCDFs expressed as TCDD equivalents.

Operational data:

For the water treatment plant

Volumetric capacity:	600 m^3/h
Materials of construction allow acidic wastewater to be treated at a pH as low as 1.5	
Sludge generated:	Approx. 350 t/a (50% water)

Cross media effects: - The sludge from the wastewater treatment plant needs to be incinerated, which again produce emissions to air and soil.

Economics: - Not available

Applicability: - To all new and existing plants

Reference literature: - [tm 204, Hydro Magnesium 1999]

The techniques listed in Chapter 2 are the techniques to consider. In a number of installations cooling water and treated wastewater including rainwater is reused or recycled within the processes.

10.3.8 Reduction of process residues

The processes that were discussed earlier as applied techniques involved in the section of present emission and consumption levels are all techniques to consider in the determination of BAT. The most important factor to reduce the environmental impact of discharging residues as waste are process-integrated measures that result in the generation of fewer residues. If the amount of process residues is minimised by using primary measures, the extended amount should be recycled or reused as much as possible. The specific feed materials will influence the final process choice. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes.

10.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector; which are for the production of alkali and alkaline earth metals, chlorine, HCl, dioxin, SF_6, dust fume, CO_2, SO_2, wastewater, residues such as sludge, aluminate, filter dust and slag;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous section. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this section are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

10.4.1 Materials storage and handling

The conclusion drawn for Best Available Techniques for the materials handling and storage are shown in section 2.17 of this document are applicable to the materials in this chapter.

10.4.2 Process selection

10.4.2.1 Pre-treatment techniques

The techniques presented in Chapter 2 for pre-processing of raw materials will partly be BAT for this sector. Where a calcination process is needed for the raw material preparation e.g. for dolomite calcining, the gas suspension calciner technique (GSC) is advantageously used. The associated emission level for dust is less then 30 mg/Nm^3 if the dust-laden off-gas from the calciner is cleaned by using an EP and 5 mg/Nm^3 by using a bag filter. Due to high investment costs for the installation of such a calciner system, the plant used to be a certain production capacity.

10.4.2.2 Core processes

According to the different alkali and alkaline metals produced, the environmental impact of the production is widely be influenced by the used metallurgical process. According to the produced metals, the following metallurgical processes are used in the industry and considered to be BAT for this sector.

Produced metal	Process	Production unit	Abatement technique	Remarks and considerations
Sodium	electrolysis of fused sodium chloride	electrolytic cell (Downs cell)	wet scrubber for cleaning the cell room air	• The possible associated level of chlorine in the ventilation air is less than 1mg/Nm^3. • Chlorine alarms should be deployed in the cell room and in the chlorine processing plant.
Lithium	electrolysis of lithium and potassium chloride	electrolytic cell (Downs cell)	wet scrubber for cleaning the cell room air	• The possible associated level of chlorine in the ventilation air is less than 1 mg/Nm^3 • Chlorine produced by the cell room is collected by partial vacuum and then absorbed in caustic soda to produce sodium hypochlorite. • Chlorine alarms should be deployed in the cell room.
Potassium	reduction of potassium chloride with sodium metal	reaction column	wet scrubber	• There are no information about a plant producing potassium metal in the EU available
Calcium	thermal reduction of calcium oxide with aluminium	electrically heated vacuum furnace		• The metal is condensed in the cooled part of the furnace • There are no significant emissions from the furnace operation
Strontium	thermal reduction of strontium oxide with aluminium	electrically heated vacuum furnace		• The metal is condensed in the cooled part of the furnace • There are no significant emissions from the furnace operation
Magnesium	Chlorination of magnesium oxide	Chlorinator shaft furnace	Multi-stage wet scrubber connected with an EP and an afterburner. The process may be combined with injection of activated carbon	• The process of chlorination can no longer be regarded as BAT for new plants producing magnesium by electrolysis •
	$MgCl_2$ brine dehydration	evaporation/prilling		• Dioxin emissions are < 10 µg/t TEQ instead of 53 µg/t TEQ for the process which needs a chlorination step. The $MgCl_2$ brine dehydration process is therefore regarded as BAT for new plants.
	electrolysis of magnesium chloride (N 1)	high-amperage electrolysis cell	bag filter to clean the chlorine gas formed by the electrolysis, which is then recycled to the chlorination stage	• The cell is operated in the rang of 300 - 400 kA • The cell is fed with liquid magnesium chloride on an intermittent basis or with solid magnesium chloride on a continuous basis . • Liquid magnesium metal is withdrawn from the cell intermittently • The amount of SF_6 used in the cast-house should be reduced as much as possible, and replaced by a less harmful substance as soon as possible (N1)
	thermal reduction of magnesium oxide by silicon	electrically heated vacuum furnace	EP and (wet) bag filter	• The possible associated level of dust using an EP is 20 - 30mg/Nm^3 • The amount of SF_6 used in the cast-house should be reduced as much as possible, and replaced by a less harmful substance when it is possible (N1)

Notes:
(N 1) Due to the high global warming potential of SF_6, it has been reported that the use of sulphur dioxide might be an alternative.

Table 10.8: Production units considered as BAT for the production of alkali and alkaline metals

10.4.2.3 Process control

The techniques presented in the different sections of Chapter 2 describing possibilities to control the process by computerised systems will be part of BAT for this sector. The most important are considered being.

- Electrolytic cell operation control to optimise operating conditions. Key parameters are cell voltage, pH-value and temperature.
- Vacuum furnace operation control to optimise operating conditions. Key parameters are pressure and temperature at various points in the furnace and gas handling system, oxygen and carbon monoxide or carbon dioxide concentrations and system pressure.
- Process control using relevant methods so that it is possible to maintain operating conditions at the optimum level and to provide alarms for conditions that are outside the acceptable operating range.
- Plant operators should be trained and given instructions about the correct operating procedures and control parameters.
- Use of good maintenance practice for process plants, abatement systems and other associated processes. A system of inspection should be adopted.
- To reduce fire hazards, fire detectors should be installed.

10.4.2.4 Post furnace operations

The techniques presented as technique to be considered in the determination of BAT are also techniques that are considered as BAT in this sector. According to the normally used post furnace operations, like casting, grinding and screening BAT is defined as follows.

- Due to the very high global warming effect of SF_6 (factor 23900 higher than CO_2), the amount of SF_6 used in the cast-house should be reduced as much as possible, and replaced by a less harmful substance as soon as it is possible.
- The different steps of grinding and screening may be closed and maintained in a pressure lightly lower than outside.
- The crushing and screening installations may be equipped with cyclones and bag filters to recuperate the ultrafines.
- The ultrafines of calcium and strontium metal may be destroyed with water to avoid fire hazards. The final product will then be a small quantity of lime.
- To reduce fire hazards, the different steps of grinding and screening should be fire isolated one from the other.
- To prevent the propagation of fire by the storage of calcium, inert material or fire safe walls may separate the different parts of the stock.
- Nitrogen bay is injected in case of fire detection.

10.4.3 Gas collection and abatement

The techniques presented in Chapter 2 for off-gas collection techniques as well as air abatement techniques will be part of BAT for this sector. According to the techniques to consider that are presented for air abatement, BAT for this sector is considered as follows.

- Bag filters are suitable for cleaning the suction air from raw material storage and handling devices. The associated level of residual particulate matter concentration for a bag filter is less than 5 mg/Nm^3. It should be noted that a bag filter could achieve very low levels of dust, which is dependent on the used filter medium. If special cases (e.g. health and safety conditions) require very low dust emissions, this can be achieved by using the appropriate membrane filter bags.

- An EP or fabric filter may clean the off-gas from a calciner, where the associated dust emission levels are in the range between 20 - 30 mg/Nm^3 for an EP and 5 mg/Nm^3 for a bag filter.
- The cell room air ("stife") needs to be cleaned in order to minimise the environmental input of Chlorine and HCl. Multi stage venturi scrubbers with subsequently a packed tower using caustic soda is suitable to remove chlorine. The associated level of chlorine is less than 1 mg/Nm^3.
- The off-gas from the chlorination furnaces is cleaned in multi-stage scrubbers connected with a wet EP and an afterburner in order to reduce dioxin and chlorinated hydrocarbon emissions to air. The total efficiency of the combination for abatement techniques should be 99.9%. To achieve lower dioxin-concentrations in the off-gas, an additional injection of activated carbon may be considered. The effluent from the scrubber and the wet EP needs to be treated in order to minimise the dioxin and chlorinated hydrocarbon emissions to water.

The following table summarises the captured emission associated with the use of best available technique and the techniques that can be used to reach these levels.

Pollutant	Emissions associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	< 5 mg/Nm^3	Fabric filter	Fabric filters are normally used for dedusting off-gases
	< 20 - 30 mg/Nm^3	EP	Cleaning the off-gas from a dolomite calciner used in the production of magnesium metal
Heavy metals		Fabric filter	High performance fabric filters (e.g. membrane fabric filters) can achieve low levels of heavy metals. The concentration of heavy metals is linked to the concentration of dust and the proportion of the metals as part of the dust.
Cl	< 1 mg/Nm^3	Multi stage venturi scrubbers with subsequently a packed tower using caustic soda	For cleaning the cell-room air
Dioxins and hydrocarbons from the chlorination in the Mg production	Total destruction efficiency > 99.9%	Multi-stage scrubbers connected with a wet EP and an afterburner	Dioxin emissions are < 10 µg/t TEQ for the $MgCl_2$ brine dehydration process instead of 53 µg/t TEQ for the process which needs a chlorination step. The $MgCl_2$ brine dehydration process is therefore regarded as BAT for new plants.

Note. Collected emissions only.
Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period.
For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.

Table 10.9: Emission levels to air associated with the use of BAT

10.4.4 Wastewater

The techniques presented in Chapter 2 for effluent treatment and water reuse will be part of BAT for this sector. According to the techniques to consider that are presented for water treatment, BAT for this sector is considered as follows:

- By producing magnesium metal, the scrubbing effluent from the chlorination stage should be treated in order to minimise the emissions of dioxin and chlorinated hydrocarbons to water by using a flocculation and solids separation and subsequently a second treatment stage by activated carbon.
- Closed water cycles are suitable for wet scrubbers, cooling systems and granulation presses.
- The bleed from closed water cycles needs to be treated to remove particulate matter and metal compounds from the water.
- Treated waste waster should be recycled and reused as much as possible
- Scrubbing liquids should also be treated and analysed before discharge.
- Containment of plant drainage systems where possible and treatment of effluents according to their content with analysis before discharge.

10.4.5 Process residues

The techniques presented in Chapter 2 for waste minimisation will be part of BAT for this sector and should therefore be taken into account in order to chose the technique or way operating the installation which results in the lowest environmental impact. The most important factor to reduce the environmental impact of discharging residues as waste are process-integrated measures that result in the generation of fewer residues. If the amount of process residues is minimised by using primary measures, the extended amount should be recycled or reused as much as possible.

According to the processes that were defined as applied techniques the following ways of utilisation, recycling and reuse are considered as BAT for this sector: The used process and the specific feed materials will influence the final process choice.

Metal produced	Residue	Utilisation, recycling and reuse
Sodium	Filter cake	• The filter cake is de-watered and then subject to incineration
	Sediment	• The sediment is de-watered and then subject to incineration
	Chlorine	• Chlorine can be sold as a by-product
Lithium	Mother liquor	• Mother liquor from crystallisation can be recycled
	Used anodes	• No information on utilisation etc, available
Calcium	Calcium aluminate	• Calcium aluminate can be used in the Bayer-process to make alumina. • It can also be used in the steel metallurgy and in the cement industry.
	Used furnace linings	• Furnace linings are high alumina bricks, which can be sold, where they can be grind and reused.
Strontium	Strontium aluminate	• Strontium aluminate can be used in the Bayer-process to make alumina. • It can also be used in the steel metallurgy and in the cement industry.
	Used furnace linings	• Furnace linings are high alumina bricks, which can be sold, where they can be grind and reused.
Magnesium (electrolytic process)	Sludge and gravel	• No information on utilisation etc, available, but a reuse in the construction industry might be possible.
	Slag	• No information on utilisation etc, available, but a reuse in the construction industry might be possible.
	Dioxin containing sludge	• Dioxin containing sludge can be incinerated where the dioxin emissions should be minimised be taking the appropriate measures
	Metal containing sludge	• Metal containing sludge can be sending for metal recovery.
	Dolime dust	• Dolime dust is a by-product and can be used in the fertiliser industry.
	Excess electrolyte	• Can be used as road salt.
Magnesium (thermal process)	Dolomite and filter dust	• Dolomite and filter dust may partly be used for agriculture uses.
	Slag from the furnace	• Slag from the furnace can partly be used in roads substratum. • Very fine slag that remains in the chill can be reused as a ladle cover in the steel industry.
	Slag from refining	• No information on utilisation etc, available, but a reuse in the construction industry might be possible.

Table 10.10: Utilisation, recycling and reuse of residues by producing alkali and alkaline metals

10.5 Emerging Technologies

The processes for the production of alkali and alkaline metals are sometimes developed directly the company who uses the processes, therefore information on emerging techniques are very limited. Research has been done in order to build large electrolytic cells for the production of lithium and sodium metal as well as the process control systems, which should reduce the high labour costs and increase the productivity.

11 PROCESSES TO PRODUCE NICKEL AND COBALT

11.1 Applied Processes and Techniques

Nickel is produced from oxidic (laterite and saprolite) or sulphidic ore, about 60% of the nickel comes from sulphide deposits and 40% from oxide deposits. There are several variations in the processes used to produce nickel from these ores and these variations are dependent on the grade of the concentrate and also on the other metals that are present in the material [tm 94, Ni Expert Group 1998].

Cobalt is usually present in nickel and copper ores and is recovered during their production. Refining of the recovered Co containing by-product is performed by a combination of processes governed by the composition of the concentrate and the physical and chemical characteristics of the final product. Cobalt arsenide ores are also sources of cobalt. These ores are roasted to remove the majority of arsenic as arsenic oxide [tm 108, Ullmanns 1996]. The process however is not used in EU.

Ore	Type	Ni%	Cu%	Co%
Murrin Murrin	Laterite	1.25		0.08
Cawse	Laterite	1		0.07
Cerro Matoso	Laterite	2.89		
Selebi-Phikwe	Sulphide	0.65	0.75	0.06
Falconbridge, Sudbury	Sulphide	1.7	1.8	0.05
Falconbridge, Raglan	Sulphide	3.2	0.9	0.05
INCO, Copper Cliff	Sulphide	1.55	2	0.04
Outokumpu, Silver Swan	Sulphide	9.8		0.11
Mount Keith	Sulphide	0.6	0	0.01

Table 11.1: Composition of some ores

Secondary nickel and cobalt are consumed directly in the form of remelted scrap and other recycled products generally in the production of ferro-nickel and stainless steel [tm 94, Ni Expert Group 1998]. Other secondary materials such as catalysts and precipitator dusts are recovered in the primary smelting processes, usually in the slag furnace.

Because these metals are so closely associated their production processes are dealt with together as far as possible [tm 94, Ni Expert Group 1998].

11.1.1 Oxidic ores

In laterite ores nickel is bound with iron oxide or silica compounds and is difficult to upgrade to a concentrate. Smelting of these ores with a source of carbon in an electric furnace can be used. Ferronickel is produced or a nickel matte can be made after the addition of sulphur.

Prior to smelting the ore is usually pre-heated or calcined in a rotary kiln [tm 109, UNEP 1993]. An electric furnace is then usually used for smelting.

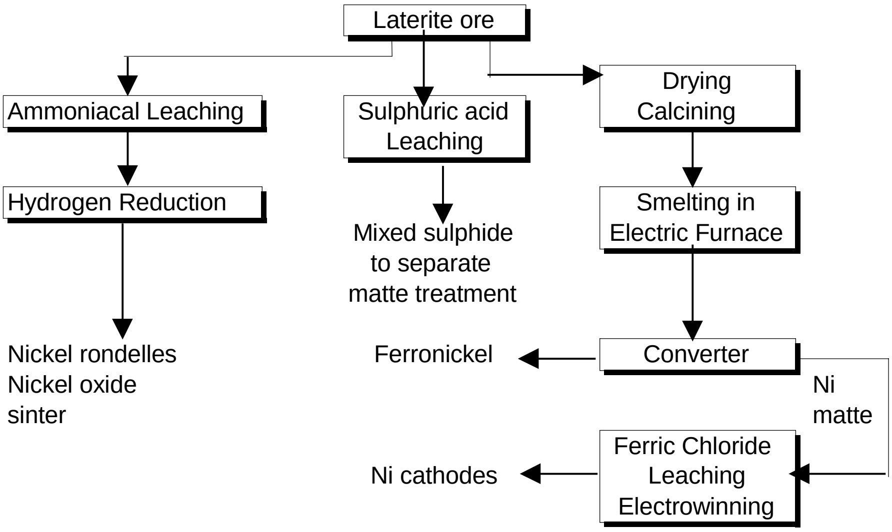


Figure 11.1: Generic flow sheet for nickel production from Laterite ores

Saprolite ores can be smelted with sulphur so that the nickel oxide is converted to a nickel sulphide matte and iron is removed as a slag [tm 109, UNEP 1993]. The matte is treated in the same manner as matte produced from sulphide ores.

Smelting to ferronickel accounts for a large proportion of nickel production from laterite ores, these processes are discussed under ferro-alloys. Leaching of laterite with ammonia is also used to extract nickel [tm 20, HMIP Ni 1993; tm 57, Outokumpu 1997; tm 96, Outokumpu 1998] and this process is becoming more important. Although conversion of nickel oxide to impure nickel and then to nickel carbonyl, which is volatile, is used to produce refined nickel, the nickel oxide is produced from the smelting of a sulphidic ore. The laterite ores generally have a maximum nickel content of 3% and are therefore not used directly in this process.

The pressure leaching of laterites with sulphuric acid is principally a simple and straightforward process. The temperature, pressure and other parameters may vary from case to case to achieve the best possible metallurgical conditions depending on the ore and products in question and other objectives. The temperature of the leaching autoclaves is usually between 230 and 260° C and pressures up to 43 bar are used. Oxygen can also be used in the process.

The resultant solution is purified either by modern solvent extraction methods or by traditional precipitation methods. For example hydrogen sulphide is used to selectively precipitate nickel and cobalt sulphides which are sent for further metal recovery. The solution can be neutralised so that iron precipitates. Nickel and cobalt will be precipitated and re- leached with ammonia.

Solvent extraction is used to separate nickel and cobalt chlorides or sulphates. Metallic nickel can be produced by electro-winning and cobalt can be precipitated as cobalt sulphide. Alternatively nickel and cobalt can be recovered as metal powders using hydrogen reduction.

11.1.2 Sulphidic ores

Nickel-bearing sulphide ores can be concentrated e.g. by flotation to upgrade the nickel content. Nickel concentrates, generally containing 7 - 25% Ni, are produced which makes further processing easier. The nickel concentrates are usually smelted under oxidising conditions to oxidise the iron sulphides, which with other gangue materials forms an iron silicate slag. The

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Outukumpu flash furnace is used in Europe; the Outukumpu and INCO Flash Furnaces and electric or shaft furnaces are used elsewhere in the World.

The nickel is recovered into a sulphide matte containing 35 - 70% Ni, Co and Cu. The matte can be treated in a Pierce Smith Converter or alternatively it can be granulated or cooled slowly before a hydrometallurgical recovery stage [tm 142, Finland N1 1999]. The converter stage is not used in Europe at the time of writing.

Important components of the nickel mattes are cobalt, copper and precious metals. The slag produced during smelting also contains recoverable metal and is treated in an electric furnace to produce more nickel matte. This can be granulated and treated separately [tm 94, Ni Expert Group 1998; tm 96, Outokumpu 1998]. Secondary materials are sometimes recovered in the electric furnace.

The following figure gives an overview of the process options.

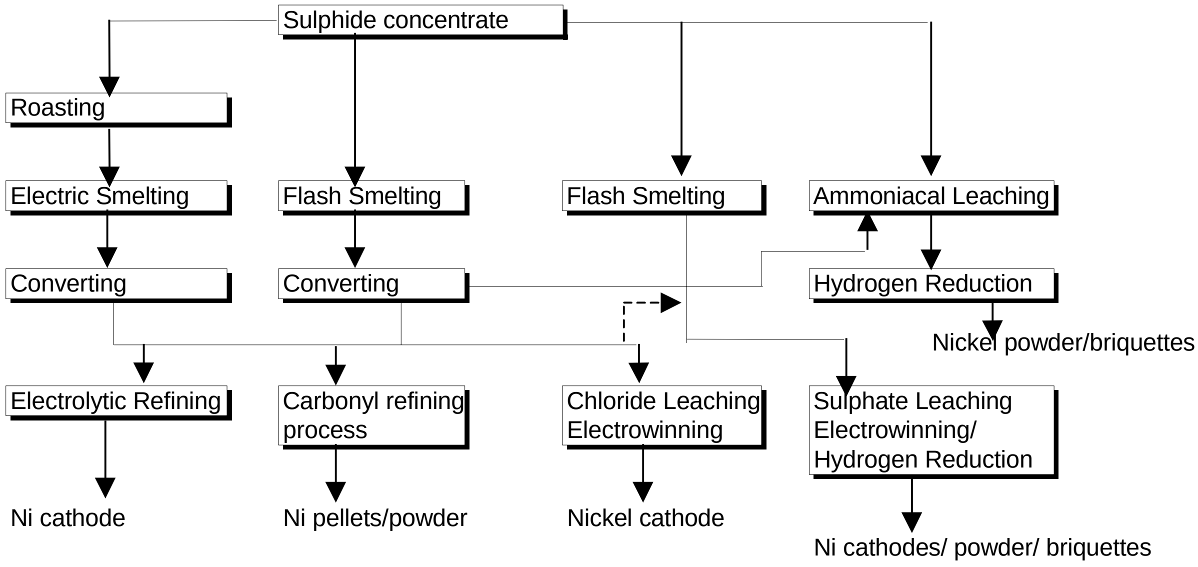


Figure 11.2: Generic flow sheet for the production of nickel from sulphide concentrates

11.1.2.1 Conventional flash smelting process

Conventional smelting processes are used to remove iron and other gangue materials from sulphide concentrates to produce nickel matte. In Europe only the Outokumpu Flash Smelting furnace is used.

Worldwide there are five other smelters, which use this process. Two of these use a flash smelting furnace designed by Western Mining Corporation, where the smelting and slag cleaning furnaces have been built together to form one larger unit.

There are differences in operations between the smelters. The most visible difference is the matte grade but variations in the raw material composition also cause some differences. The generic flow sheet is shown below.

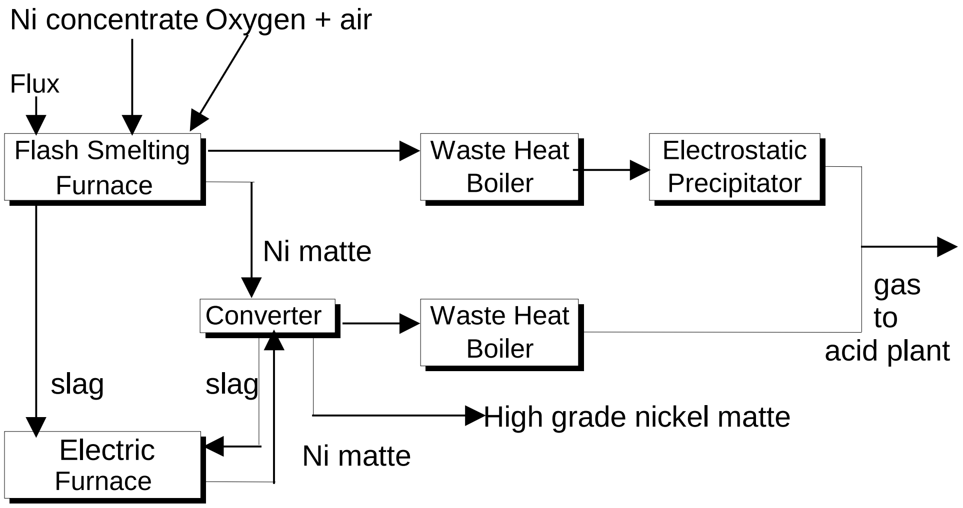


Figure 11.3: Conventional flash smelting

More recent process developments have exploited the concept of separate treatment of the mattes that are produced during smelting and slag treatment stages.

The Direct Outokumpu Nickel process (DON process) uses an Outokumpu flash furnace with oxygen enriched air and produces a copper- nickel matte with a metal content of ~75% Cu+Ni and 2 - 6% iron. The matte is granulated and ground before passing to the leaching stage. The slag passes by launder to an electric slag-cleaning furnace where it is treated with coke to produce more nickel matte and a cleaned slag for disposal. The two mattes have different compositions and are treated separately.

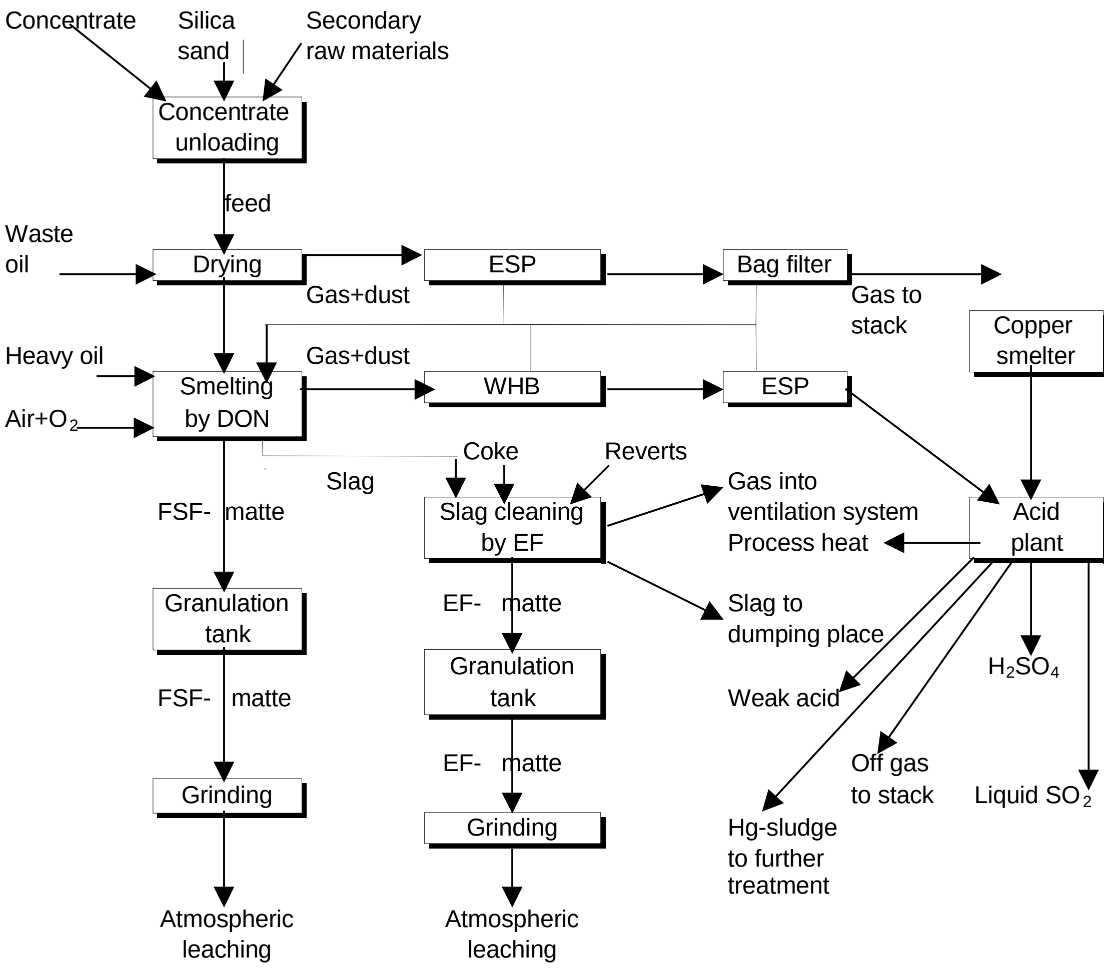


Figure 11.4: The DON process

11.1.3 Matte refining processes

The mattes produced by the smelting processes must be treated further in order to recover and refine the metal content. Nickel matte must go through a multi-stage refining process to reject iron and recover copper, cobalt and precious metals. Matte can be treated pyro-metallurgically but hydro-metallurgical processes are more commonly used. A variety of electro-refining, leaching-reduction and precipitation processes are carried out. Nickel is recovered from purified solutions by electro-winning or by hydrogen reduction.

The following diagram shows the generic processing routes.

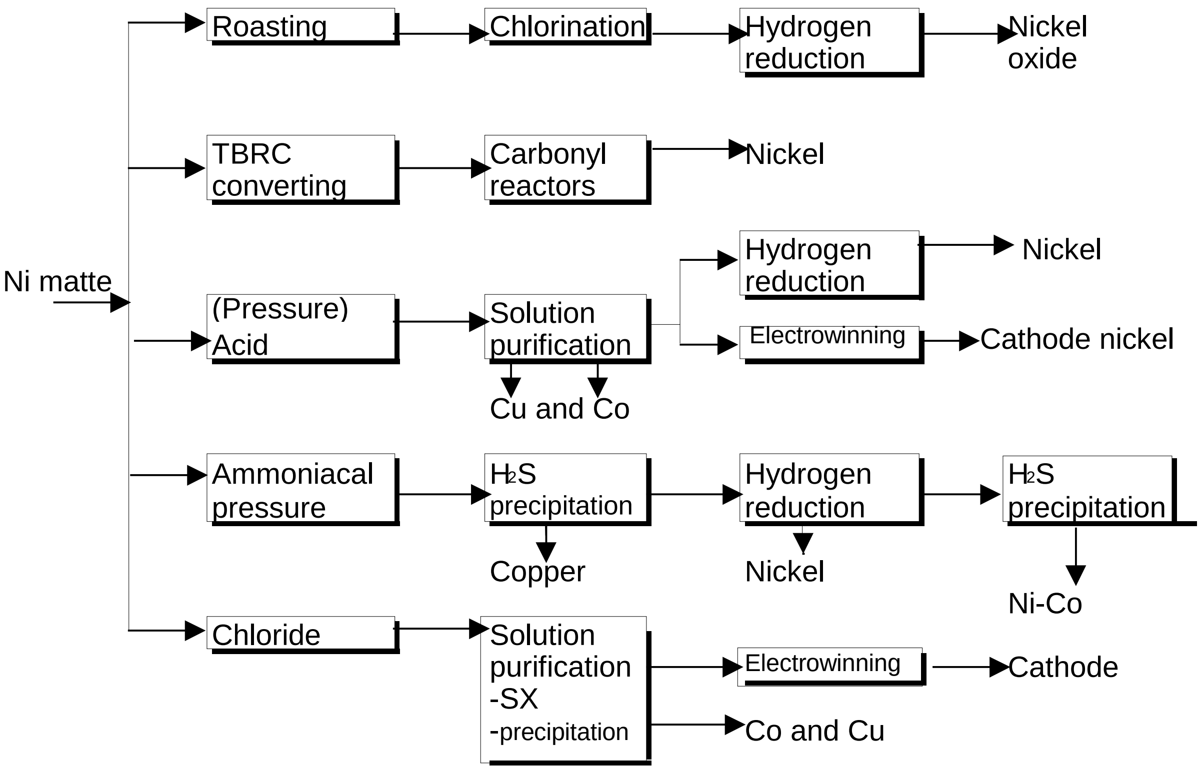


Figure 11.5: Generic flow sheet for nickel matte refining processes

11.1.3.1 Chloride leaching of matte followed by electro-winning

Matte is leached in a chloride solution in several stages at high temperature and pressure using chlorine gas as an oxidant. The chlorine gas is generated in the electro-winning cells. Copper is precipitated as the sulphide and then iron and arsenic are precipitated as hydroxides and arsenates to purify the leachate. Copper sulphide is roasted in a fluidised bed furnace and the resulting calcine is leached with spent copper electrolyte, copper is then electro-won.

Cobalt is removed by solvent extraction of the chloride solution using an organic solvent and is electro-won. The nickel solution is then purified further using chlorine to remove lead and manganese and is then electro-won in diaphragm cells using titanium anodes. The cells are sealed to recover the chlorine that is formed at the anode.

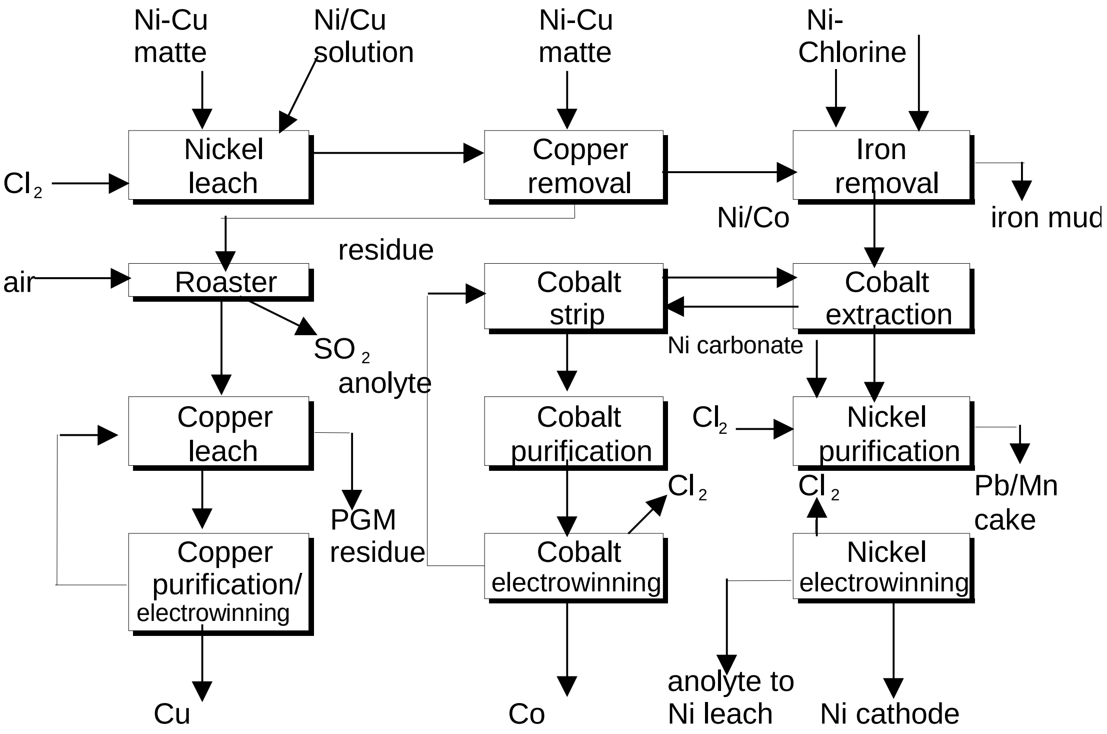


Figure 11.6: Falconbridge process
Chlorine from electrolysis is returned to the leach and purification stages

11.1.3.2 Sulphate based atmospheric - pressure leaching followed by electro - winning/hydrogen reduction

Matte is leached in a sulphate based anolyte recycled from nickel electro-winning [tm 58 & 59, Outokumpu 1997]. Nickel sulphide matte is leached in an atmospheric leaching stage using oxygen or air-sparged leach vessels with the aid of copper ions. Dissolved iron is oxidised to form iron oxide, which precipitates.

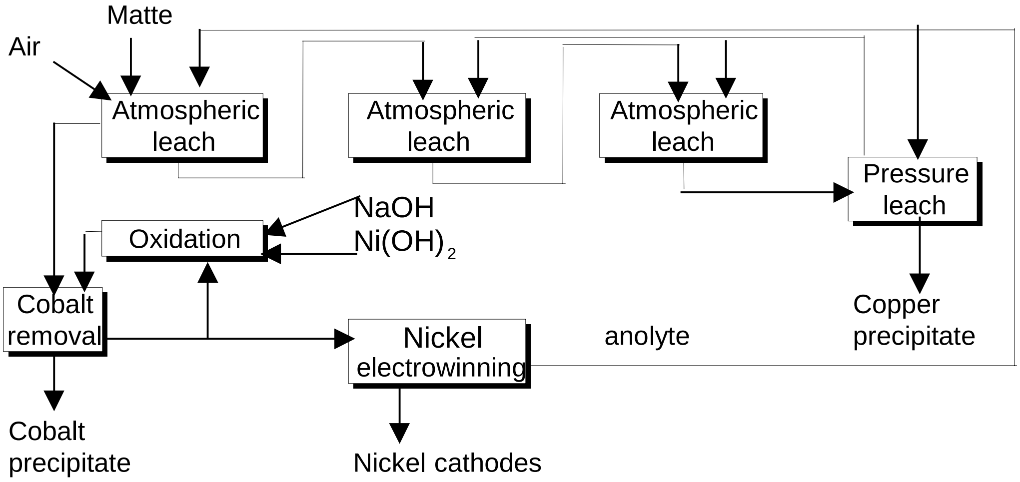
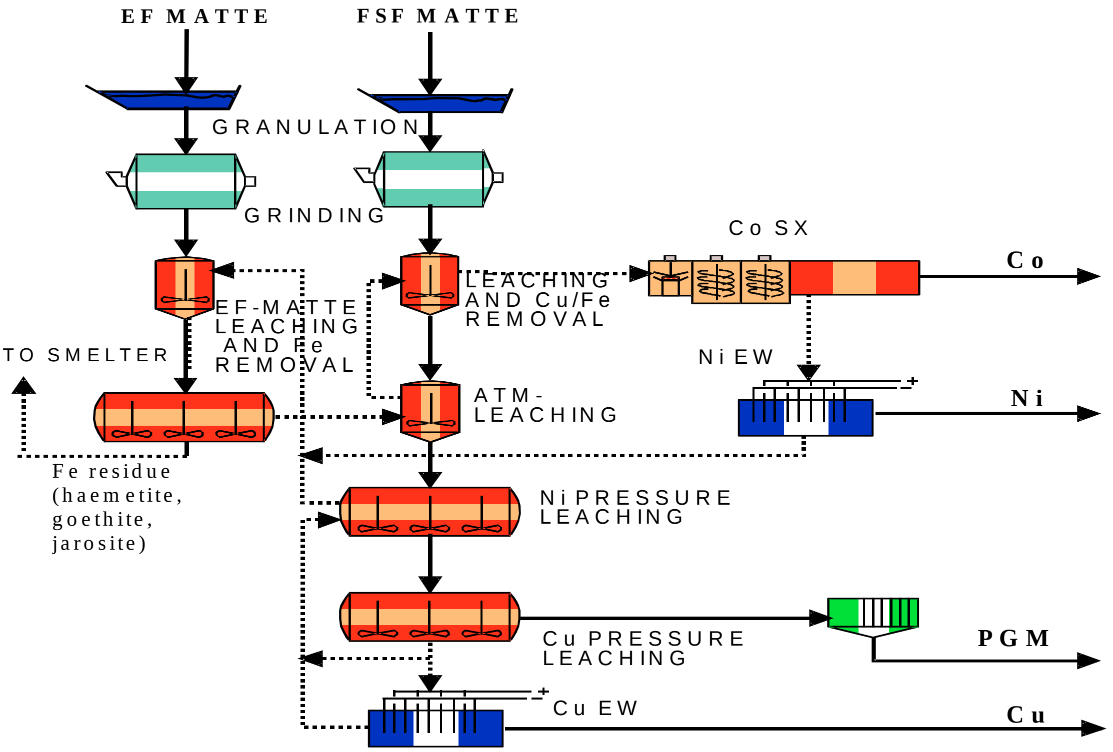


Figure 11.7: Sulphate based leaching process

The residue from the atmospheric leaching is passed to pressure leaching stage where the nickel content is dissolved and copper is precipitated as copper sulphide, which is returned to the copper smelter. The iron oxide precipitate is returned to the nickel smelter. The nickel solution from the atmospheric leach is purified by solvent extraction to remove cobalt and impurities. Cobalt can be electro-won or reduced to cobalt powder using hydrogen. Nickel can be electro-won from the purified sulphate solution to produce cathodes.

Nickel powder can be produced by adding ammonia and ammonium sulphate to the solution. The mixture is then reduced in an autoclave using a hydrogen atmosphere. The powder is sold or can be sintered into briquettes. The sulphuric acid present is neutralised by ammonia. The ammonium sulphate is recovered for sale or reuse in the process.



EF = Electric Furnace. FSF = flash smelting furnace. SX = solvent extraction. EW = electro-winning.

Figure 11.8: Flow sheet of the DON refinery process

This process has been developed into a two-stream process to allow separate treatment of the mattes produced from the smelter and the slag cleaning furnaces in the process shown above.

11.1.3.3 Ammonia pressure leach and hydrogen reduction

Matte is leached into ammoniacal ammonium sulphate solution in pressure autoclaves using air as an oxidant. After the precipitation of copper sulphide, nickel solution is reduced with hydrogen in the autoclaves to produce metallic nickel powder. The ammonium sulphate formed in the hydrogen reduction stage is recovered by crystallisation. After the hydrogen reduction the rest of the dissolved nickel and all the cobalt are precipitated with hydrogen sulphide for further treatment [tm 94, Ni Expert Group 1998; tm 96, Outokumpu 1998].

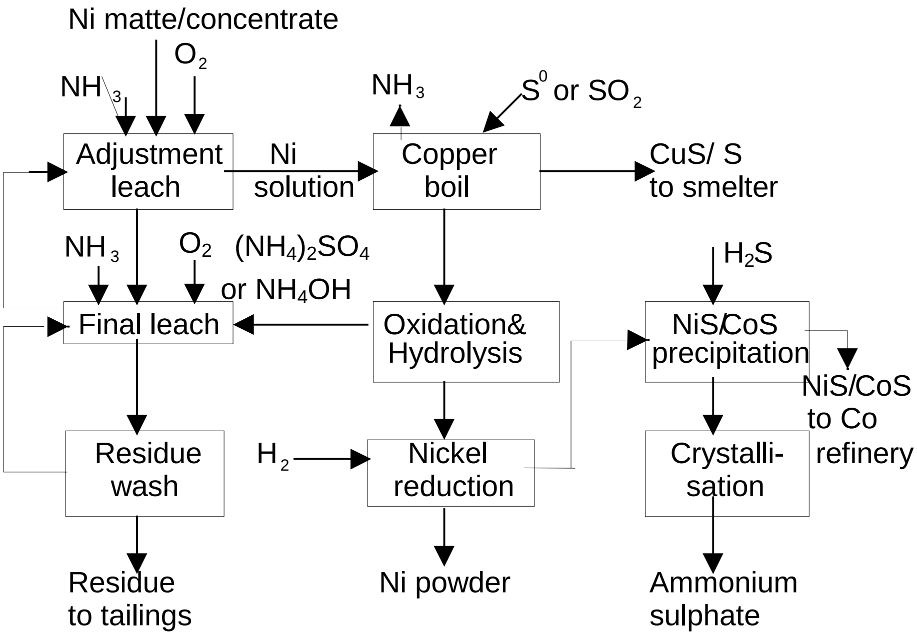


Figure 11.9: Sherritt ammoniacal leaching

11.1.3.4 Ferric chloride leaching

Matte is leached in several stages using recycled ferric chloride in the presence of chlorine (which is generated from the electro-winning cells) near to boiling point. Sulphur remains in the elemental state and is filtered from the final solution. Iron is then removed by solvent extraction using tri-butyl phosphate allowing ferric chloride to be recovered. Cobalt is removed in a further solvent extraction stage using tri-iso octyl amine. Cobalt chloride solution is sold [tm 94, Ni Expert Group 1998; tm 96, Outokumpu 1998].

Other minor impurities such as Cr, Al, Pb are removed using a combination of electrolysis, ion exchange and active carbon. Nickel is then electro-won from the purified solution in diaphragm cells using titanium anodes and nickel cathodes. Chlorine is collected and returned to the leach circuit.

11.1.3.5 Carbonyl process

The low-pressure carbonyl process uses an impure oxide produced by smelting sulphide ore as the raw material to refine the nickel. This oxide is reduced to an impure metal using hydrogen and the metal is then activated. Nickel carbonyl is then formed by the reaction of the metal with carbon monoxide at low temperature and pressure. Nickel carbonyl is volatile and is refined by separation from the solid impurities. The solid residue is returned for further processing to the primary smelter to recover other metals that are present [tm 20, HMIP Ni 1993; tm 26, PARCOM 1996].

Nickel carbonyl gas passes from the reactor and is then decomposed using heat to form powders and pellets. It can also be decomposed onto other substrates such as carbon fibres to produce nickel-coated materials. During decomposition carbon monoxide is released and is recovered and reused to produce more nickel carbonyl. Pure nickel salts are produced by the reaction of nickel pellets with acids. Any waste gases from the process are incinerated to destroy any nickel carbonyl and carbon monoxide. Dust from the afterburner is removed.

11.1.3.6 Matte electro-refining

Nickel matte can be cast into anodes. These are dissolved in a diaphragm electrolysis cell using a chloride/sulphate electrolyte. The electrolyte from the anode compartment is purified and circulated through the cathode bag. The anodes are also bagged to collect the sulphur-containing anode slime of the anode. Elemental sulphur and precious metals are recovered from the slime. This process is limited to mattes that have a low copper content. [tm 96, Outokumpu 1998].

11.1.3.7 Solvent extraction

Most of the processes described above use a solvent extraction stage to remove iron and to separate nickel and cobalt prior to electro-winning or transformation. Metal ion-complexes are formed using chelating agents so that the desired metal ions can be extracted into an organic phase. The desired ions are then back extracted into a second aqueous phase by altering the conditions of a second aqueous phase.

The choice of solvent and chelating (complexing) agent allows specific metal ions to be removed from aqueous solution and to be concentrated. The solvent/chelating mixture is recycled between the extraction and winning baths. The baths comprise a mixer/settler to allow solvent/water contact and then phase separation. Sealed or covered systems are used to prevent the emission of solvent fumes. The following figure shows a generic process outline.

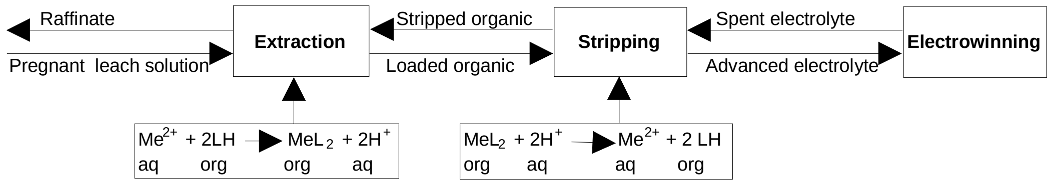


Figure 11.10: Solvent extraction (SX) process outline

11.1.4 Nickel alloy production from secondary materials

The process includes raw materials preparation, melting (including tapping and casting), ingot stripping and dressing, scrap recycling and “electroslag refining” with a throughput about 7000 t/year.

Raw materials for the process consist of recycled scrap, purchased scrap and virgin material. Scrap in the form of turnings, swarf off-cuts etc. is treated to remove oil by centrifuging and/or degreasing. Raw materials are weighed into charging vessels to the desired alloy composition. The charging vessels are then transported to the relevant furnace.

Air melting is carried out in an induction furnace, with fume captured by one of two extraction systems fitted with bag filters. Some of the air-melted metal is further refined in vacuum refining furnaces. Vacuum is provided by steam ejectors and gases from the ejectors are cooled using spray condensers.

Three casting techniques are used: top casting, uphill casting and durville casting. Casting fluxes and anti-piping compounds are used during casting. Ladles used for casting are pre-heated by gas fired burners.

Vacuum induction melting (VIM) is carried out in a 7.5 tonnes capacity furnace. Casting from the furnace is carried out either under vacuum or argon.

Vacuum arc refining (VAR) is carried out producing solid ingots under vacuum.

Slag is refined in an electric furnace.

The ingots from casting are stripped of any residual refractory material etc. Solid waste from the casting processes, casting/ladle refractories, slags etc are collected for recovery of residual metal. The stripped ingots may then be subjected to various processes: machining, sawing, grinding and shot blasting. The scrap from these processes in the form of dust, swarf and turnings is collected for reprocessing or sale.

11.1.5 Cobalt production

Cobalt is produced during the recovery of nickel after separation by solvent extraction (SX) and is described above. Cobalt can be electro-won from the solution to produce saleable cathodes using diaphragm cells in the same manner are nickel.

Cobalt can also be recovered from the solution as a powder by hydrogen reduction. Alternatively the solution can be treated to precipitate an impure cobalt by-product for further refining, or may be sold.

Further refining of these and other cobalt containing by-products, intermediates and recycled materials is performed using atmospheric and oxygen pressure leaching in sulphuric or hydrochloric acid medium. Separation using hydroxides, carbonates and amine or ammonium complexes is also used [tm 108, Ullmanns 1996].

Precipitation, solvent extraction and ion exchange techniques are used to purify the solutions. Cobalt is then recovered as metal powder, metal oxide or salts. The products are made with a wide variety of very specific physical and chemical characteristics. Pyrolysis of carboxylates, high temperature reduction of oxides, precipitation and crystallisation techniques are used depending on the particle size or other characteristics that are required [tm 108, Ullmanns 1996].

These processes are commercially confidential and very site specific in nature.

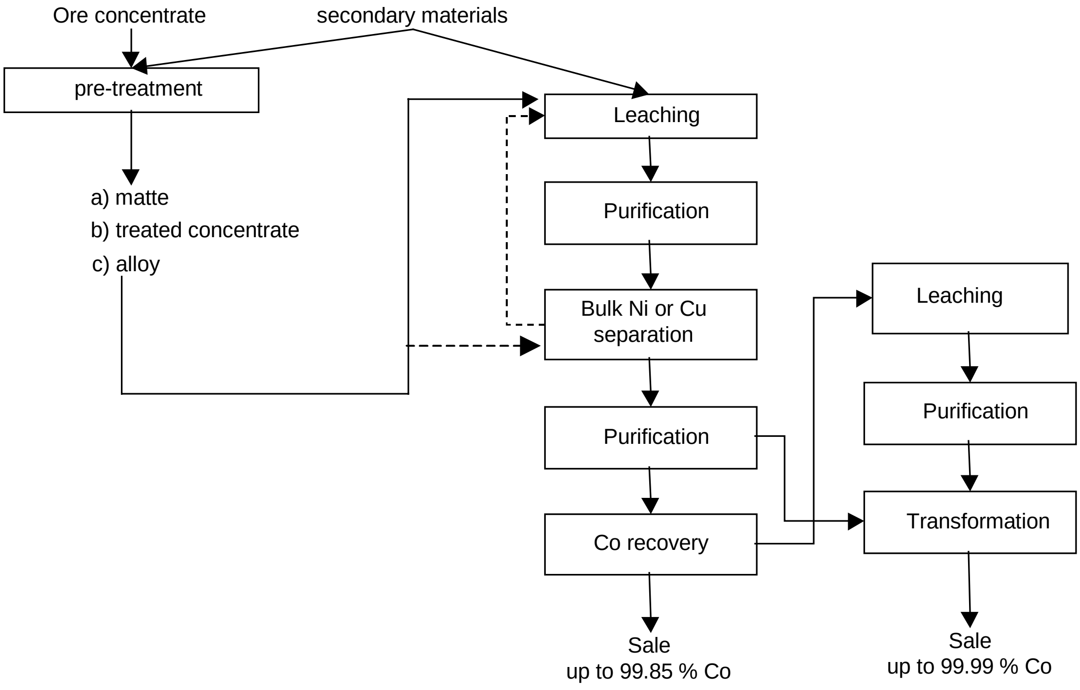


Figure 11.11: Generic flow sheet showing possible process steps for cobalt production

11.2 Present Emission and Consumption Levels

Some emission and consumption data for sulphidic ore processes operated worldwide are shown below.

Smelter	Process Units	Capacity t/h	Annual Prodn. t/a	Oxygen Enrich-ment%	Gas Strength SO_2%	SO_2 Emission
Selebi-Phikve, Botswana	Spray dry, OK flash smelt furnace (FSF), 3 PSC, electric slag cleaning, whb and 2 EPs	100	46000 Matte	24.5		
Nadezhda, Norilsk, Russia	Spray dry, OK FSF, PSC, slag cleaning furnace, whb, 3 EPs, Sulphur prodn.	170 – 180		45 – 55		
Kalgoorlie, Australia	Modified OK FSF, 3 PSC, whb, EP, acid plant	110	100000 Matte	35 – 40		35000 t/a 350 kg/t
Jinchuan, China	Roary drier modified OK FSF, WHB, EP, acid plant	~ 45	21000 Ni	44 – 46		
Harajvalta, Finland	Rotary drier, OK FSF, DON process, WHP, EP, acid plant.	40	30000 Ni	70 – 92	19	18 kg/t
Fortaleza, Brasil	Steam drier, OK FSF, DON process, quench cooling, acid plant	~ 20	19000 Matte	60 – 70		
Copper Cliff, Ontario, Canada	Fluid bed drier, INCO FSF, 6 PSC, Cu plant, acid plant and SO_2 plant.	~ 150	127000 Ni	100	10 – 11	230000 t/a 1000 kg/t
Sudbury, Ontario, Canada	FB roaster, Electric furnace, 3 PSC, PS slag converter, spray cooler, 3 EPs, acid plant	n.a.	45000 Ni		6 - 9	50000 t/a 500 kg/t
Thompson, Canada	FB roaster, electric furnace, 3 PSC	n.a.	81600 Ni			
Pechenganickel Russia	Electric smelting, converting, electric slag cleaning	n.a.	n.a.			

Note. FB = Fluidised Bed. OK = Outokumpu. PSC = Pierce – Smith Converter. EP = Electrostatic Precipitator. DON = Direct Outokumpu Nickel process. whb = waste heat boiler. Acid plant refers to a sulphuric acid plant icluding the relevant gas cooling and cleaning train. n.a. = not available.

Table 11.2: Example input and output data for worldwide nickel production

11.2.1 Energy use

The energy used for the production of matte from sulphidic ores is reported to be in the range 25 to 65 GJ per tonne of nickel for ores containing 4 to 15% Ni. The energy used in the various refining stages is reported to be 17 to 20 Gj per tonne of nickel.

11.2.2 Emissions to air

The potential emissions of concern to air from nickel and cobalt production are:

- sulphur dioxide (SO_2) and other acid gases;
- oxides of nitrogen (NO_x) and other nitrogen compounds;
- metals and their compounds including As;
- dust;
- Chlorine;
- VOCs and odours.
- CO and carbonyls (alarm levels set at 80 ppb).

The relevance of the potential substances emitted from the major sources is given in the following table and are discussed later in this section:

Component	Roasting or smelting	Leaching and purification	Electrolysis	Solvent Extraction	Sulphuric acid plant
Sulphur dioxide and trioxide *. HCl	•••*	•	•	•	•••
VOC (incl. CO and odours)	•	•		••	
Chlorine		••	••		
Nitrogen oxides	•*				•
Dust and metals	•••*	•	•		

Note. * The direct emissions from the roasting or smelting stages of sulphidic ores are treated and/or converted in the gas cleaning steps and sulphuric acid plant; the remaining emissions of sulphur dioxide and nitrogen oxides of the sulphuric acid plant are still relevant. Fugitive or non-captured emissions are also relevant from these sources.

••• More significant…………..• less significant

Table 11.3: Significance of potential emissions to air from cobalt and nickel production

The sources of emissions from the process are: -

- roasting;
- other pre-treatment;
- smelting, converting and slag treatment;
- leaching and purification;
- solvent extraction;
- electrolysis;
- final recovery or transformation stage;
- sulphuric acid plant.

11.2.2.1 Sulphur dioxide and other acid gases

The major sources of sulphur dioxide emission are fugitive emissions from the roaster or smelter. Uncaptured emissions from the ladle transfer and blowing stages of the converter and direct emissions from the sulphuric acid plant are significant. Good extraction and sealing of the furnaces prevents fugitive emissions and the collected gases are passed to a gas cleaning plant and then to the sulphuric acid plant. The gas collection from the converter stages is a significant source and this aspect is discussed in Chapter 3 copper and its alloys.

After cleaning, the sulphur dioxide in the gas from the roasting stages is converted to sulphur trioxide (SO_3) with an efficiency of between 95 to 99.8% depending on the sulphuric acid plant used (single or double absorption) and the concentration of sulphur dioxide in the feed gas. SO_2 concentrations in the off gas from 200 - 1300 mg/Nm^3 are emitted. A very small amount of SO_3 is not converted and is emitted together with the SO_2. During start up and shut down there may be occasions when weak gases are emitted without conversion. These events need to be identified for individual installations, many companies have made significant improvements to process control prevent or reduce these emissions.

During electrolysis there are emissions of aerosols (diluted hydrochloric and sulphuric acids and metal salts) to the tank house. These emissions leave the tank house via the (natural) ventilation or from the cooling towers and are classed as fugitive emissions. Cells can be covered by foams or plastic beads to reduce the production of mists. Cell room ventilation air can be de-misted and the solution returned to the electrolysis stage.

Chlorine is formed during the electrolysis of chloride solutions. This is collected in the sealed anode compartment and is returned to the leaching stage. Chlorine monitors are used to detect leaks and scrubbers are used to remove traces of chlorine from ventilation air and other sources.

Process	**Product**	**Metal Production Tonnes per year**	**Sulphur Dioxide kg per tonne of metal produced.**
Grinding/ Leaching	Co and Compounds	5000	0.01
Ni Smelter	Ni, Co, Cu	200000	18
Note. Table refers to specific raw materials – Grinding of matte produced from sulphidic ore – smelting of Cu/Ni sulphidic concentrates.			

Table 11.4: Sulphur dioxide production from some nickel and cobalt processes

11.2.2.2 VOCs

VOCs can be emitted from the solvent extraction stages. A variety of solvents are used and they contain various complexing agents to form complexes with the desired metal that are soluble in the organic layer. Emissions can be prevented or minimised by using covered or sealed reactors and in this case emissions in the order of 30 mg/Nm^3 have been reported.

The solvents can be aliphatic or aromatic in nature but usually a mixture is used. VOCs can be classified according to their toxicity but aromatic and chlorinated VOCs are usually considered to be more harmful and require efficient removal. Solvent vapours are emitted depending on the temperature of the extraction stage and the vapour pressure of the solvent components at that temperature. VOC concentrations of up to 1000 mg/Nm^3 (~1 kg/h) have been reported but the operating conditions are not known [tm 94, Ni Expert Group 1998]. The nature of the solvents and conditions of use need to be determined locally so that the hazard can be assessed.

VOCs can be removed using condensers or by cooling the ventilation air and recovering the solvent for further use. Mass emissions of 0.2 kg per tonne of metal produced have been reported following condensation [tm 94, Ni Expert Group 1998]. Carbon filters or bio-filters can also be used to reduce VOC emissions further but do not allow the solvent recovery.

11.2.2.3 Dust and metals

Dust carry over from the roasting, smelting and converting processes are potential sources of direct and fugitive emissions of dust and metals. In some processes the gases are collected and treated in the gas cleaning processes of a sulphuric acid plant. Dust is removed and returned to the leaching process.

Process	Product	Production (tonnes)	Dust kg per tonne of metal	Ni kg per tonne of metal	Co kg per tonne of metal
Grinding/Leaching	Co		0.2	0.05	0.03
Matte grinding	Ni		0.01	0.005	
Carbonyl process	Ni	41000	0.28	0.007	
DON process and copper smelter	Ni, Co, Cu	200000	0.37	0.03	

Table 11.5: Mass release of metals from some European processes

11.2.2.4 Chlorine

Chlorine is used in some leaching stages and is produced during the subsequent electrolysis of chloride solutions. The leach vessels are sealed and there is provision of chlorine gas scrubbing to remove uncaptured chlorine.

The anodes in the electrolysis cells are contained in a membrane and enclosed by a collection hood. The chlorine evolved is collected and re-used in the leach stage. The systems are sealed and fugitive emissions occur only during membrane or pipe work failure. Chlorine alarms are used extensively in leach and cell rooms to detect such failures and there are normally no emissions of chlorine.

The presence of chlorine in wastewater can lead to the formation of organic chlorine compounds if solvents etc are also present in a mixed wastewater.

11.2.2.5 Hydrogen, carbon monoxide and carbonyls

Carbon monoxide and hydrogen are used in the vapo-metallurgical refining of nickel to produce crude nickel and then nickel carbonyl. These gases are explosive or very toxic and so sophisticated reactor seals and control equipment is used to prevent emissions, comprehensive monitoring and alarm systems are used. Hydrogen is also used as a reducing agent in hydrometallurgical or pyrometallurgical recovery or transformation processes. Robust process design including scaled equipment and appropriate gas exhaust systems are used to avoid explosive gas mixtures.

Carbon monoxide is recovered and waste process gases are finally incinerated to destroy any carbon monoxide or carbonyl that may be present, nickel carbonyl is converted to nickel oxide, which is recovered.

11.2.2.6 Nitrogen oxides

The roasting and smelting stages are potential sources of nitrogen oxides (NO_x). NO_x may be formed out of nitrogen components that are present in the concentrates or as thermal NO_x. The sulphuric acid produced can absorb a large part of the NOx and this can therefore affect sulphuric acid quality. If high levels of NO_x are present after the roasting stages, treatment of the roasting gases may be necessary for reasons of product quality and environment. Direct smelting uses oxygen enrichment except for slag fuming and can reduce the thermal NO_x. Other furnaces that use oxy-fuel burners also show a reduction in NO_x the reverse may be true at lower levels of oxygen enrichment when the temperature increase and nitrogen content are significant. The range for all of the processes is 20 to 400mg/Nm^3.

11.2.2.7 Fugitive emissions

Besides process emissions, fugitive emissions occur. The major fugitive emission sources are:

- dust from storage and handling of concentrates
- leakage from roasters, smelters and converters;
- dust from the exhaust gases of leaching and purification vessels;
- exhaust gases (including HCl, Cl_2 and VOCs) from the solvent extraction and electro-winning units;
- dust from the exhaust gases of casting furnaces;
- miscellaneous including building ventilation air.

Although fugitive emissions are difficult to measure and estimate there are some methods that have been used successfully (section 2.7). The following table gives some estimates from a primary smelter where the smelter and converter ventilation gases are collected and treated with the dryer gases.

Emissions	**[t/a] from**		
	Primary capture	**Secondary capture**	**Fugitive**
Sulphur dioxide	523	2242	147

Table 11.6: Significance of secondary fume capture and fugitive emissions
[tm 142, Finland Ni 1999]

The table above shows that fugitive emission can be significant in primary smelting if ventilation gases are not collected and treated. In this case they would be much higher than abated emissions. Refining processes are reported to have lower fugitive emissions and the carbonyl process is particularly well sealed. Action to reduce fugitive emissions may needed in many processes.

11.2.3 Emissions to water

Metals and their compounds and materials in suspension are the main pollutants emitted to water. The metals concerned are Cu, Ni, Co, As and Cr. Other significant substances are fluorides, chlorides and sulphates.

Possible wastewater streams are:

- Hydrometallurgical purification processes;
- Waste water from wet scrubbers;
- Waste water from wet electrostatic precipitators;
- Wastewater from slag granulation;
- Anode and cathode washing liquid effluent;
- sealing water from pumps;
- general operations, including cleaning of equipment, floors, etc.;
- discharge from cooling water circuits;
- Rainwater run-off from surfaces (in particular storage areas) and roofs.

Wastewater from wet gas cleaning (if used) of the smelter, converter and fluid-bed roasting stages are the most important sources. Other sources are cleaning and miscellaneous sources. The leaching stages are usually operated on a closed circuit and drainage systems are isolated but there are potential problems unless good leak prevention and detection systems are used, electrolyte bleed liquors are used in the leaching stage.

11.2.3.1 Waste waters from abatement plant

If wet scrubbers are used after the leaching and roasting processes an acidic solution is produced. The scrubber removes fluorides, chlorine, chlorides, most mercury and selenium and some particles that pass the mechanical gas treatment. To avoid the build up of contaminants, some liquid needs to be bled continuously from the scrubber and then treated. Dissolved SO_2 is removed prior to the discharge.

Wet electrostatic filters will also produce an acidic scrubber liquid. This is recycled after filtering. Some liquid needs to be bled from this circuit to remove build up of contaminants. This bleed liquor is treated and analysed before discharge.

The following table provides an indication of the composition of the gas cleaning liquids before treatment.

Pollutant	Concentration (dissolved)	Composition of Suspended solids
Solids		250 – 1500 mg/l
Sulphate	13 – 25 g/l	
Chloride	1.3 - 1.8 g/l	
Fluoride	0.3 - 0.5 g/l	
Cobalt	0.1 - 9 mg/l	5 - 30% of suspended solids
Nickel	0.1 – 10 mg/l	10 – 60% of suspended solids
Copper	5 – 15 mg/l	< 0.05% of suspended solids
Zinc	0.1 - 2.5g/l	2 – 6% of suspended solids
Cadmium	1 – 5 mg/l	
Lead	1 – 3 mg/l	5 – 50% of suspended solids

Table 11.7: Typical gas cleaning effluents

11.2.3.2 Miscellaneous sources

The electrodes and membrane bags used during electrolysis need to be rinsed periodically to remove deposited material upon the surface. Manganese dioxide can be formed on the surface of the anodes by the reaction of oxygen with dissolved manganese. After rinsing of the anodes, the manganese is separated from the rinse water for external re-use. Cathodes are cleaned after removal of the Co or Ni sheets. The anode and cathode washing liquid effluents are acidic and likely to contain copper, nickel, cobalt and suspended solids.

Cooling water from the granulation of matte or slag is usually re-circulated in a closed circuit system. There have been reports of the formation of persistent organic chlorine compounds and dioxins in some cooling circuits of chlorine leach processes.

Filters and wastewater from the hydrometallurgical separation and transformation processes are treated for metal and suspended solid removal. The products of this treatment may be returned to upstream operations, depending on their composition and value.

Process unit	Operation/source	Use/treatment options
General	Rain water from roads, yards, roofs Wet cleaning of roads Cleaning of lorries, ...	Waste water treatment plant/reuse Waste water treatment plant Recirculation, waste water treatment plant
Smelting operation	Cooling water from furnace, machinery and equipment	Recirculation
Matte or slag granulation	Wet ESP effluent (if needed) Granulation water	Recirculation, waste water treatment plant Recirculation
Gas cleaning system	Condensate from gas cooling, wet ESP Condensate from mercury removal Leakage	Removal of suspended dusts and reuse as feed, waste water treatment plant After mercury removal to waste water treatment plant Recirculation
Sulphuric acid plant	Cooling water equipment Leakage	Recirculation Waste water treatment plant
Feed storage	Surface water (rain/wetting)	Waste water treatment plant
Sinter plant	Scrubber (sinter fine cooling)	Waste water treatment plant
Roast gas cleaning	Wet gas cleaning	Waste water treatment plant
Roasting/roast gas cleaning	Wet cleaning of roast gases	Waste water treatment plant
Leaching	General operations including wet gas cleaning	Recovery of metals
Purification	General operations Filter Cakes	Recovery of metals Counter-current washing
Electrolysis	Cleaning of cells, anodes and cathodes	Recovery of metals
All process units	Maintenance	Waste water treatment plant
Waste water treatment plant	Effluent treatment	Reuse for certain applications/discharge

Table 11.8: Summary table of potential wastewater sources and options

Process	Effluent [m³/t]	Flow [m³/h]	Main components [mg/l]					
			Cu	Zn	As	Co	Ni	COD
Co		200	< 0.1	< 1.5	< 0.1	< 1.5	< 1.0	25
Cl Leach		55	0.1			0.2	0.7	
Cl Leach			1.0	1.0		0.25	1.0	
Carbonyl		450	0.4			0.1	1.4	
Smelter + Leach	135		17 g/t	9 g/t	2 g/t		16.5 g/t	

Table 11.9: Examples of wastewater analyses

11.2.4 Process residues and wastes

The production of metals is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). The most important process specific residues are listed below.

Residues arise as the result of the treatment of liquid effluents. The main residue is gypsum waste ($CaSO_4$) and metal hydroxides that are produced at the wastewater neutralisation plant. These wastes are considered to be a cross-media effect of these treatment techniques but many are recycled to the metallurgical process to recover the metals, depending on their value.

Dust or sludge from the treatment of gases are used as raw materials for the production of other metals such as precious metals and Cu etc or can be returned to the smelter or into the leach circuit for recovery.

11.2.4.1 Precipitates from purification processes

The production of iron based solids accounts for a significant volume of waste depending on the process used. The composition is shown in the following table.

Process	**Fe%**	**Zn%**	**Co%**	**Cu%**	**Ni%**
Iron hydroxide residues in chloride leaching process	40		0.1	< 0.1	1 - 2
Gypsum residues		25	2 – 3		
Waste water treatment	< 10	< 10	< 0.5	< 1	< 0.05

Table 11.10: Example-compositions of different types of residues

The disposal of these residues can be a considerable cost as specially constructed, lined ponds are used to contain the material. Particular care is taken about leakage and these ponds have a major need to monitor groundwater. There is a significant cross media effect. One site deposits the waste in underground rock caverns.

11.2.4.2 Pyrometallurgical slags and residues

Slags from smelting processes usually contain very low concentrations of leachable metals after slag cleaning. They are therefore suitable for use in construction. The slag output is between 4 and 10 times the weight of the metal produced depending on the source of the concentrate.

The following table gives examples of the composition of some nickel slags. The exact composition will also depend on the source of the concentrate.

Component	**Reverberatory furnace**	**Electric furnace**	**Outokumpu flash***
Nickel%	0.2	0.17	0.1 - 0.3
Cobalt%	0.1	0.06	0.1 - 0.25
Copper%	0.08	0.01	0.05 - 0.25
Iron%	38		35 - 43
Silica%	36	35	30 - 39
Lime%	2		0.5 - 7
Note. *After cleaning in electric furnace			

Table 11.11: Composition of typical nickel slags

A number of standard leachability tests are used by Member States and these are specific to the Country in question. Nickel slags are listed in EU on the Amber List of the Trans-frontier Shipment of Waste Regulations.

The drosses and solids, removed during the melting and refining stages, contain metals that are suitable for recovery. The following table shows some of the treatment or re-use options.

Process step	Solid output	Use/treatment options
Autoclave	Residue	Smelting furnace
Iron removal	Precipitate	Smelting furnace or disposal
Abatement	Filter dust	Smelting furnace
Pressure Leaching	Sulphide residue	Cu recovery
De-copperising	Cu cement	Cu smelter
Nickel and Cobalt regeneration	Impure nickel carbonate	Pure nickel sulphate production
Slag treatment	Clean slag	Construction
Removal of As etc	Gypsum ferri-arsenate	Special disposal or As recovery
Effluent treatment	Precipitate	Recovery of other metals or disposal

Table 11.12: Solid residues from Ni and Co processes

11.2.4.3 Other materials

Other residues or sludges arising from the different process stages or from general waste water treatment, depending on their composition and value may be recycled or sent for final disposal.

11.3 Techniques to Consider in the Determination of BAT

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in Chapter 2 "common processes" apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

The general techniques described in Chapter 2 "common processes" apply in a large extent to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated. Techniques used by other sectors are also applicable particularly those relating to the use of sulphur recovery systems.

The techniques to consider on a site by site basis are strongly influenced by the raw materials that are available to a site, in particular the type and variability of the concentrate, intermediate product (e.g. matte) or secondary raw materials. The other metals that they contain can also be crucial to the choice of process. In a similar manner the standard of collection and abatement systems used worldwide in the industry reflects local, regional or long-range environmental quality standards and direct comparison of the environmental performance of process combinations is therefore difficult. It is possible however, to judge how a particular process can perform with the appropriate, modern abatement equipment.

The processes described above are applied to a wide range of raw materials of varying quantity and composition and are also representative of those used worldwide. The techniques have been developed by the Companies in this sector to take account of this variation. The choice of pyro-metallurgical or hydrometallurgical technique is driven by the raw materials used, their quantity, the impurities present, the product made and the cost of the recycling and purification operation. These factors are therefore site specific. The basic recovery processes outlined in the section on applied techniques therefore constitute techniques to consider for the recovery processes when used with appropriate abatement stages. The techniques to consider for collection and abatement stages and other aspects of process operation and control are covered in section 2.6, 2.7 and 2.8.

11.3.1 Materials storage, handling and pre-treatment processes

The raw materials are concentrates, chlorine and other gases, intermediate products, fluxes and fuel, other important materials are products, sulphuric acid, slags and process residues. Important aspects are the prevention of leakage of dust and wet material, the collection and treatment of dust and liquids and the control of the input and operating parameters of the handling and feeding processes.

The issues specific to this group are: -

- The potentially dusty nature of concentrates and fluxes means that enclosed storage, handling and treatment systems are techniques to consider in these instances.

- The dust generated by some crushing operations means that collection and abatement may be applicable for this process.

- Concentrates are mixed with fluxes to produce a fairly constant feed therefore the general practice is sampling and analysis to characterise the concentrates and store individual concentrates separately so that an optimum blend can be prepared for smelting. This is a technique to consider.

- Intermediate products such as matte may also need to be handled in this way depending on the potential to form dust.

- Chlorine and other gases will be handled according to specific safety requirements to prevent leaks and contain the gases.

Process gases such as chlorine, hydrogen or carbon monoxide can be stored in approved pressure vessels or can be produced on site. The production of these gases is covered elsewhere. Gases are usually regenerated and recycled during the processes and are returned to the process or storage.

Acid produced during the process should be stored in double walled tanks or tanks placed in chemically resistant bunds. The treatment of acid slimes from the sulphuric acid plant and weak acid from scrubbing systems depends on local processing or disposal requirements unless there is a local use for the material.

Sludges and other metallic residues that are destined for recovery off site should be stored drums or other suitable ways depending on the material.

There are a variety of secondary raw materials used and they range from fine dusts to large single items. The metal content varies for each type of material and so does the content of other metals and contaminants. The techniques used for storage, handling and pre-treatment will therefore vary according to the material size and the extent of any contamination. These factors vary from site to site and the techniques discussed in Chapter 2 will be applied on a site and material specific basis. The specific issues that apply to this group are shown in table 11.15 in the section on BAT.

The storage of raw materials depends on the nature of the material described above. The storage of fine dusts in enclosed buildings or in sealed packaging is used. Materials that contain water-soluble components are stored under cover. The storage of non-dusty material in open stockpiles and large items individually in the open is used.

11.3.2 Primary smelting processes

The only smelting process used for direct production of nickel or cobalt in Europe is the Outokumpu Flash Smelter using oxygen enrichment. This is used to produce a nickel matte and a slag that is treated further in an electric furnace to produce more matte and an inert slag. The mattes are granulated for hydrometallurgical processing and the slag is granulated or cooled and used for civil engineering purposes. The use of the Outokumpu Flash furnace in this manner is characterised by low energy consumption of the overall process (7 mWh per tonne of Ni) and reliable furnace operation. The process features heat recovery in the form of steam and electricity and also the collection and recovery of sulphur dioxide as sulphuric acid. The furnace lining life is reported to be greater than 5 years. The other processes used worldwide are also techniques to consider.

The Pierce-Smith converter is not used for the production of nickel or cobalt in Europe. The use of this converter would be a technique to consider when used in conjunction with an intelligent secondary fume collection system and furnace blowing control system (see Chapter 3 Copper).

Cobalt is generally recovered in conjunction with nickel. The process that is used to produce ferro-nickel is covered in Chapter 9, ferro-alloys.

The abatement system used for primary smelting of sulphide concentrates is the recovery of sulphur dioxide usually by conversion to sulphuric acid in double contact process with four or more passes, sometimes a caesium-doped catalyst is used. Conversion of part of the SO_2 into liquid SO_2 is also practised with the balance being converted into sulphuric acid. The gases are cooled (with heat/energy recovery) and cleaned before conversion. A combination of coolers and hot electrostatic precipitators or a combination of scrubbers (radial or jet) and wet EPs are used. Mercury recovery systems are employed if necessary using the techniques discussed in section 2.8.

11.3.3 Refining and transformation processes

11.3.3.1 Leaching, chemical refining and solvent extraction

The refining processes described in applied techniques are applied to a wide range of raw materials of varying quantity and composition. The techniques have been developed by the Companies in this sector to take account of this variation. The choice of pyro-metallurgical or hydrometallurgical technique is driven by the raw materials used, the impurities present and the product made. In particular the morphology of the final product can be crucial for example when powders are produced for battery manufacture or when metal coatings are applied to a variety of substrates such as foams.

The basic refining processes outlined above therefore constitute the techniques to consider for the recovery processes. The application of the reactor sealing, abatement, control and management techniques that are covered in Chapter 2 of this document are techniques to consider.

EXAMPLE 11.01 MINIMISATION OF THE EMISSIONS OF VOCS

Description: - Use of low shear mixer for the solvent/aqueous mixture to optimise droplet size and minimise contact with air. Covered mixer and separate, covered settlement zone reduces emissions of VOC to air and carryover in aqueous phase. Use of low shear and variable speed pumping reduces energy consumption of the system.

Main environmental benefits: **-** Prevention of VOC emissions

Operational data: - Concentration of VOC in occupational air < 5 ppm (< 30 mg/Nm^3) when kerosene was used as solvent.

Cross media effects: - Positive effect by prevention of VOC emissions, reduction of energy use.

Economics: - Not available but the process operates viably in several installations.

Applicability: - All solvent extraction processes.

Example plants: - Finland

Reference literature: - [tm 94, Nickel Expert Group 1998]

11.3.3.2 Electro-winning

Electro winning may produce gases that are evolved at the anode and will produce chlorine or an acid mist. This needs to be collected and removed, extraction and mist elimination are used and collected mist returned to the process, scrubbing the collected gases does not allow reuse of the mist and contributes to wastewater. Cell coverings can be used to reduce the amount of mist formed but are not as effective as de-misting, organic coatings or plastic bead layers can be used. In the case of electro-winning processes based on chloride, the recovery and reuse of chlorine produced from the cells is considered to be part of the process.

EXAMPLE 11.02 COLLECTION AND REDUCTION OF CHLORINE GAS.

Description: - Collection of gases produced during electro-winning and leaching processes. The electrolysis cells are fitted with an integral hood, which collects chlorine gas. Leaching reactors are sealed. The gas from electro-winning is collected and blown into a central system and returned to the leaching stage.

Main environmental benefits: - Reduces the need for an extensive gas scrubbing system.

Operational data: - Not available.

Cross media effects: - Positive effect by preventing of emissions of chlorine. Reuse of chlorine minimises the amount of chlorine purchased. Reduction in the amount of gas scrubbing prevents effluent discharges.

Economics: - Not available. The system is viable in most electro-winning process using chloride solutions.

Applicability: - All electro-winning.

Example plants: - Norway, France

Reference literature: - [tm 94, Nickel Expert Group 1998]

The processes and the techniques for control, mist collection and acid gas recovery and removal are suitable for use with new and existing installations.

Sealed tank house drainage systems, the recovery of electrolyte bleed are also techniques to be considered.

11.3.3.3 Other metals

Precious metals and copper are often associated with the raw materials and they are either recovered on site or the residues sent to other refineries. The processes that were discussed earlier as available techniques are all considered being techniques to consider in the determination of BAT. The specific feed materials will influence the final process choice. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes.

11.3.3.4 Production of metal powders ingots and other products

The processes that were discussed earlier as available techniques are all considered being techniques to consider in the determination of BAT.

The specific feed materials and the final products will influence the choice of process and the factors of product size and shape are the main influencing factors. The techniques discussed in Chapter 2 should also be considered in conjunction with these processes.

11.3.4 Fume/gas collection and abatement

The techniques discussed in section 2.7 of this document are techniques to be considered for the various process stages involved in the production of cobalt and nickel etc. The use of containment or secondary hoods is also a technique to be considered. There are several site-specific issues that will apply to the abatement techniques used. This depends on the reagents used in the process and the components present in the off gas. Some of the techniques are summarised in the following table.

Reagent Used.	Component in off - gas.	Treatment Method.
Solvents, VOC	VOC, odours	Containment, condensation. Activated carbon, Bio-filter
Chlorine, HCl	Cl_2	Collection and re-use. Caustic scrubber system
Sulphides	Sulphur dioxide	Sulphuric acid plant or scrubber.
Nitric Acid	NO_x	Oxidise and absorb, recycle, scrubber system.
Ammonia	NH_3	Recovery, scrubber system.
Hydrogen	H_2	Process control, afterburner.
Carbon monoxide	CO	Recovery and re-use. Afterburner and dust removal.

Table 11.13: Chemical treatment methods for some gaseous components

Essentially the process technologies discussed in this chapter, combined with suitable abatement will meet the demands of stringent environmental protection. An example is given of the collection of chlorine gas that is evolved at the anode during electro-winning and leaching. Other techniques include the containment of solvent vapours using closed solvent extraction reactors and the collection and re-use of solvents and CO. The significance of the components of any VOC depend on the solvent used and these can only be determined locally.

The use of hoods for tapping and casting and the use of secondary fume collection from the smelter and converter stages are also techniques to consider. Tapping fume will consists of fumes from oxygen lancing, dust from drilling, fumes from the vaporised slugs if a tapping gun is used and fumes from all exposed metal and slag surfaces. These fumes will consist mainly of oxides of the metals that are involved in the smelting process. The design of the hooding system needs to take account of access for charging and other furnace operations and the way the source of process gases change during the process cycle.

11.3.5 Process control and management

The principles of process control and management discussed in Chapter 2 are applicable to the production processes used in this Group. Some of the processes are capable of improvement by the adoption of many of these techniques.

11.3.6 Wastewater

This is a site-specific issue, existing treatment systems are reported to be to a high standard. All wastewater should be treated to remove dissolved metals and solids. The techniques listed in section 2.9 are the techniques to consider. In a number of installations cooling water and treated wastewater including rainwater is reused or recycled within the processes. Similarly granulation water may require settlement or other treatment prior to discharge to water.

11.3.7 Process residues

This is a site and process specific issue but the minimisation and re-use of residues where practicable should be considered. The techniques to consider in section 2.10 are techniques to consider in the determination of BAT.

11.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector; which for the production of nickel and cobalt are VOCs, dust, fume, odours, SO_2, chlorine CO and other acid gases, wastewater, residues such as sludge, filter dust and slag;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous section. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this section are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

Best Available Techniques are influenced by a number of factors and a methodology of examining the techniques is needed. The approach that has been used is given below.

First of all the choice of process depends strongly on the raw materials that are available to a particular site. The most significant factors are the chemical composition, the presence of other included metals, their size distribution (including the potential to form dust) and the degree of contamination by other material. There may be primary materials available from single or multiple sources, secondary raw materials of varying quality or an intermediate product that requires refining or transformation.

Secondly, the process should be suitable for use with the best gas collection and abatement systems that are available. The fume collection and abatement processes used will depend on the characteristics of the main processes, for example some processes are easier to seal. Other processes may be able to treat recycled materials more easily and therefore reduce the wider environmental impact by preventing disposal.

Finally, the water and waste issues have been taken into account, in particular the minimisation of wastes and the potential to reuse residues and water within the process or by other processes. Energy used by the processes and abatement is also a factor that is taken into account in the choice of processes.

The choice of BAT in a general sense is therefore complicated and depends on the above factors. The varying requirements mean that BAT is influenced mainly by the raw materials available to the site, the physical and chemical properties of the products to be made and the required throughput of the plant. The issues are therefore site specific.

The following points summarise the recommended methodology that has been used in this work: -

- Is the process industrially proven and reliable?
- Are there limitations in the feed material that can be processed?
- The type of feed and other metals contained in it influences process selection.
- Are there production level constraints? - e.g. a proven upper limit or a minimum throughput required to be economic.
- Can latest and efficient collection and abatement techniques be applied to the process?
- Can the process and abatement combinations achieve the lowest emission levels? The achievable emissions are reported later.
- Are there other aspects such as safety that are related to processes?

At the time of writing several process and abatement combinations are able to operate to the highest environmental standards and meet the requirements of BAT. The processes vary in the throughput that can be achieved and the materials that can be used and so several combinations are included. All of the processes maximise the reuse of residues and minimise emissions to water. The economics of the processes vary. Some need to operate at a high throughput to achieve economic operation, while others are not able to achieve high throughputs.

The collection and abatement techniques used with these processes were discussed under techniques to consider in the determination of BAT and when applied in combination with the metallurgical process will result in a high level of environmental protection.

As indicated in the general preface to this document, this section proposes techniques and emissions that are considered to be compatible with BAT in general. The purpose is to provide general indications of the emission and consumption levels that might be considered as an appropriate benchmark of BAT based performance. This is done by quoting achievable levels in ranges that are generally applicable to both new and upgraded plants. Existing installations may have factors, such as space or height limitations that prevent full adoption of the techniques.

The level will also vary with time depending on the condition of the equipment, its maintenance and the process control of the abatement plant. The operation of the source process will also influence performance as there are likely to be variations in temperature, gas volume and even the characteristics of the material throughout a process or batch. The achievable emissions are therefore only a basis from which actual plant performance can be judged. Process dynamics and other site specific issues need to be taken into account at a local level.

11.4.1 Materials handling and storage

The conclusions drawn for Best Available Techniques for the materials handling and storage stages are shown in section 2.17 of this document and are applicable to the materials in this chapter.

The following table summarises the techniques.

Material	Storage	Handling	Pre-treatment	Comment
Coal or Coke.	Covered Bays, Silos.	Covered conveyors if non-dusty. Pneumatic.		
Fuel and other oils. Solvents.	Tanks or drums in bunded areas.	Secure pipeline or manual system.		Back venting of storage tanks.
Fluxes.	Enclosed (Silo)	Enclosed conveyors with dust collection. Pneumatic.	Blending with concentrates or other material.	
Concentrates, intermediate products.	Enclosed if dust forming	Enclosed with dust collection. Closed conveyor or pneumatic.	Blending using conveyors. Drying or sintering	
Process gases	Approved pressure vessels	Secure gas pumping or vacuum systems		Gas alarms in storage and process areas.
Fine dust.	Enclosed.	Enclosed with dust collection. Pneumatic.	Blending, Agglomeration.	
Coarse dust (raw material or granulated slag)	Covered Bays	Mechanical loader.	Grinding or milling	Oil collection if necessary
Lump (raw material or slag).	Open	Mechanical loader.	Grinding or milling	Oil collection if necessary
Whole Items	Open or Covered Bays	Mechanical loader.		Oil collection if necessary
Acids: - Waste acid Product Acid	 Acid resistant tanks. Acid resistant tanks.		 Sale or neutralisation. Sale	
Products – Cathodes, billets and cake. Powders.	Open concrete area or covered storage. Drums or bags.			
Process residues for recovery.	Covered or enclosed depending on dust formation.	Depends on conditions.		Appropriate drainage system.
Wastes for Disposal.	Covered or enclosed bays or sealed (drums) depending on the physical and chemical state of the material.	Depends on conditions.		Appropriate drainage system.

Table 11.14: Storage, handling and pre-treatment methods for nickel and cobalt

11.4.2 Process selection

It is not possible to conclude that a single production process can be applied to all stages for the production of metals in this group.

11.4.2.1 Pyrometallurgical processes

The pyrometallurgical processes that are described as techniques to consider form the basis of BAT. At the time of writing the Outokumpu Flash Furnace that forms part of the DON process is considered to be BAT for the smelting of nickel concentrates when used with effective collection and abatement equipment. Similarly the INCO flash furnace and the sealed electric furnace with converter can also be considered.

11.4.2.2 Refining and transformation processes

The refining and transformation processes that are described as techniques to consider in the determination of BAT form the basis of BAT when used with effective gas and liquid collection and treatment techniques. Table 11.16 summarises the techniques used and the treatment options.

11.4.3 Gas collection and abatement

The use of sealed reactors where possible for the leaching and solvent extraction stages allow gases and vapours to be contained and re-used. These techniques are considered to be BAT.

There are occasions when sealing is not possible for example covered settlement baths. Fume collection from semi-sealed equipment is a very important component of BAT as the mass of fugitive emissions can be greater than abated emissions. This is illustrated in table 11.6.

The correct use of furnace sealing and fume collection techniques is also considered to be BAT and is associated with the use of proper prevention and maintenance techniques. The techniques are reported in section 2.7 and some examples are given in the section on techniques to consider.

The following table provides an overview of some of the recovery and abatement techniques that can be used for the various process stages operating to the standard of BAT.

Process stage	Component in off-gas	Abatement option
Materials handling and storage.	Dust and metals.	Correct storage, handling and transfer. Dust collection and fabric filter if necessary.
Grinding, drying.	Dust and metals.	Process operation. Gas collection and fabric filter.
Smelting and converting. (Sulphidic ore)	Dust, metals and sulphur dioxide.	Gas collection, gas cleaning and sulphuric acid plant.
Slag treatment.	Dust and metals. Sulphur dioxide. Carbon monoxide.	Gas collection, cooling and fabric filter. Scrubber. Afterburner.
Leaching and chemical refining.	Chlorine.	Gas collection and reuse, wet chemical scrubber.
Carbonyl refining.	Carbon monoxide. Hydrogen.	Sealed process, recovery and reuse. Afterburner and dust removal in fabric filter for tail gas.
Solvent extraction.	VOC. (depends on the solvent used and should be determined locally to assess the possible hazard).	Containment, gas collection, solvent recovery. Carbon adsorption if necessary.
Thermal refining.	Dust and metals. Sulphur dioxide.	Gas collection and fabric filter. Scrubber if necessary for SO_2.
Powder production	Ammonia	Gas collection and recovery. Acid medium scrubber.
High temperature reduction	Hydrogen.	Sealed process, reuse. Afterburner.
Electro-winning.	Chlorine. Acid mist.	Gas collection and re-use. Wet scrubber. De-mister.
Melting and casting.	Dust and metals.	Gas collection and fabric filter.

Note. * Dust arrestment using a fabric filter may require the removal of hot particles to prevent fires. Hot electrostatic precipitators would be used in a gas cleaning system prior to a sulphuric acid plant.

Table 11.15: Summary of the abatement options considered as Best Available Techniques

11.4.3.1 Emissions to air associated with the use of BAT

Emissions to air comprise the captured/abated emissions from the various sources, plus the fugitive or uncaptured emissions from these sources. Modern, well operated abatement systems result in efficient removal of pollutants and the information at the time of writing indicates that the fugitive emissions can be the largest contributor to the total emissions to air.

a) For smelting of nickel concentrates the total emissions to air are based on the emissions from:

- The material reception, storage, blending and sampling.
- The smelting, converting and slag cleaning furnaces with the associated hot gas handling and cleaning system.

- The slag handling system.
- The wet gas cooling and cleaning section and the sulphuric acid plant.

b) For the refining of nickel matte the total emissions to air are based on:

- The matte preparation and grinding process.
- The leaching and precipitation stages.
- The solvent extraction and purification stages.
- The electro-winning process.

c) For the carbonyl refining process the total emissions to air are based on:

- The material reception and storage.
- The hydrogenation and refining reactors.
- The decomposers with the associated gas handling and after-burning system.

d) For sheet or ingot production the total emissions to air are based on:

- The material reception and storage.
- The melting, refining and holding furnaces with the associated hot gas handling and cleaning system.
- The casting machinery, the fabrication units and auxiliary equipment.

Measurements have been carried out at one major copper/nickel smelter. The results clearly show that fugitive emissions would predominate if they were not collected and treated (Table 11.6). The following tables summarise the emissions associated with the use of BAT.

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 - 5 mg/Nm^3	Fabric filter	High performance fabric filters can achieve low levels of heavy metals. The concentration of heavy metals is linked to the concentration of dust and content of the metals in the dust.
NO$_x$	< 100 mg/Nm^3 < 100 - 300 mg/Nm^3	Low NO$_x$ burner Oxy-fuel burner	Higher values are associated with oxygen enrichment to reduce energy use. In these cases gas volume and mass emission is reduced.
Total organic carbon as C	< 5 - 15 mg/Nm^3 < 5 - 50 mg/Nm^3	Afterburner. Optimised combustion.	
Dioxins	< 0.1 - 0.5 ng TEQ/Nm^3	High efficiency dust removal system (i.e. fabric filter), afterburner followed by quenching. Other techniques are available (e.g. adsorption by activated carbon, oxidation catalyst).	Treatment of a clean de-dusted gas is required to achieve low levels
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 11.16: Emissions to air associated with the use of BAT from materials pre-treatment incineration or after-burning, roasting, smelting, thermal refining, and melting for nickel and cobalt production

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Acid mists Acid gases Ammonia	< 50 mg/Nm³ < 50 mg/Nm³ < 5 mg/Nm³	De-mister Wet alkaline scrubber. Acidic scrubber	A de-mister will allow the collected acid to be reused.
Chlorine	0.5 mg/Nm³	Collection and re-use. Alkaline scrubber	
CO and carbonyls	5 mg/Nm³	Process control and sealed reactor.	For the carbonyl process only - See above for the incineration stage.
NO_x	< 100 mg/Nm^3	Oxidising scrubber	
VOC or solvents as C	< 5 - 15 mg/Nm^3	Containment, condenser, carbon or bio filter	
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 11.17: Emissions to air associated with the use of BAT from leaching, chemical extraction and refining, electro-winning and solvent extraction for nickel and cobalt production

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Low SO_2 off-gas streams (~ 1 – 4%)	> 99.1	Single contact sulphuric acid plant or WSA, (tail gas SO_2 content depends on feed gas strength)	For low-grade SO_2 gases. Combined with dry or semi-dry scrubber to reduce SO_2 emission and produce gypsum if a market is available.
SO_2 – rich off-gas streams (> 5%)	> 99.7% conversion factor	Double contact sulphuric acid plant (tail gas SO_2 content depends on feed gas strength). A de-mister may be appropriate for the final removal of SO_3	Very low levels for other air-borne pollutants will be reached due to intensive gas treatment prior to the contact plant (wet scrubbing, wet EP and, if necessary, mercury removal to ensure H_2SO_4 product quality
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 11.18: Emissions to air associated with the use of BAT from the roasting and smelting of sulphide concentrates and intermediates for nickel and cobalt production

The metal content of the dust varies widely between processes. In addition for similar furnaces there are significant variations due to the use of varying raw materials. It is therefore not accurate to detail specific achievable concentrations for all metals emitted to air in this document. The issue is site specific.

Some metals have toxic compounds that may be emitted from the processes and so need to be reduced to meet specific local, regional or long-range air quality standards. It is considered that low concentrations of heavy metals are associated with the use of high performance, modern abatement systems such as a membrane fabric filter provided the operating temperature is correct and the characteristics of the gas and dust are taken into account in the design.

11.4.4 Wastewater

This is site specific issue. All wastewater will be treated to remove solids, metals, oils and organic material and absorbed components and should be neutralised if necessary. The following basic principles apply.

- Closed water cycles are suitable for wet scrubbers, cooling systems
- The bleed from closed water cycles needs to be treated to remove particulate matter and metal compounds from the water.
- Treated waste waster should be recycled and reused as much as possible
- Scrubbing liquids should also be treated and analysed before discharge.
- Containment of plant drainage systems where possible and treatment of effluents according to their content with analysis before discharge.

For cobalt and nickel production the total emissions to water are based on:

- The slag treatment or granulating system.
- The refining process used, the electro-winning circuit and the leaching section.
- The wastewater treatment system.

11.4.5 Process residues

The production processes have been developed by the industry to maximise the re-use the majority of process residues in the production units or to produce residues in form that enables them to be used in other non-ferrous metal production processes. Table 11.12 gives an overview of the potential end uses for residues and some specimen quantities.

The quantity of residues produced is strongly dependent on the raw materials in particular the iron content of primary materials, the content of other non-ferrous metals in primary and secondary materials and the presence of other contaminants such as organic materials. The emissions to land are therefore very site and material specific and it is therefore not possible to produce a realistic, typical table of quantities that are associated with the use of BAT.

The techniques presented in section 2.10 for waste minimisation will be part of BAT for this sector.

11.4.6 Costs associated with the techniques

Cost data has been compiled for a variety of process variations and abatement systems. The cost data is very site specific and depends on a number of factors but the ranges given may enable some comparisons to be made. The data is provided in an appendix to this note so that costs for processes and abatement systems over the whole of the non-ferrous metal industry can be compared.

11.5 Emerging Technologies

Various developments have been reported for the use of low pressure and atmospheric leaching for the production of nickel from sulphidic ores. The main processes are [tm 142, Finland Ni 1999]: -

- Activox leaching – fine grinding and leaching at 100 °C, 10 bar.
- Bio-leaching for mixed ores containing copper or gold using iron and sulphur oxidising bacteria.
- CESL process - chloride leaching in sulphate solution using ferric chloride.

  The processes have been proven at the pilot stage.

- Three new plants are under construction or are at the commissioning stage for the pressure leaching of laterites using sulphuric acid [tm 142, Finland Ni 1999]. The processes are similar to the established process used in Cuba but different purification stages are used to remove other metals. An atmospheric chloride leaching process for laterites is also being developed.

- A process is being commissioned in Germany to recover nickel and zinc from residues using a oxy fuel furnace and a solvent extraction refining system from sulphate solutions. Data is not available at the time of writing.

12 PROCESSES TO PRODUCE CARBON AND GRAPHITE ELECTRODES ETC.

12.1 Applied Processes and Techniques

There are a number of processes that are used to produce a wide range of carbon and graphite products. Carbon or graphite electrodes (anodes and cathodes) and furnace linings are produced for a variety of ferrous and non-ferrous metal production processes in particular primary aluminium smelting, ferro-alloy and steel production.

More than 2000 products of varying sizes, shapes and properties are produced for other applications.

All of the process use coke or carbon and other raw materials such as pitch to produce pastes, electrodes and shapes. Raw material storage and handling stages use enclosed coke delivery and handling systems and integral dust filters. Coal tar pitch and tar delivery and storage systems use tank back venting and condensers for tank breathing. The main product types and process stages are: -

12.1.1 Processes to produce electrodes.

Søderberg paste, Søderberg electrodes, prebaked anodes and graphite electrodes are made either in dedicated installations or in processes associated with primary aluminium smelting.

Raw Materials	**Process**	**Products**
Anthracite coal	Calcining	Calcined anthracite coal
Coke Additives (Solids)	Storage, Handling, Grinding, Sieving	Coke grain fractions
Pitch, Additives (Liquids)	Storage, Handling,	Pitch, Additives (Liquids)
Coke Pitch Additives	Mixing	Paste e.g. Tapping pastes, Søderberg Paste
Paste	Forming	Green Shapes e.g. Søderberg Electrodes
Green Shapes, Impregnated Shapes	Baking	Baked Shapes e.g. Prebaked Anodes
Baked Shapes Pitch, Resins other additives	Impregnation	Impregnated shapes
Baked shapes	Graphitising	Graphite Shapes
Baked and graphitised Shapes	Machining	Graphite &Carbon components

Figure 12.1: Overview of process steps

12.1.1.1 Green paste, Søderberg paste, Søderberg electrodes and green shapes

Green paste production is the starting point for the production of all carbon and graphite products. All green pastes are manufactured from a mixture of calcined petroleum coke and up to 28% coal tar pitch, which acts as a binder. The petroleum cokes are a residue from the distillation of crude oils and can therefore be contaminated with substances like metals (e.g. nickel) and sulphur compounds. Highly annealed metallurgical and lignite cokes are used as auxiliaries for packing. Calcined and annealed cokes by themselves are free of hydrocarbon and PAH.

Coke is normally transferred by sealed conveyor or dense phase pneumatic systems and is stored in silos. Pitch is transported in the molten state and is transferred by pumping and is stored in heated tanks, the tank ventilation gases contain hydrocarbon fume and are usually cleaned. Condensers or oil scrubbers are used [tm 77, Al Expert Group 1998] and back venting of the tank gases is also used. Petroleum coke is ground and then mixed with pitch in heated mixers. The ratio of coke and pitch is adjusted according to the application and to allow the paste to be handled.

In the case of Søderberg paste the blend is produced to allow it to be added to the electrode shell. Dry electrode paste (low pitch content) is preferred to minimise the amount of hydrocarbon released during use [tm 6, HMIP Al 1993]. Dry paste also improves electrical conductivity but a stud hole paste is required for the electrical connections and this paste uses up to 40% pitch. Søderberg paste is normally used for electrodes in the primary aluminium industry but the paste can be made into electrodes by pressing and forming for use in other applications for example in electric furnaces for the production of ferro-alloys.

Søderberg electrodes are also produced from the paste by a forming process. In this case the green electrodes are formed into the size and shape required and sold [tm 77, Al Expert Group 1998]. These electrodes are commonly used in submerged arc electric furnaces. A number of variants exist, for example hollow electrodes can be made to allow furnace feeding through the electrode and composite electrodes can be made to overcome production problems.

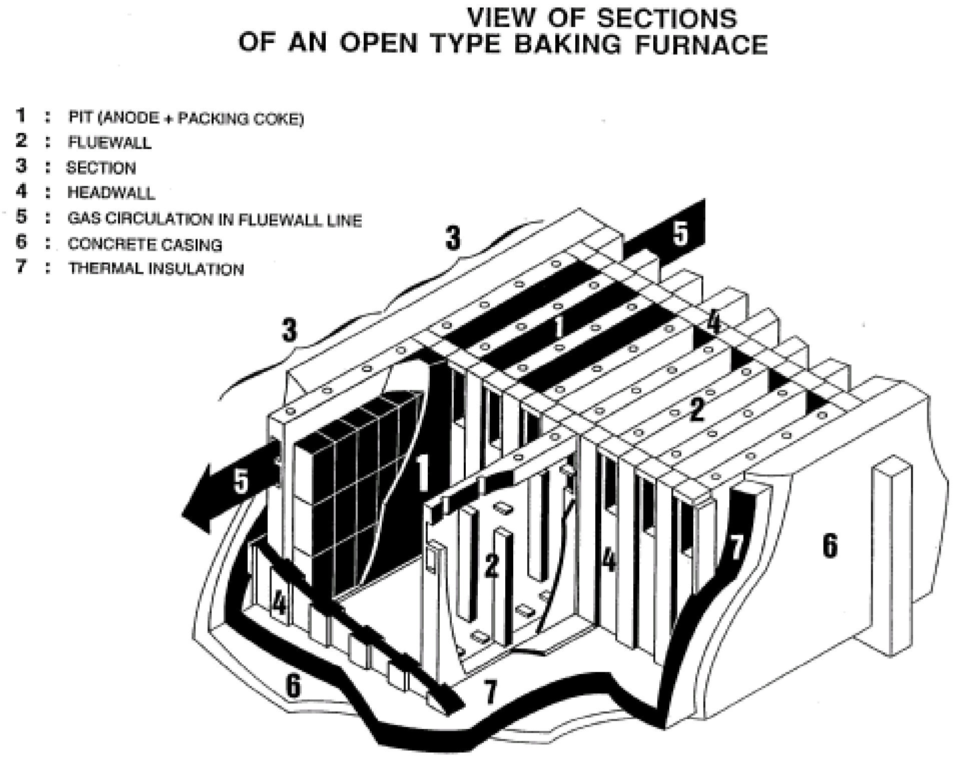
12.1.1.2 Prebaked anodes, electrodes and carbon shapes

The primary aluminium prebake process uses prebaked anodes, which are manufactured by anode production plants. These anode production plants can be associated within the site of the aluminium smelter and several of these plants produce anodes that are sold to other plants and processes. Other dedicated production sites produce a range of electrodes including cathodes and furnace linings.

These electrodes are also manufactured from a mixture of petroleum coke and 14 to 18% coal tar pitch and residual material from old anodes [tm 77, Al Expert Group 1998; tm 119, VDI 1998].

Electrode production involves crushing, grinding and mixing of the raw materials. The mixed materials are then formed into green electrodes. The green electrodes are then baked in ring furnaces comprising a large number of pits, which contain the electrodes. Refractory brick walls separate the pits and ducts are formed for the flue gases. Green electrodes are stacked in the anode furnace in rows and the heating ducts are formed. Layers of packing coke separate the anodes and prevent oxidation. This coke is consumed during the heating and cooling cycle at a rate of 12 to 18 kg per tonne of electrodes, the remaining coke is re-used. At any one time, pits in separate sections of the furnace are being filled, heated, cooled or emptied [tm 93, PARCOM 1992].

Hot air is passed through the ducts using movable gas fired burners and the electrodes are baked at 1100 °C in the absence of air. The ducts are kept under negative pressure to contain the fumes. At the end of the heating cycle the ducts are then connected to blowers to cool the section. Hot air passing from the furnace section being cooled is then recycled through the burners or through other furnace sections to preheat that part of the system.



VIEW OF AN OPEN TYPE BAKING FURNACE

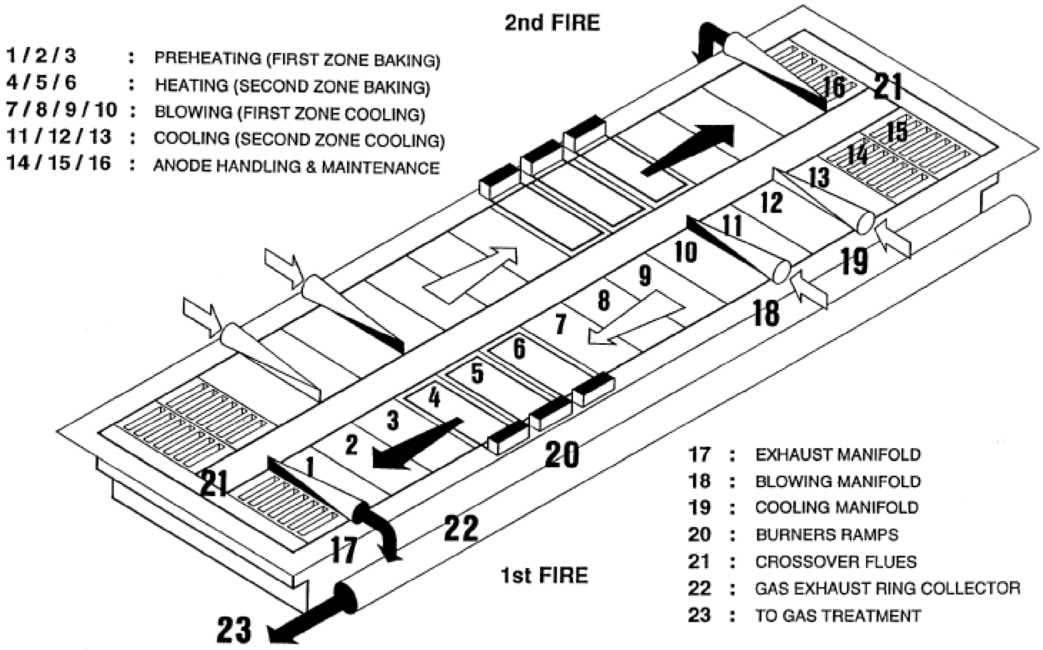


Figure 12.2: General views of an open baking furnace for anodes

Two types of furnace are used for anode baking; open and closed ring furnaces. Open furnaces use a horizontal duct and closed furnaces use a vertical flue. Open furnaces account for 60% of capacity. The horizontal ducts of the open furnace are separate and parallel, this allows the heating cycle to be optimised for each duct and so reduces fuel consumption [tm 93, PARCOM 1992]. The use of multiple chambers in the furnace allows heat from one section to be used in other sections as outlined below.

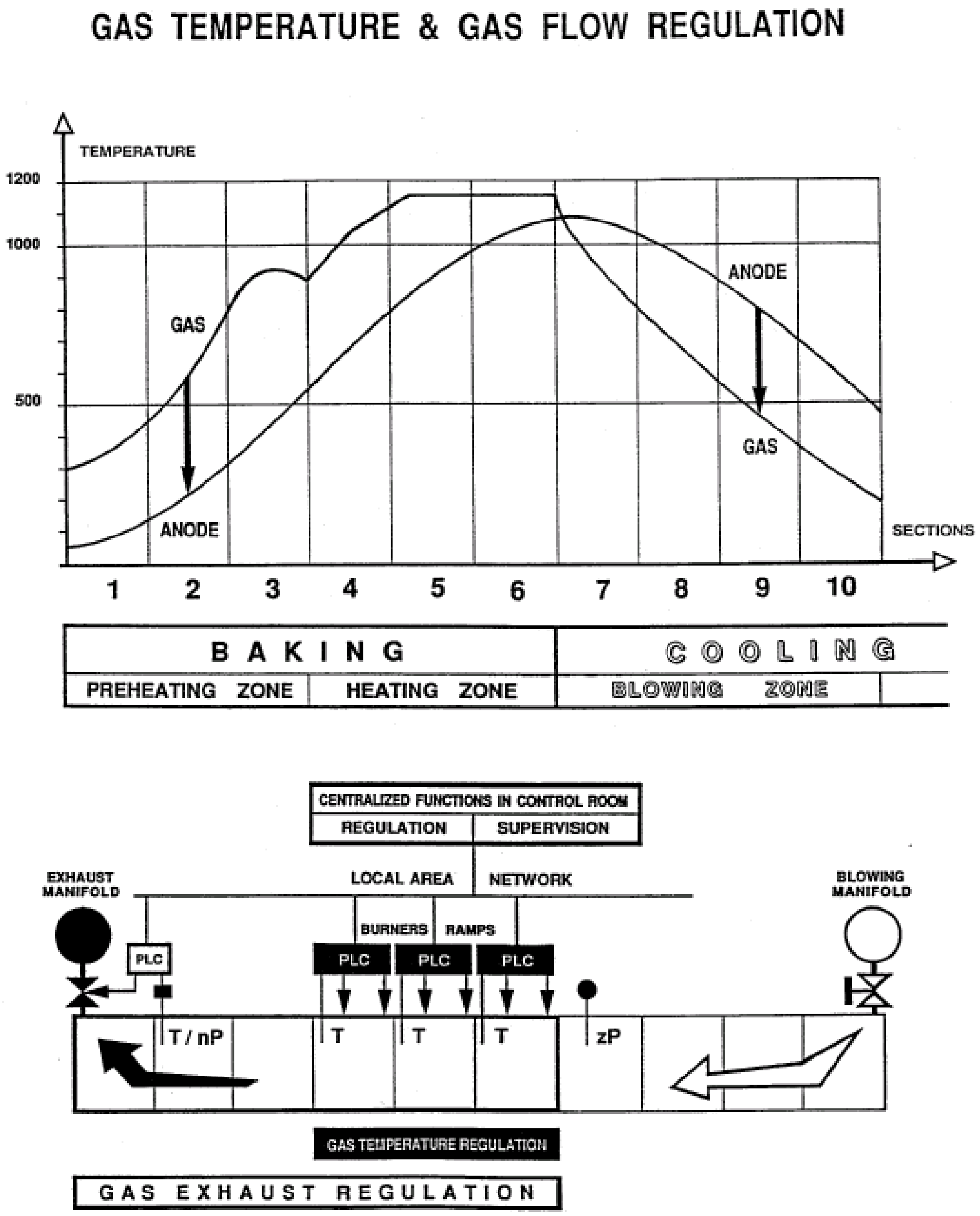


Figure 12.3: Temperature profile during the baking of anodes

During the baking process the coal tar pitch is converted into coke, making the material electrically conductive. There is a 5% loss in weight during baking [tm 77, Al Expert Group 1998], the baking process takes approximately 18 to 21 days.

In the aluminium industry the prebaked anodes are connected to the anode studs using rods. These are fixed into the anode in a rodding plant allowing the anodes to be placed in the top of the electrolysis pot using hangers. The anodes are consumed during the electrolysis and have to be replaced after about 80% of the anode is consumed [tm 6, HMIP Al 1993; tm 29, PARCOM 1997]. The anode residues (20% of original anode weight) are re-used for anode production after residual electrolyte has been removed. The steel rods are reconditioned for further use although a small proportion is scrapped if corroded.

12.1.1.3 Graphite electrodes

The production process for graphite electrodes (anodes and cathodes) is very similar to the production of the pre-bake electrodes; normally no residual anode material is used in the blend. Green shapes are first of all baked, the baking temperature used is ~ 1000 °C and the loss in weight during baking is increased to 15%.

Single chamber furnaces or pit furnaces are used as well as closed ring furnaces for the baking stage during graphite electrode production. Tunnel furnaces are used for small-scale production of speciality carbon.

Baked electrode material is then subject to impregnation with pitch, re-baking and graphitising. Machining and finishing stages follow to produce graphite electrodes.

Graphite is formed when prebaked carbon is heated to approximately 2800 °C. Graphitising of electrodes is usually carried out in Acheson or Castner furnaces.

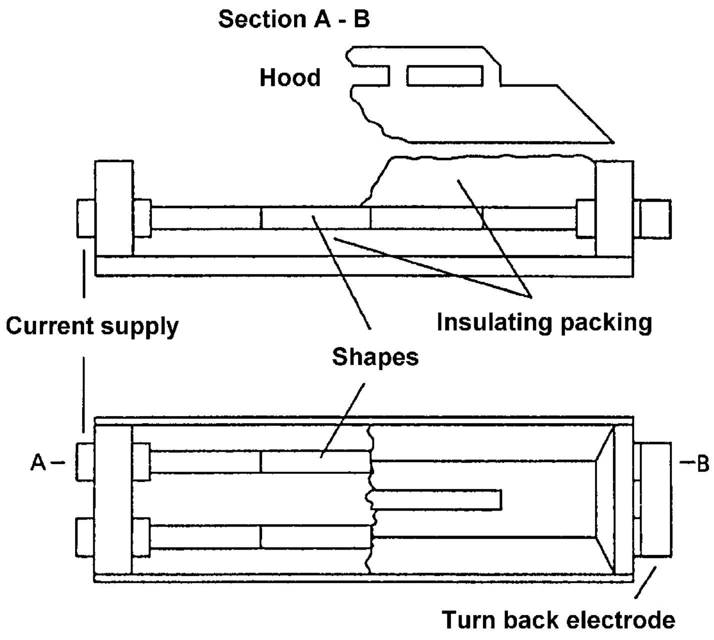


Figure 12.4: Castner graphitising furnace

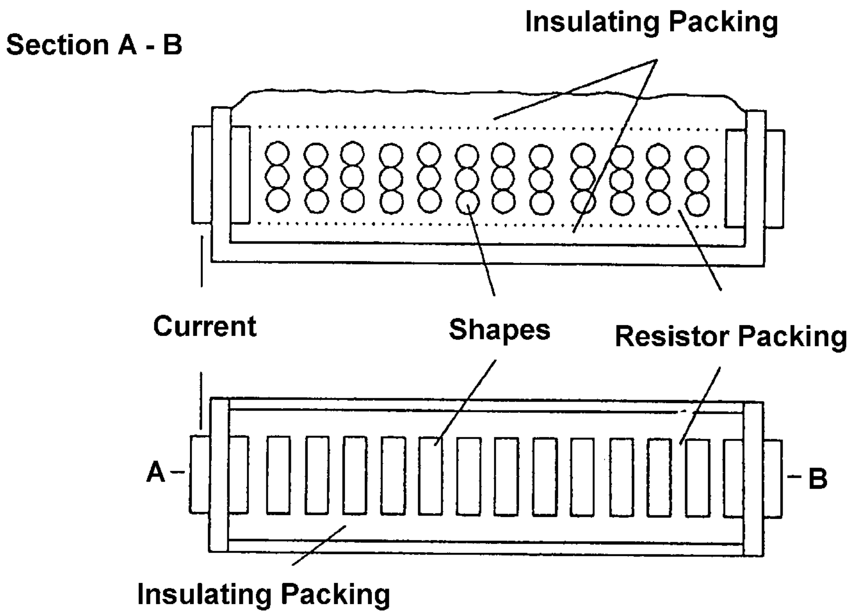


Figure 12.5: Acheson graphitising furnace

In some cases no hoods are used where there are only minor fugitive dust emissions and the carbon oxides are well dispersed at the roofline.

The Acheson furnace is used for carbon shapes with irregular dimensions and cross sections and the Castner furnace is used for shapes with parallel faces and equal cross sections. Both furnaces are electric resistance furnaces constructed from refractory material. They differ in the way the current is applied to the furnace. In the Acheson furnace shapes are placed inside the furnace body and the interstices filled with a carbon/graphite mixture (resistor packing), the current is passed through the resistor packing and the shapes. In the Castner furnace the shapes form the entire current path and can lead to gains in the current efficiency.

In the Acheson furnace thermal insulation is provided by a mixture of silicon carbide, coke, sawdust and sand. In the Castner furnace only coke is used. Heating cycles vary from 2 to 7 days and the cooling cycle takes up to 14 days. At the end of the cycle the insulation and resistor packing are processed and re-used [tm 119, VDI 1998].

The graphitised shapes are finished by turning, drilling, milling and similar processes to customers' requirements. The resultant final shapes are then polished. Dusts produced by these processes are collected and re-used as far as possible. The specific process depends on the final product.

These electrodes are used in electric arc furnaces in a variety of processes. Furnace linings are also produced in the same process and may be used in aluminium cells as cathodes (cathode blocks can be made from pre-baked, graphite or mixed prebake/graphite material). Carbon cathodes are also used in electric arc furnaces.

12.1.2 Processes to produce other carbon and graphite products

Other graphite products such as seals, brushes, crucibles and similar products are produced in a similar way to graphite electrodes. There are differences in the size and complexity of the products and this affects the processes that are used. Other additives such as sulphur and metals can be added to the blend of raw materials to give the desired physical properties to the product. Sometimes resins are used instead of pitch.

The grinding and mixing stages are important, as there are a wide variety of graphite products and specifications. The characteristics of these products often depend on a particular grain size. The choice of grinding or milling technique is made according to particle size of carbon required for a particular product. Green shapes are formed by moulding and these may be baked, re-baked and graphitised.

Heating the shapes to 2800 °C then produces graphite, which is then subjected to a number of finishing process such as machining and polishing [tm 119, VDI 1998].

The baked or graphitised components may be impregnated with other materials e.g. resins or metals. Impregnation is carried out by “soaking”, sometimes under vacuum and sometimes under pressure, autoclaves are used. Components that have been impregnated or bonded with coal tar pitch are re-baked. If resin bonding has been used they are cured.

Porous graphite is also produced in the basic process by blending sawdust with the raw materials. During baking the sawdust is combusted and a porous matrix of carbon or graphite remains.

High purity graphite is produced in a similar way but the graphitising process is used to remove included impurities such as metals. In this case Freons are used in the gas stream and they decompose to produce chlorine and fluorine, which react with metallic impurities to form volatile salts therefore removing the metals from the graphite. Current practice includes the use of Freons that are recovered from appliances and the process therefore provides a useful method for dealing with these materials. Excess halogens and the metal salts are removed from the off gas by dry scrubbing.

Special products such as carbon fibre reinforced carbon (CFRC), carbon fibres and carbon fabrics are also made, and an induction or pit furnace is used. The processes used to produce carbon fibres and associated materials can include acrylonitrile as a pre-cursor in the form of Poly Acrylonitrile cloth (PAN cloth) or as an impregnating agent [tm 131, Davies 1998]. In these cases hydrogen and sodium cyanides can be produced during the heating stages in a furnace. Sodium cyanide can be converted at high temperatures in the presence of carbon oxides into sodium carbonate. An afterburner is used to oxidise the gases emitted.

The process stages are described further below and are also shown in the following diagram.

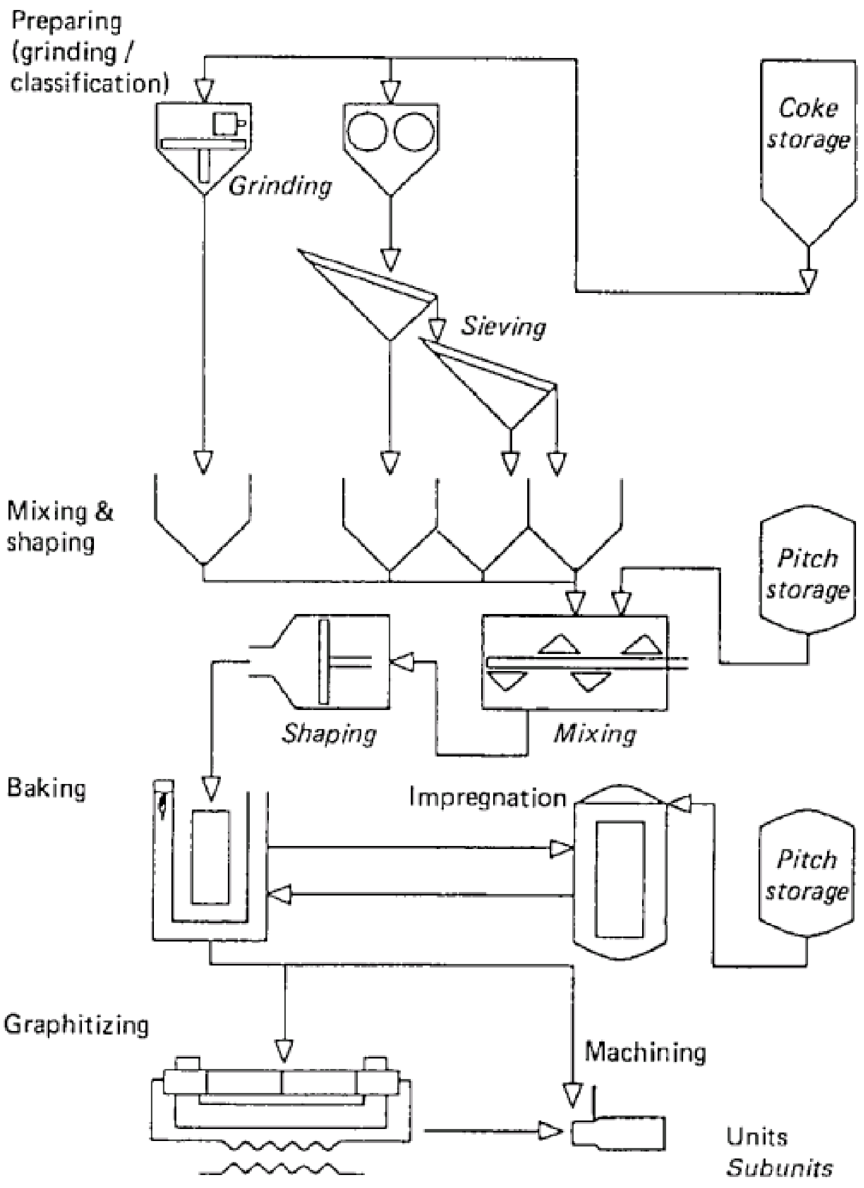


Figure 12.6: Graphite shape production

12.1.2.1 Blending and forming

Raw materials are mixed to produce a constant feed, weighing systems are used to fulfil a particular recipe depending on the product. A variety of mixers are used depending on the product required, the particle size of the raw material and the throughput required. Heated mixers and screw conveyors (typically at 200 °C) are used to prevent batches from solidifying and allow efficient discharge of contents. Kneading mixers, paddle mixers and continuous action mixers are used. Continuous or batch operation is practised and can depend on the scale of the operation.

The green mixture is passed to a forming process to produce the shapes required. Die moulding, extrusion and vibrating systems are used. During special carbon production, green shapes may be washed with alcohol to remove excess resin. Large shapes may also be cooled in a closed circuit water bath.

12.1.2.2 Baking and re-baking

Green shapes (or impregnated shapes) are baked at temperatures up to 1300 °C using a variety of furnaces such as tunnel, single chamber, multiple chamber, annular and push rod furnaces depending on the size and complexity of the product. Continuous baking is also carried out. The furnace operations are similar to those used for electrode baking but the furnaces are usually smaller.

The tunnel furnace is fed by pre-shaped forms that are carried through the fired zone in a metal sagger surrounded by packing material. The furnace is usually gas or oil fired and a recuperator is usually incorporated to preheat fuel or combustion air.

12.1.2.3 Impregnation

Tars, pitches, resins, molten metals (Si, Sb) can be added to the baked shapes and other reagents are used to fill the voids formed in the carbonised material. Soaking with or without vacuum and autoclaving are used. Various impregnating techniques are used depending on the product but batch or quasi-continuous operations are used. The impregnation cycle usually involves pre-heating, impregnation and cooling. A hardening reactor may also be used.

Only special carbons are impregnated with various metals.

12.1.2.4 Graphitising

Graphite is formed when prebaked carbon is heated to approximately 2800 °C. Graphitising is carried out tunnel, Acheson, Castner or induction furnaces depending on the size or shape of the component and the raw material used. Other specialised furnaces are also used for example the vacuum graphitising furnace for special products such as carbon composites.

The Acheson furnace is used for carbon shapes with irregular dimensions and cross sections and the Castner furnace is used for shapes with parallel faces and equal cross sections. Both furnaces are electric resistance furnaces constructed from refractory material. They differ in the way the current is applied to the furnace. In the Acheson furnace shapes are placed inside the furnace body and the interstices filled with a carbon/graphite mixture (resistor packing), the current is passed through the resistor packing and the shapes. In the Castner furnace the shapes form the entire current path and can lead to gains in the current efficiency. In the Acheson furnace thermal insulation is provided by a mixture of silicon carbide, coke, sand and sometimes sawdust. In the Castner furnace only coke is used. Heating cycles vary from 2 to 7 days and the cooling cycle takes up to 14 days. Energy use is in the range 9 to 20 GJ/t. At the end of the cycle the insulation and resistor packing are processed and re-used [tm 119, VDI 1998].

12.1.2.5 Product shaping

Sawing, turning, drilling, milling and similar processes are used to process the graphite shapes. The resultant final shapes are then polished. Dusts produced by these processes are collected and re-used as far as possible. The specific process depends on the final product.

12.1.2.6 Special processes.

Other processes such as resin or metal impregnation, graphite expansion and carbon fibre formation using controlled heat treatment are also used. A range of tailor made processes are employed that are not reported here.

12.2 Present Emission and Consumption Levels

About 40% of the coal tar pitch is volatilised during baking and more than 95% of the volatile hydrocarbons are burnt off at the high temperature in the furnace. Baking therefore results in a residual emission of hydrocarbons and PAHs due to their presence in the coal tar pitch. The potential emissions points from the various process stages are shown in the following figure.

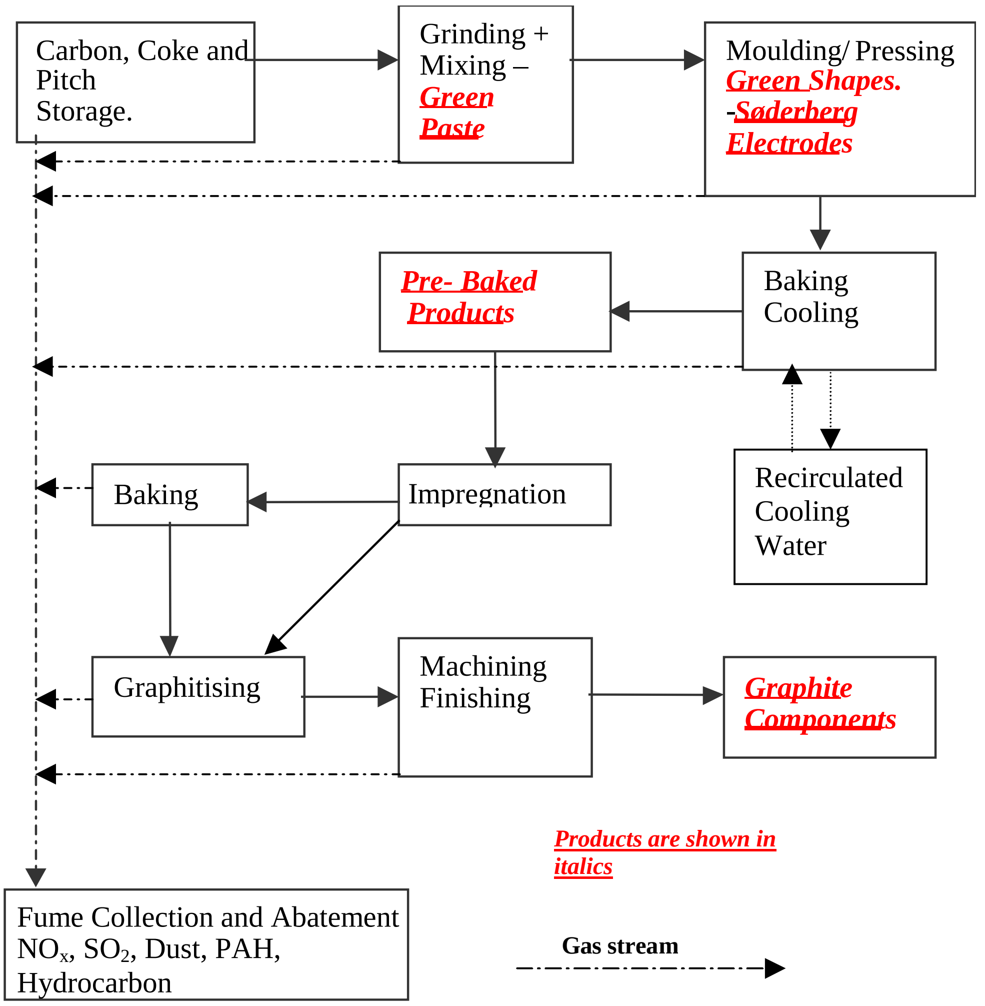


Figure 12.7: Generic emission diagram of the processes used

The furnace gases are treated by after-burning, wet scrubbing, dry scrubbing using coke, wet EPs or in the case of production of electrodes at a primary aluminium smelter, by contact with alumina in a scrubber/bag filter system [tm 77 & 90, Al Expert Group 1998]. Dust from handling and mechanical processes are collected in fabric filters. Solvents from washing stages of special carbon production are collected and re-used if possible or removed in bio filters.

The energy input to anode production is ~ 2300 MJ per tonne and is accounted for by the fuel used. There are also losses from the electrode, packing coke, refractory and fumes, the total is equivalent to 5500 to 6000 MJ per tonne [tm 93, PARCOM 1992]. Packing coke is consumed at a rate of ~12 to 18 kg per tonne of electrodes [tm 119, VDI 1998]. Energy use in graphitising is 9 to 20 GJ/t.

12.2.1 Emissions to air

The emissions can escape the process either as stack emissions or as fugitive emissions depending on the age of the plant and the technology used. Stack emissions are normally monitored continuously or periodically depending on the component measured and reported by on-site staff or off-site consultants to the competent authorities.

There are potential emissions to air of hydrocarbons and PAHs, sulphur dioxide, dust, fluorides (only for anode production if spent anodes form a source of carbon), Hydrocarbons (if solvents are used) and cyanide (only for fibre production from acrylonitrile). The formation of SO_2 is influenced by the fuel and raw materials used whereas the formation of NO_x is determined by the combustion temperature.

When an anode plant is associated with a primary aluminium smelter the process gases can be combined with the electrolysis cell gases and reacted with alumina in a dry scrubber. A fabric filter serves the scrubber and the alumina collected is used in the electrolysis cells. The data for combined processes is included with the data reported in chapter 4.

In stand alone processes or other carbon and graphite processes a combination of techniques such as afterburners, electrostatic filters and fabric filters are used. Coke filters have been recommended [tm 29, PARCOM 1997] but it is concluded that the tar fraction that is emitted by the baking process is the light condensable fraction. This may not be fully carbonised during the subsequent early stages of the baking of the coke (or if it is been formed into Søderberg paste). The fate of the various fractions is shown in the following figure.

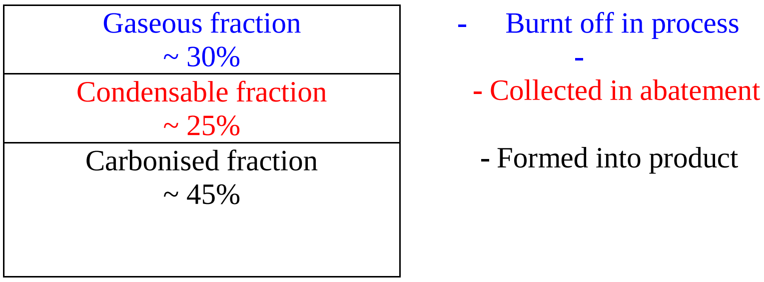


Figure 12.8: Fate of coal tar pitch fractions

There is therefore a distinct possibility that all of the condensable fraction may not be collected if absorption onto coke only is used for the baking stages. A significant portion of the tars can recycle from the coke filter material during the temperature gradient of the pre-heating stage of the baking furnace (fig. 12.3). When alumina is used as the scrubbing medium in an associated aluminium process, it is reported that the constant high temperatures in the cell bath destroy any hydrocarbons that have been collected on the recycled alumina provided that is not used as bath covering material [EAA]. A coke filter is appropriate for the mixing and forming stages when the pitch has not been broken down.

12.2.1.1 VOCs, Hydrocarbons and PAHs

Paste for anodes other electrodes and most special carbon products are produced from petroleum coke and coal tar pitch. Emissions of hydrocarbons as tars can occur during delivery, transfer, mixing and baking. Coal tar pitch also contains PAHs, which will also be emitted. PAHs are potentially hazardous in the environment as well as inside industrial plants and this is an important issue within the carbon industry. According to an investigation made in 1989, the total (uncontrolled) emission of PAHs by anode baking is 0.432 kg per tonne anode [tm 29, PARCOM 1997]. In modern plants, emissions from mixing and baking are therefore cleaned e.g. in condensing systems followed by dry scrubbing systems using alumina in a plant associated with a primary aluminium smelter or coke/lime, where the hydrocarbons and PAHs are returned to the production process [tm 119, VDI 1998]. Alternatively afterburners and wet EP's can be used depending on the site and scale of production.

12.2.1.2 Dust

During production dust emissions occur during all process stages (storage, transfer, mixing, grinding, baking, graphitising and shaping). The emission is mainly caused by dust generated during the grinding and screening and shaping processes and from the carbonisation gases. The mechanical handling and treatment stages are usually enclosed and extracted [tm 119, VDI 1998]. The source of dust and its characteristics influence the abatement method used to remove it, carbon dust can be very fine and abrasive.

In some cases of manufacturing special carbon and graphite products, absolute filers are used to remove it; the cleaned air is then used in the workplace.

The techniques and achievable emissions are described in Chapter 2.

12.2.1.3 Combustion gases

Gases produced from the combustion of gas or fuel oil will be emitted from the process. There are potential emissions of carbon oxides and the oxides of sulphur and nitrogen. Optimisation of combustion conditions and the use of low NO_x burners is commonly practised and fuel choice is made according to site conditions.

12.2.1.4 Sulphur dioxide

The raw materials from which the products are made contain sulphur and the fuel used for heating can also contain sulphur. This results in an emission of sulphur dioxide during baking [tm 6, HMIP Al 1993]. The emission of SO_2 is in the range 0.5 (gas) to 2 kg (fuel oil) per tonne aluminium depending on the fuel (based on an anode consumption of 0.4 tonne per tonne aluminium). This is far less than the emission of sulphur dioxide produced during electrolysis [tm 100, NL Al 1998]. Sulphur is also added to the blend to produce desired characteristics in special graphite products. This can be a significant source of sulphur dioxide and wet scrubbers are used to remove this.

12.2.1.5 Fluorides (Anode production if anode remnants are used)

Fluorides are emitted when spent anodes from the aluminium electrolysis process are used in the blend for anode production. The spent anodes are slightly contaminated with fluorides from the electrolyte. Emissions of particulate fluoride from anode baking plants are negligible. The HF emissions from the anode baking (if scrubbed) equal about 1% of the emissions generated by aluminium electrolysis [tm 100, NL Al 1998].

12.2.1.6 VOCs (Manufacture of special carbon and graphite products)

VOCs may be emitted from vacuum and other systems used for impregnation. After - burning or adsorption techniques are used to control these, [tm 119, VDI 1998]. Washing and drying stages in special carbon use solvents such as ethanol. These materials are potential sources of odours and are usually removed at source. Bio filters are used to absorb and decay the organic components and remove odours from the gas stream. The gas is pre-wetted and usually passes through a number of filters in series. The bio-filters operate on a batch basis and the biological substrate (peat, twigs etc.) is replaced periodically.

12.2.1.7 Cyanides (poly acrylo nitrile (PAN) based carbon fibre production)

Cyanides are produced during the decomposition of acrylonitrile (in PAN cloth) used in the production of carbon fibres. HCN concentrations of 55 mg/Nm^3 have been reported during periods when abatement has not been available [tm 131, Davies 1998]. Afterburners are used to decompose hydrogen cyanide.

Sodium cyanide can also be formed if sodium thiocyanate is used as a solvent for acrylonitrile. In this case the sodium is driven off the carbon fibre during the high temperature treatment stage and sodium cyanide solid is formed during cooling. In the presence of CO_2 at high temperatures it is mainly converted into sodium carbonate.

12.2.1.8 Dioxins

Current test results on emission sources and abatement units in this sector indicate that dioxins are not relevant for the conventional carbon and graphite manufacturing processes. This will need to be examined if chlorine compounds or additives are used.

12.2.1.9 Summary of main air pollutants.

Component	Raw gas content (kg/tonne aluminium*)	Remarks
Fluorides (gaseous)	0.05 - 0.6	Emission of solid fluoride is usually negligible
PAHs Hydrocarbons	0.15 - 0.5 25 – 40	Estimated value based on a weight loss of about 5% during baking
Dust	5 – 10	Estimated value
Note. For a process associated with primary aluminium production. Raw gas masses of various pollutants. Captured emissions are treated in the alumina scrubber/fabric filter that is used for the electrolysis gases.		

Table 12.1: Raw gas from anode production in a plant associated with a primary aluminium smelter

Component	Typical range	Comment
Fluoride kg/t	0.01 - 0.1	
Dust kg/t	0.01 - 1.0	
BaP g/t	0.0015 - 3.0	
SO_2 kg/t	0.1 - 6.0	
NO_x kg/t	0.1 - 0.4	

Table 12.2: Mass releases from the production of prebake anodes

Source	**Abatement type**	**Pollutant**	**Concentration range mg/Nm^3**
Material storage and Handling Coke	Cyclone	Dust	20 - 150
	Fabric filter	Dust	1 - 90
Material storage and Handling Pitch	Re-venting, Condensation	Hydrocarbon	1 - 75
Grinding and mixing	Afterburner	Dust	1 - 15
		Hydrocarbon	1 - 100
		PAH VDI $_{I+II}$	0.007 - 8.0
		Benzene	0.06 - 0.25
	Adsorber	Dust	1 - 50
		Hydrocarbon	19 - 150
		PAH VDI $_{I+II}$	0.1 - 1.0
	Scrubber	Dust	10 - 50
		Hydrocarbon	20 - 150
		PAH	0.1 - 1.0
Baking and re - baking	EP adsorber	Dust	2.5 - 90
		Hydrocarbon	50 - 250
		PAH	0.003 - 6
		Benzene	1 - 11
	Afterburner - conventional thermal oxidiser (CTO)	Dust	1 - 40
		Hydrocarbon	2 - 17
		PAH VDI $_{I+II}$	0.003 - 0.2
		Benzene	0.15 - 7.5
		SO_2	20 - 100
		NO_x	50 - 250
	Afterburner - Regenerative thermal oxidiser (RTO)	Dust	1 - 60
		Hydrocarbon	6 - 100
		PAH VDI $_{I+II}$	0.01 - 0.5
		Benzene	0.1 - 3.5
		SO_2	2 - 150
		NO_x	10 - 40
	Dry scrubber. (alumina or carbon/lime)	Dust	<1 - 14
		Hydrocarbon	1 - 135
		PAH	0.002 - 55
Impregnation	Afterburner - (CTO)	Dust	1 - 40
		Hydrocarbon	3.5 - 7.5
		PAH	0.0002 - 0.2
		Benzene	0.4 - 7.5
		SO_2	20 - 100
		NO_x	50 - 250
	Cooler and filter	Dust	1 - 4
		Hydrocarbon	4 - 40
		PAH VDI $_{I+II}$	0.001 - 0.1
Graphitising	Fabric filter	Dust	1 - 20
		Hydrocarbon	1 - 25
Machining and shaping	Fabric filter	Dust	1 - 35
		Hydrocarbon	1 - 25

Table 12.3: Emission ranges for a number of carbon and graphite processes
The regenerative afterburner (regenerative thermal oxidiser RTO) is still being developed

Component	Calcining	Storage and Handling	Grinding and Milling	Mixing and Forming	Baking	Impregnation	Graphitising	Machining
Sulphur dioxide	••[1&2]				••[1&2]		••[2]	
Halides		• (if anodes reclaimed)	• (if anodes reclaimed)	• (if anodes reclaimed)	• (if anodes reclaimed)		••[3]	
Hydrocarbon inc. PAH	•	•••[5] •[6]	•	••	•••	•••		
Cyanide					••[4]		••[4]	
Nitrogen oxides					••[2]		••[2]	
Dust	•	••	•••	••	•		••	•••

••• More significant…………..• less significant

1 With sulphur containing raw materials.
2 Combustion gases.
3 With high purity graphite.
4 With carbon fibres.
5 High concentration during loading. Solid pitch.
6 High concentration during loading. Liquid pitch

Table 12.4: Significance of potential emissions to air from carbon and graphite production

PAH values are subject to some uncertainty. Several standardised methods exist to measure and report PAH, the following groups of PAHs have been included in the reported data: - VDI-group I(2), VDI-group II (7), OSPAR 11 (11), EPA (16). Low molecular weight PAHs are very sensitive to the sampling and testing conditions and procedures. There is therefore some uncertainty in EPA data due to the possible incompleteness of their collection. The PAH compounds measured and reported for these conventions are shown in table 12.10.

The following table gives the ranges reported for PAH emissions from a variety of abatement systems using these conventions.

Abatement method	**BaP µg/Nm^3**	**VDI-I µg/Nm^3**	**VDI-I+II µg/Nm^3**	**OSPAR 11 µg/Nm^3**	**EPA µg/Nm^3**
CTO	0.03	0.04	3.35*	64.6	75.6
CTO		< 1	10		260 - 330
RTO		< 1 - 4	10 - 50		
RTO		0.08 – 0.92	10 - 20		
Wet scrubber		1 - 27			1670 - 2980
Dry scrubber		1 - 12	14		
Dry scrubber		6.7 – 9.2	11 - 1350		2320 - 3754
Dry scrubber	1.3	1.4	153*	46875	55383
Dry scrubber	0.6 – 2.6	0.8 – 2.8	150 - 293*	38831 - 46865	47794 - 55334
Electrostatic precipitator	34	43.8	471	6251	8049
Electrostatic precipitator	10.6 – 45.3	13.7 – 56.5	199 – 613		
Electrostatic precipitator	1 - 8	1 - 8	200 - 800		2650 – 6300

Table 12.5: Examples of some ranges of PAH reported using different groups of compounds
***) VDI –I+II without benzo(b)naphol(2,1-d)thiophene.**

12.2.2 Wastewater

The production of electrodes and graphite shapes are inherently dry processes. Discharge of process wastewater is usually limited to cooling water but most processes use a sealed cooling system. Rainwater run-off from surfaces and roofs may contain carbon dust and associated material. Open storage of raw materials and deposited solid emissions are the source of potential contamination. Typical values for processes associated with primary aluminium production for this contamination are < 0.03 kg/tonne for suspended solids and < 0.02 kg/tonne for dissolved fluoride [tm 100, NL Al 1998]. Current practice is to use vacuum systems for material transfer and closed silos for storage. Contamination of runoff is therefore reduced.

Considerable amounts of wastewater can be discharged when wet systems are used for air pollution control. The wastewater produced by wet systems is regarded to be a cross-media effect of the abatement techniques. Wet EPs are used frequently to remove hydrocarbons from the furnace exhaust and this is a potential source of contaminated wastewater. Some bio filters may also produce wastewater depending on the biological process that is used.

The processes can account for the production of wastewater consisting of cooling water, used to cool the green anodes or from the flue gas treatment. The cooling process can be performed using indirect water systems, resulting in a discharge of clean cooling water. Indirect water systems can also be used to cool the flue gases, to make them suitable for abatement with regular techniques [tm 93, PARCOM 1993] (bag filters, electrostatic precipitators).

12.2.3 Process residues

The production of carbon and graphite is related to the generation of several by-products, residues and wastes, which are also listed in the European Waste Catalogue (Council Decision 94/3/EEC). The most important process specific residues are listed below.

Refractory bricks from the baking furnaces. These bricks can be re-used in other applications after cleaning or can be landfilled as waste. Typical furnace lining life for prebaked anodes is about 100 cycles and this represents approximately 10 kilograms of bricks per tonne of anode produced.

Other residues include the material removed during the shaping, cutting and grinding stages together with tar or pitch fractions. Depending on the material, they are usually suitable for recycling within the process as raw materials or in other processes as fuel or carburant. In some cases carbonised or graphitised material is deliberately produced so that it can be ground and returned as raw material so that the properties of the product can be controlled.

Used biological substrate is also disposed but has some value as a soil conditioner provided that toxic components have been decayed.

12.3 Techniques to Consider in the Determination of BAT

This section presents a number of techniques for the prevention or reduction of emissions and residues as well as techniques reducing the overall energy consumption. They are all commercially available. Examples are given in order to demonstrate techniques, which illustrate a high environmental performance. The Techniques that are given as examples depend on information provided by the industry, European Member States and the valuation of the European IPPC Bureau. The general techniques described in chapter 2 “common processes” apply to a large extent, to the processes in this sector and influence the manner in which the main and associated processes are controlled and operated.

The particular techniques that are pertinent to this group are outlined below. The raw materials handling and pre-treatment processes and the process control and abatement systems are particularly relevant. The control of furnace operating parameters and the prevention of fugitive emissions from furnaces is also important. Techniques used by other sectors are also applicable particularly those relating to the use of hydrocarbon and PAH removal systems.

The techniques to consider on a site by site basis are strongly influenced by the product specification and this influences some of the raw materials and processes used. The basic processes outlined in the section on applied techniques therefore constitute techniques to consider for the production processes when used with appropriate abatement stages. The techniques to consider for collection and abatement stages and other aspects of process operation and control are covered in section 2.

12.3.1 Materials storage, handling and pre-treatment processes

The raw materials are carbon, coke, pitch, sawdust, fillers and resins. Important aspects are the prevention of leakage of dust and wet material, the collection and treatment of dust and liquids and the control of the input and operating parameters of the handling and feeding processes.

The issues specific to this group are: -

- The potentially dusty nature of some raw materials means that enclosed storage, handling and treatment systems are used in these instances.

- The dust generated by some crushing, grinding operations means that collection and abatement may be applicable for this process.

- The storage of raw materials depends on the nature of the material described above. The storage of fine dusts in enclosed buildings or in sealed packaging is used. Liquid pitch storage in tanks with condensers to remove hydrocarbons during breathing and venting of displaced gases back to the tanker during delivery.

- Materials that contain water-soluble components are stored under cover.

- The storage of non-dusty, non-soluble material in open stockpiles and large items individually in the open.

The following table summarises the techniques to consider for the material storage, handling and pre-treatment stages.

Material	Storage	Handling	Pre-treatment	Comment
Carbon or Coke.	Silos.	Pneumatic. Covered conveyors if non-dusty.	Grinding or milling. Blending	
Fuel, pitch and other oils. Solvents or resins.	Tanks or drums in bunded areas.	Secure pipeline or manual system.	Grinding or milling. Blending, Impregnation	Oil collection if necessary. Back venting of tanks recovery of solvents
Fine carbon and graphite dust and grained material	Enclosed.	Enclosed with dust collection. Pneumatic.	Grinding or milling. Blending	
Coarse carbon and graphite grains and lumps	Covered or open bays.	Mechanical loader	Grinding or milling. Blending	
Products: – Shapes Powders.	Covered or open store. Drums or bags.		Impregnation	
Process residues for recovery.	Covered or enclosed depending on dust formation.	Depends on conditions.		Appropriate drainage system.
Wastes for Disposal.	Covered or enclosed bays or sealed (drums) depending on the material.	Depends on conditions.		Appropriate drainage system.

Table 12.6: Techniques to consider for storage, handling and pre-treatment methods

12.3.2 Other process stages

The processes used are strongly influenced by the product and its specification. These factors are therefore site specific. The blending and forming, baking (production of anodes), impregnation, graphitisation, product shaping and fume collection and abatement systems described as applied techniques are therefore techniques to consider in the determination of BAT. Essentially the process technologies discussed in this chapter, combined with suitable abatement discussed in chapter 2 will meet the demands of stringent environmental protection [tm 207, TGI 1999]. The following are the most important techniques to consider: -

- Enclosed and extracted grinding and blending of raw materials, fabric filters for abatement.
- Use of furnaces with adequate extraction of process gases. Furnaces operated on planned basis to allow cooling and heating periods to maximise heat recovery from the gases.
- Destruction of cyanides, tars and hydrocarbons in an afterburner if they have not been removed by other abatement.
- Use of low NO_x burners or oxy-fuel firing. Control of the firing of furnaces to optimise the energy use and reduce PAH and NO_x emissions.
- Adequate maintenance of the furnaces to maintain the sealing of off-gas and air ducts.
- Monitoring of the off-gas collection system to identify blockages or potential explosive mixtures caused by condensing hydrocarbons.

- Use of wet or semi-dry scrubbing to remove sulphur dioxide if necessary.
- Use of coke bed filters or dry scrubbers plus fabric filters.
- Electrostatic precipitators to remove tars hydrocarbons and PAHs emitted from pitch storage, blending, impregnation, forming and baking stages. Use of afterburners to reduce their levels further if necessary.
- Use of bio filters to remove odorous components if necessary (special carbon production).
- Use of sealed or indirect cooling systems.

Reagent Used.	**Component in off - gas.**	**Treatment Method.**
Solvents, VOCs	VOC	Condensation. Activated carbon, Bio-filter
Freons, Halides	Cl_2, F_2, HF, HCl	Collection. Caustic scrubber system
Nitric acid	NO_x	Oxidise and absorb, recycle, scrubber system
Tars, pitches	Hydrocarbons, PAH	Afterburner, condensation, EP, carbon filter, alumina scrubber.
Sulphur	SO_2	Wet or dry scrubber system
Poly acrylo-nitrile (PAN)	HCN	After-burning

Table 12.7: Treatment methods for gaseous components

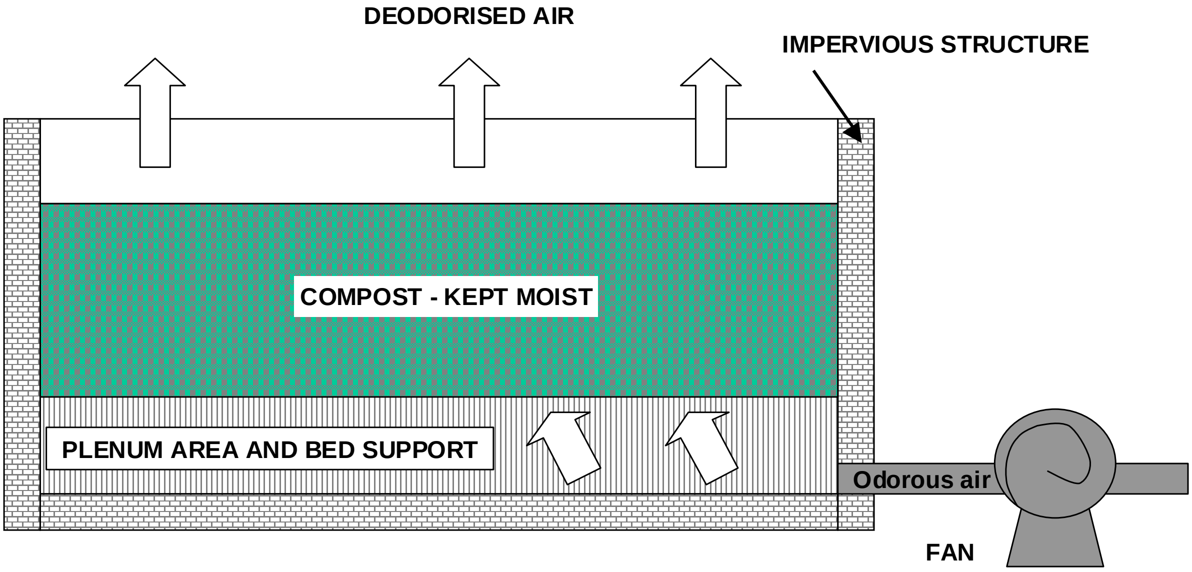


Figure 12.9: Example of a Bio-filter

EXAMPLE 12.01 DRY ABSORPTION OF FLUORIDES AND PAHS

Description: - The emissions from the production of green anodes and anode baking can be reduced by dry adsorption combined with dust removal. The dry adsorption technique is based on the principle that the pollutants are adsorbed on the surface of a medium, consisting of particulates. Fluorides, hydrocarbons and especially PAHs tend to adhere to these particulates. The particulates with the adsorbed pollutants are removed from the flue gas by regular dust abatement techniques like fabric filters.

Main environmental benefits: - Removal of hydrocarbons, PAHs and dust

Operational data: - Alumina is often applied as adsorption medium by aluminium plants with an integrated anode production facility. Coke dust and lime can also be used as adsorption medium. The adsorption medium is often removed from the flue gas by fabric filters. These fabric filters have the advantage that an additional adsorption layer is build up on the filter surface. The application of fabric filters is limited by both humidity and temperatures of gas-laden streams. Hence, the flue gases are often pre-treated by a conditioning tower. Electrostatic precipitators can also be used as a pre-treatment to remove particulate matter from the flue gas prior to the dry adsorption.

The adsorption medium has to be removed periodically from the system and is often re-used within the production processes. Alumina can be re-used for the electrolysis and coke dust for anode production. The PAHs and condensable hydrocarbons are burned at the high temperatures of these processes. SO_2 is also initially removed, but is released again during the re-use of the adsorption medium and will in due course be emitted to the atmosphere.

As most of the aluminium plants already apply dry adsorption with alumina combined with dust removal to reduce their emissions from the electrolysis, this technique is also often applied for the flue gases from the anode production. Other plants apply systems based on cokes dust as adsorption medium that is re-used within the anode production (e.g. stand-alone anode production). It should be noted that the dry adsorption combined with dust removal is often applied within a combination of techniques (condensation, dry adsorption and in some situations wet scrubbing) to reduce the emissions of the anode production.

Cross media effects: - Depends on the reuse of the adsorbent within the process. The dry adsorption combined with the dust removal accounts for an additional energy consumption. No information could be retrieved on the specific energy consumption of this technique for the abatement of the emissions caused by the anode production.

Economics: - Based on data of two anonymous plants, the operational costs for dry scrubbing range from ECU 2 to 5 per tonne aluminium.

Applicability: - Alumina scrubber - Anode or paste plants associated with primary aluminium smelter. Coke scrubber - Provided that the coke adsorbent is reusable within the process as powder or grains.

Example plants: - France, Germany

Reference literature: - [tm 100, Nl Al 1998]

EXAMPLE 12.02 USE OF CONDENSATION AND EPS

Description: - The volatile hydrocarbons emitted during anode baking can be condensed and the condensed hydrocarbon particulates are removed from the flue gas. As the PAHs tend to adhere to the condensed hydrocarbon particulates, the PAH emission is also reduced. Condensation can be achieved by external and/or internal cooling with air and/or water systems. Condensation is often achieved within conditioning towers.

The condensed hydrocarbon particulates can be removed from the flue gas by regular dust abatement techniques like fabric filters or electrostatic precipitators.

Main environmental benefits: - Removal and recovery of the condensable hydrocarbon

Operational data: - Not available

Cross media effects: - Beneficial effect by recovering hydrocarbon for use in the process. Some energy costs for cooling.

Economics: - Not available but several installations are operating viably.

Applicability: - Pre-treatment stage for several process abatement stages.

Example plants: - Germany

Reference literature: - [tm 106, Farrell 1998]

EXAMPLE 12.03 USE OF REGENRATIVE AFTERBURNER.

Description: - A regenerative afterburner has been used in a number of applications. The process depends on an alternating cycling of gases through a series of support zones where heating, cooling and cleaning cycles take place. The combustible fraction is heated in the heating zone and passes to a common residence chamber where combustion is completed, the hot gases then pass into a cooling section which is heated to become the next heating zone. The zones are change using a manifold system to allow cleaning.

Main environmental benefits: - The energy content of the contaminants (hydrocarbon and PAH) is used to heat the support materials and auto-thermal operation is therefore possible.

Operational data: - Not available but < 0.1 ng/Nm^3 dioxins have been reported for an installation serving a blast furnace.

Cross media effects: -Auto-thermal operation.

Economics: - Not available but several installations are operating viably.

Applicability: - Applicable to a variety of processes. The basic principle is good but the changeover to the cleaning phase may cause the emission of un-combusted material if the design is poor. It is considered to be emerging for high molecular weight, condensable hydrocarbons.

Example plants: - Germany, UK.

Reference literature: - [tm 106, Farrell 1998]

12.3.3 Wastewater

This is a site-specific issue, water recirculation is practised extensively. Existing treatment systems are reported to be to a high standard. All wastewater will be treated to remove hydrocarbon and solids. The techniques listed in chapter 2 are the techniques to consider. In a number of installations cooling water and treated wastewater including rainwater is reused or recycled within the processes.

12.3.4 Process residues

The principles of the minimisation and re-used of process residues are techniques that form part of BAT.

12.4 Best Available Techniques

In understanding this section and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector; which for the production of carbon and graphite are PAHs, Hydrocarbons, dust, fume, odours, SO_2, wastewater prevention, residues such as filter dust;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous section. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this section are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

Best Available Techniques are influenced by a number of factors and a methodology of examining the techniques is needed. The approach that has been used is given below.

First of all the choice of process depends strongly on the products that are made, in particular their size and additives needed.

Secondly, the process should be suitable for use with the best gas collection and abatement systems that are available. The fume collection and abatement processes used will depend on the characteristics of the main processes, for example some processes are easier to seal.

Finally, the water and waste issues have been taken into account, in particular the minimisation of wastes and the potential to reuse residues and water within the process or by other processes. Energy used by the processes is also a factor that is taken into account in the choice of processes.

The choice of BAT in a general sense is therefore complicated and depends on the above factors. The varying requirements mean that BAT is influenced mainly by the desired products and their properties.

The following points summarise the recommended methodology that has been used in this work: -

- Is the process industrially proven and reliable?
- Are there limitations in the feed material that can be processed?
- The type of feed and other materials contained in it influences process selection for particular products.
- Are there production level constraints? - e.g. a proven upper limit or a minimum throughput required to be economic.
- Can latest and efficient collection and abatement techniques be applied to the process?
- Can the process and abatement combinations achieve the lowest emission levels? The achievable emissions are reported later.
- Are there other aspects such as safety that are related to processes?

At the time of writing several process and abatement combinations are able to operate to the highest environmental standards and meet the requirements of BAT. The processes vary in the throughput that can be achieved, the materials that are used and the products that can be made and so the process stages that are described as techniques to consider form the basis of BAT. The collection and abatement techniques used with these processes were discussed under techniques to consider in the determination of BAT and when applied in combination with the process will result in a high level of environmental protection.

As indicated in the general preface to this document, this section proposes techniques and emissions that are considered to be compatible with BAT in general. The purpose is to provide general indications of the emission and consumption levels that might be considered as an appropriate benchmark of BAT based performance. This is done by quoting achievable levels in ranges that are generally applicable to both new and upgraded plants. Existing installations may have factors, such as space or height limitations that prevent full adoption of the techniques.

The level will also vary with time depending on the condition of the equipment, its maintenance and the process control of the abatement plant. The operation of the source process will also influence performance as there are likely to be variations in temperature, gas volume and even the characteristics of the material throughout a process or batch. The achievable emissions are therefore only a basis from which actual plant performance can be judged. Process dynamics and other site specific issues need to be taken into account at a local level. The examples given in the section on techniques to consider in the determination of BAT give the concentrations associated with some existing processes.

12.4.1 Materials handling and storage

The conclusions drawn for Best Available Techniques for the materials handling and storage stages are shown in section 2.17 of this document and are applicable to the materials in this chapter. The following table summarises the methods considered to be BAT.

Material	**Storage**	**Handling**	**Pre-treatment**	**Comment**
Carbon or Coke.	Silos.	Pneumatic. Covered conveyors if non-dusty.	Grinding or milling. Blending	
Fuel, pitch and other oils. Solvents or resins.	Tanks or drums in bunded areas.	Secure pipeline or manual system.	Grinding or milling. Blending, Impregnation	Oil collection if necessary. Back venting of tanks recovery of solvents
Fine carbon and graphite dust and grained material	Enclosed.	Enclosed with dust collection. Pneumatic.	Grinding or milling. Blending	
Coarse carbon and graphite grains and lumps	Covered or open bays.	Mechanical loader	Grinding or milling. Blending	
Products: – Shapes Powders.	Covered or open store. Drums or bags.		Impregnation	
Process residues for recovery.	Covered or enclosed depending on dust formation.	Depends on conditions.		Appropriate drainage system.
Wastes for Disposal.	Covered or enclosed bays or sealed (drums) depending on the material.	Depends on conditions.		Appropriate drainage system.

Table 12.8: Storage, handling and pre-treatment methods considered to be BAT

12.4.2 Process selection

It is not possible to conclude that a single production process can be applied to this group. The choice of process is highly dependent on the required physical and chemical characteristics of the final product. The techniques outlined above when used with well designed and operated abatement systems can all achieve similar environmental performance.

12.4.3 Gas collection and abatement

The fume collection systems used should exploit furnace or reactor sealing systems and be designed to maintain a reduced pressure that avoids leaks and fugitive emissions. Systems that maintain furnace sealing or hood deployment are considered to be BAT. Examples are the use of robust rotary valves on feed systems. Secondary fume collection is expensive and consumes a lot of energy but is needed in the case of some furnaces. The system used should be an intelligent system capable of targeting the fume extraction to the source and duration of any fume.

Best Available Techniques for gas and fume treatment systems are those that use cooling and heat recovery if practical before a fabric filter. Fabric filters that use modern high performance materials in a well-constructed and maintained structure are applicable. They feature bag burst detection systems and on-line cleaning methods.

Gas treatment for the process stages using sulphur additives should include a sulphur dioxide removal stage and those that produce hydrocarbons or PAHs such as pit, tunnel or single chamber furnaces, should use after-burning or dry scrubbing.

The acid gas and solvent recovery systems applied especially for the special carbon and graphite products and the associated dust recovery stages are those described in chapter 2 of this document. Fume collection systems should follow the best practice outlined in techniques described in section 2.6. The use of or the recycling of filter dusts is considered to be part of the processes.

Other abatement systems are considered to be applicable for other parts of the process and an overview is shown in the following table.

Source	Abatement option	Components in off-gas
Materials handling and storage	Prevention, Cooler, Afterburner, Back venting of tanks	Dust, hydrocarbon and PAH. Potentially significant –
Grinding,	Cyclone and fabric filter	Dust Handling dried material –
Mixing and forming.	Afterburner. Coke filter	Dust, hydrocarbon and PAH. Handling dried material –
Anode baking	Afterburner. Cooler, lime/carbon adsorption and fabric filter. Alumina scrubber and fabric filter if integrated with primary aluminium smelter	Dust, SO_2, hydrocarbon and PAH EP can be used to remove condensable materials.
Baking or re-baking of other electrodes.	Cooler and coated filter. Afterburner (and fabric filter).	Dust, SO_2, hydrocarbon and PAH EP can be used to remove condensable materials. Depends on gas collection from furnace.
Washing and drying	Gas collection and Bio-filter.	Odours, organic solvents
Impregnation	Afterburner. Gas collection and filter (carbon or bio filter for solvents).	Hydrocarbon and PAH, Odours, organic solvents, metal fume
Graphitising	Gas collection and fabric filter (SO_2 scrubber if necessary).	Dust, SO_2. Depends on gas collection from furnace.
Machining and shaping	Cyclone and fabric filter.	Dust - collected dust and particles returned as raw material.
Note. Modern, well-designed electrostatic precipitators may be able to achieve the same performance as a dry scrubber.		

Table 12.9: Sources and treatment of abated and fugitive emissions from carbon and graphite production

12.4.3.1 Emissions to air associated with the use of BAT

Emissions to air comprise the captured/abated emissions from the various sources, plus the fugitive or un-captured emissions from these sources. Modern, well operated systems result in efficient removal of pollutants and the information at the time of writing indicates that that the fugitive emissions can be the largest contributor to the total emissions.

For all processes the emissions to air are based on the emissions from:

- The materials handling and storage,
- The blending and mixing stages,
- The baking, impregnation, graphitising and finishing stages.

Fugitive emissions may be highly significant and can be predicted from the fume capture efficiency and can be estimated by monitoring (see Chapter 2.6).

PAH values are subject to some uncertainty. Several standardised methods exist to measure and report PAH and the following groups have been used for this report: - VDI-group I (2), VDI-group II (7), VDI-group I+II (9), OSPAR 11 (11), EPA (16).

Low molecular weight PAHs are very sensitive to the sampling and testing conditions and procedures. There is therefore more uncertainty in EPA data due to the possible incompleteness of their collection. Abatement techniques designed to remove PAHs however are generally expected to achieve similar removal efficiencies for each of the reporting conventions although the numerical values are different for each convention.

The PAH compounds measured and reported for these conventions are shown below.

PAH Compounds	**VDI-I**	**VDI-II**	**VDI-I+II**	**OSPAR 11**	**EPA**
Naphthalene					**X**
Acenaphthylene					**X**
Acenaphthene					**X**
Fluorene					**X**
Phenanthrene				**X**	**X**
Anthracene				**X**	**X**
Fluoranthene				**X**	**X**
Pyrene					**X**
Benzo (a) pyrene	**X**		**X**	**X**	**X**
Dibenzo (a,h) anthracene	**X**		**X**	**X**	**X**
Benzo (a) anthracene		**X**	**X**	**X**	**X**
Benzo (b) fluoranthene		**X**	**X**	**X**	**X**
Benzo (j) fluoranthene		**X**	**X**		
Benzo (k) fluoranthene		**X**	**X**	**X**	**X**
Chrysene		**X**	**X**	**X**	**X**
Indeno (1,2,3,-cd) pyrene		**X**	**X**	**X**	**X**
Benzo(ghi)perylene				**X**	**X**
Benzo (b) naptho (2,1-d) thiophene		**X**	**X**		

Table 12.10: Reporting conventions for PAHs

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 - 5 mg/Nm^3	Cyclone and/or bag filter	Depends on the characteristics of the dust.
	< 30 mg/Nm^3	Isolated filter units used for storage silos only	
Hydrocarbons (volatile)	< 10 mgC/Nm^3	Condenser, adsorber. Back venting of gases during delivery.	
Hydrocarbons (condensable)	< 50 mgC/Nm^3		
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 12.11: Emissions to air associated with the use of BAT in the storage and handling of coke and pitch

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 - 5 mg/Nm^3	Cyclone plus fabric filter	Depends on characteristics of dust.
PAH (VDI I)	< 10 µg/Nm^3	Afterburner (CTO/RTO)*	
PAH (VDI I+II)	< 100 µg/Nm^3	Afterburner (CTO/RTO)* Adsorber/dry scrubber	
Hydrocarbons (Total)	< 5 mgC/Nm^3	Afterburner*	
	< 25 mgC/Nm^3	Adsorber/dry scrubber	
SO_2	< 50 - 200 mg/Nm^3	Wet or semi-dry alkaline scrubber	If sulphur is added to the blend or the fuel contains high %S.
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used. *A regenerative afterburner has been used in a number of applications and requires less energy input and can have a lower gas volume, however the process is still being developed. The measurement and reporting of PAH is complex, the value reported depends on the number of individual PAHs that are determined and reported.			

Table 12.12: Emissions to air associated with the use of BAT in the grinding and mixing, stages

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 - 5 mg/Nm^3	Fabric filter	Depends on characteristics of dust.
PAH (OSPAR 11)	< 200 µg/Nm^3	*Cooler, lime/carbon adsorption and fabric filter.	
PAH (EPA)	200 - 500 µg/Nm^3	Afterburner	
Hydrocarbons (volatile)	< 10 - 25 mgC/Nm^3	Afterburner	
	< 10 - 50 mgC/Nm^3	*Cooler, lime/carbon adsorption and fabric filter	
Hydrocarbons (condensable)	< 1 - 5 mgC/Nm^3	Afterburner or *Cooler, lime/carbon adsorption and fabric filter	

Note. Collected emissions only.
Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period.
For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.
An electrostatic precipitator can be used for special applications with special products and/or low specific furnace loadings. In these cases the emissions should be equivalent to those reached with those the dry scrubbing techniques.
The measurement and reporting of PAH is complex, the value reported depends on the number of individual PAHs that are determined and reported, the ratio of the individual PAHs will vary.
* Modern, well-designed electrostatic precipitators may be able to achieve the same performance as a dry scrubber.

Table 12.13: Emissions to air associated with the use of BAT in the production of prebaked anodes where it is not feasible to share the abatement with smelter cell gases and in the baking, impregnating and re-baking for the production of carbon and graphite anodes

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 – 5 mg/Nm^3	Alumina scrubber and fabric filter	Depends on characteristics of dust.
BaP *	< 0.5 µg/Nm^3	Alumina scrubber and fabric filter,	BaP is an indicator
PAH (OSPAR 11)	< 200 µg/Nm^3	Alumina scrubber and fabric filter	
Hydrocarbons (Total)	< 1 - 10 mgC/Nm^3	Alumina scrubber and fabric filter	
HF	< 0.2 mg/Nm^3	Alumina scrubber and fabric filter	
Total fluoride	< 0.5 mg/Nm^3		

Note. Collected emissions only. The levels given are for the combined gases from the cell room and anode plant after treatment in an alumina scrubber/fabric filter.
Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period.
For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.
* The measurement and reporting of PAH is complex, the value reported depends on the number of individual PAHs that are determined and reported, BaP is used as an indicator only, the ratio of the individual PAHs will vary.

Table 12.14: Emissions to air associated with the use of BAT in the production of prebaked anodes from a process sharing the abatement system with a primary aluminium smelter

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
Dust	1 - 5 mg/Nm^3	Cyclone plus fabric filter	Depends on characteristics of dust.
Hydrocarbons (Total)	< 10 mgC/Nm^3	Fabric filter	Only relevant if green material is used
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 12.15: Emissions to air associated with the use of BAT in the machining and graphitising stages

Pollutant	Range associated with the use of BAT	Techniques that can be used to reach these levels	Comments
VOC or solvents as C	< 20 mg/Nm^3	Containment, condenser, carbon or bio filter	
Cyanide	< 2 - 5 mg/Nm^3	Afterburner	Only for carbon fibre production using PAN
Note. Collected emissions only. Associated emissions are given as daily averages based on continuous monitoring during the operating period. In cases where continuous monitoring is not practicable the value will be the average over the sampling period. For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.			

Table 12.16: Emissions to air associated with the use of BAT in the mixing and impregnation stages if solvents are used and in the production of carbon fibres

12.4.4 Emissions to water

The processes described above are capable of being operated on a closed cycle and this is considered to be BAT. No releases to water are expected for a new installation. Sludges from sealed circuits and blow-down water are wastes for special disposal.

12.4.5 Process residues

Residues from the production processes are capable of re-use within the process or in other processes.

12.4.6 Costs associated with the techniques

Cost data has been compiled for a variety of process variations and abatement systems. The cost data is very site specific and depends on a number of factors but the ranges given may enable some comparisons to be made. The data is provided in an appendix to this note so that costs for processes and abatement systems over the whole of the non-ferrous metal industry can be compared.

12.5 Emerging Technologies

A regenerative afterburner has been used in a number of applications and requires less energy input for similar performance. The process depends on an alternate cycling of gases through a series of support zones when heating cooling and cleaning cycles take place. The basic principle is reported to be good but development is still taking place to improve the cleaning stage. There may be applications in other processes in this section when this work is complete.

13 CONCLUSIONS AND RECOMMENDATIONS

13.1 Timing of the work

The work to produce this BREF document was started in December 1997 when background papers describing the scope of the work and key environmental issues were prepared.

The first Technical Working Group Meeting was held over 4 days between 20 to 23 January 1998 combining the Primary and Secondary Industries so that the actual structure of the Industry was reflected. The scope and key issues were agreed. The 42 metals involved were arranged in 10 groups that have the same or very similar production processes.

A first draft of the report covering was produced in October 1998 and TWG Members made comments. New data and reports were supplied.

A second draft of the complete document was produced in July 1999 and comments from this round of consultation produced additional data and reports.

The final TWG meeting was held 24 to 26 November 1999 and a high level of consensus was obtained. Some issues such as emission levels associated with the use of BAT for SO_2, dioxins and VOC were strongly debated. Additional information provided during the consultation and after the TWG meeting have been incorporated in this final BREF.

This BREF has met a high level of support from the TWG and participants at the 7th meeting of the Information Exchange Forum. Critical remarks have mainly related to information gaps and presentational aspects (calls for more BAT associated emission and consumption levels to be included in the Executive Summary).

The main conclusions on BAT for the various production stages and the metallurgical process are presented in the BAT sections of chapters 2 to 12.

13.2 Sources of information

The 42 metals (plus ferro alloys and carbon and graphite) were arranged into 10 groups and Lead Experts from Industry represented 7 of these groups. Member State representatives took part in meetings of these expert groups and this was a source of useful data and reports. The experts involved are recognised as some of the most knowledgeable and experienced in the World. The expert groups representing Cu; Al; Zn/Pb; precious metals; Ni/Co and ferro alloys presented high quality sub-sector reports.

Major, high quality reports on specific sectors within the Member States were submitted by Germany (Cu and Pb/Zn), Finland (Cu, Ni, ferro alloys and primary Zn), NL (primary Al and primary Zn), Austria (secondary Cu and Al), Spain (all sectors).

Existing reports produced for the European Commission; UK; UNEP; Economic Commission for Europe; PARCOM; OSPARCOM; USEPA and Norway were used together with a range of reference material, which are listed under references.

Data for process descriptions, achievable emissions, effectiveness of techniques and factors relating to supervision, management and policy were obtained from 60 site visits and 21 Expert Group Meetings.

The combination of these sources of information allowed the data and information to be thoroughly audited. The quality of all of the reports were very high and the data supplied was found to be reliable and accurate.

As reported above, further data and information was submitted during the consultation stage for the first and second drafts. Additional information was also provided after the Second TWG Meeting to support a revised method of reporting emission levels associated with the use of BAT.

13.3 Recommendations for Future work

As reported, the quality of the reports submitted by the various sources was high but some gaps in the data were identified. Areas were identified where further work needs to be carried out to help define the BAT associated emission levels or to help in the next revision of this document. The following areas have been identified.

- The best abatement system and the associated emission level to air for gases containing mercury mists needs to be established. Work is currently being carried and information could be available by the autumn of 2000. An early report is needed so that this data can be included in the next revision of this document.

- The use of afterburners to remove total carbon (VOC) is established in the sector. Recent developments include a regenerative afterburner applied to a cleaned gas . This uses the energy content of the final off gases and so reduces the use of additional fuel required to heat the gas to the reaction temperature. Very good results have been demonstrated for a secondary copper installation but variable results have been reported in other sub-sectors. It is understood that the data from the other sectors related to early versions of the technique and data will be available from more developed afterburners by the spring of 2001. This data should be reported and included in the next revision of this document.

- The range of performance of other afterburner systems is required for the next revision of this document to confirm the associated emissions of afterburners or optimised combustion systems. The existing data is very limited and data from other sectors has been used to provide a wider background of data for this document.

- Fugitive emissions have been identified as potentially the most significant emissions to air in this sector. More work is needed to measure and report on fugitive emissions from installations and on the reductions that are achieved using the methods of fume collection reported in this document. This data should be provided for the next revision of this document.

- More data is required for the next revision of this document to confirm the operational performance of wet and semi-dry alkaline scrubbers for SO_2 removal. The existing data is very limited and data from other sectors has been used to provide a wider background of data for this document.

- Emerging techniques have been reported for most of the metal groups and the next revision of this document should investigate progress. In particular the use of inert anodes for the primary production of Al appears to be slow to emerge but could offer several major environmental advantages if the work is successful.

- Emission data for air, water and residues, together with energy use should be provided for the next revision of this document. Collection of this data should start as soon as possible and should include specific volumes (i.e. volume per tonne of product) of gases or wastewater so that specific emissions can be calculated for BAT processes and process stages. Energy usage should also be reported on this basis. Specific emission data will allow the comparison of the various installations to be made across the Member States.

- Cross media issues have been identified in many cases but the information provided for this document may not be comprehensive. Comments on cross media issues of the various processes should be provided where possible for the next revision of the document.

- The measurement of PAH has been based on a number of parameters such as BaP, total PAH, VDI and the OSPAR 11 to air and Borneff 6 to water. In some cases the basis of the reported values has not been made available, data for the next revision of this document should include information about the components that are measured. The protocol for the measurement and reporting of PAH is currently being studied by an OSPARCOM group lead by Norway.

- Process control equipment for some furnaces and processes, particularly some blast furnaces, is capable of improvement. It is recommended that this work is carried out and reported for the next revision of this document.

- Data and information about small and medium sized companies was not fully available during the exchange of information. This information should be provided for the next revision of the document so that the situation particular to these companies can be taken into account.

It is recommended that this document be revised in 4 years time to assess the above points in particular.

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ANNEX I SPECIFIC COST DATA FOR METAL PRODUCTION AND ABATEMENT

This annex compiles data to allow cost evaluations for some process and abatement installations. The data given focuses on the process plant and main consumption data. Site-specific cost factors have been eliminated as far as possible. The information gives an order of magnitude of the cost range and allows a limited comparison of costs between techniques.

Data is not available for all of the metal groups and so this data is presented as an annex so that some costs e.g. for furnaces, abatement etc can be referred to for these groups. Costs are mainly presented on the basis of cost per annual tonne of production. Reference is made where possible to the size of the process or of the abatement plant so that the data can be used to provide rough estimates for sectors that may not be represented.

Several sources presented data and all give the specific investment cost per tonne of metal produced per year. The data was supplied in a variety of currencies effective at the time of purchase. For the sake of direct comparisons, these currencies have been converted into Euros, using the exchange rate that was effective on 16th June 1999 – 1.06 $ = 1 € (Euro). The various exchange rates that operated since 1950 are given below so that the original costs can be derived if required.

Year	**DM / £**	**DM / US $**	**US $ / £**	**DM / ECU ***	**US $ / ECU ***
1950	11.76	4.20	2.80	-	-
1960	11.71	4.17	2.81	-	-
1970	8.74	3.65	2.40	-	-
1980	4.23	1.82	2.33	2.48	1.36
1990	2.88	1.62	1.79	2.07	1.26
1993	2.48	1.65	1.50	1.90	1.15
1996	2.35	1.50	1.56	1.90	1.27
1998	2.91	1.76	1.66	1.97	1.12

* since 1979 only.

Table I.1: Some currency exchange rates

The cost data shown in this annexe are an order of magnitude indication only.

Some sources also reported financing and operating costs for the particular installation. These may not be applicable to other sites because the costs of individual operations would include a substantial percentage of site and corporate specific cost components.

I.1 Influences on cost data

Some of the site-specific influences on costs referred to above are listed as follows: -

- Transport:
    - Feed material transport costs (effect on treatment and refining charge).
    - Transport costs for product(s).

- Direct operating costs:
    - Labour legislation, climatic conditions, arrangement of unit operations (in-plant transport costs), energy availability, available infrastructure, special environmental protection requirements.

- Sales costs:
    - Market access, infrastructure, climatic conditions.

- Capital costs:
    - Feed material shipment options, market access and market conditions/product sale, corporate structure.

- Investment costs:
    - Climatic conditions, available infrastructure, energy and consumables, specific local environmental protection requirements.

The above factors indicate that it is very difficult to give reliable cost data which could be used in a more general sense without the danger of misleading results. A complete and reliable economic calculation /evaluation can only be done for a site-specific investment. Only on such a basis is definite cost data available. For example the following factors have an overwhelming influence on the economics of a project and cannot always be estimated in this annex –

- treatment and refining charges for concentrate,
- costs for concentrate, flux etc. and other purchases,
- purchase price (after deductions) of secondary materials,
- purchase price for refined metal,
- sale of by-products like sulphuric acid or similar,
- the selected country (taxes, labour, disposal and energy costs, inflation),
- the specific site (transport of pure materials and products),
- the infra-structure (availability of energy, water, oxygen, maintenance),
- the plant capacity,
- type and composition of feed,
- time schedule and time of investment,
- financing of the investment,
- costs for construction and erection (inland execution).

Where costs are known accurately for specific installations they have been included but they are provided separately so that site variation can be taken into account. Comments have also been made where possible to illustrate how cost variations e.g. waste disposal costs, can account for a significant variation in the costs.

I.2 Specific Investment Costs for Copper Process Plants

As explained above, the investment costs for copper plants are influenced also by a number of site-specific factors and not only by the process technology and abatement techniques selected. The following tables give some technology-related data.

The tables indicate for green-field plants: -

- the year of investment or cost determination;
- the key plant sections covered;
- the production capacity related to the cost indication.

The normal plant related abatement techniques are included in the cost indication. The investment costs are indicated as specific cost per tonne of copper. The cost data shown are to be understood as an order of magnitude indication. Not included are costs for land, finance, inside and outside plant infrastructure, owner’s costs during construction and all other investments, which are not directly connected with the plant sections mentioned.

Year	Installed Cost € per t/a production capacity.	Product made and Design Capacity in t/a	Plant sections included
1977	2250 – 2450	Anode copper 70000 t/a	Material handling/storage, partial roasting & electric furnace smelting, PS converter, anode plant, EF slag cleaning, double catalysis acid plant
1980	2450 – 2650	Anode copper, 150000 –160000 t/a	Material handling/storage, Outokumpu flash, PS converter, anode plant, EF slag cleaning, double catalysis acid plant.
1981	1700 – 1850	Anode copper, 280000 t/a	Material handling/storage, Outokumpu flash, PS converter, anode plant, EF slag cleaning, double catalysis acid plant.
1981	2850 – 3000	Anode copper 100000 t/a	Material handling storage, Mitsubishi continuous smelting, anode plant, double contact acid plant.
1981	2250 – 2550	Anode copper 120000 t/a	Material handling/storage, Inco flash, PS converter, anode plant, double catalysis acid plant.
1992	2150 – 2250	Anode copper 150000 t/a	Material handling/storage, ISA Melt, PS converter, anode plant, EF slag cleaning, double catalysis acid plant.
1994	2250 – 2350	Anode copper 285000 t/a	Material handling/storage, Outokumpu flash smelter, Flash converter, anode plant, double catalysis acid plant. Slag flotation not included.
1995	2350 – 2750	Anode copper 120000 t/a	Material handling/storage, Outokumpu flash, PS converter, anode plant, EF slag cleaning, double catalysis acid plant.
1997	1950 - 2150	Anode copper 160000 t/a	Material handling storage, Mitsubishi continuous smelting, anode plant, double contact acid plant.
1998	2550 – 2650	Anode copper 303000 t/a	Outokumpu flash smelter, Flash converter, anode plant, double catalysis acid plant.
1998	2950 – 3150	Anode copper 200000 t/a	Material handling storage, Mitsubishi continuous smelting, anode plant, double contact acid plant.

Note. * Cost indications are in year indicated without consideration of escalation or adjustment! Original costs were in $ and have been converted using € = 1.06$.

Table I.2: Primary copper smelter / acid plant complexes
Source Copper industry – [tm 92, Copper Expert Group 1998, Copper Conference 1999]

Ronnskar Project,

Description of Project components: -:

- Extension to quay for raw materials unloading.
- Enclosed conveyors for raw material handling.
- Mixing plant and conveyors.
- Outokumpu flash furnace.
- Converter aisle with 3 Pierce-Smith converters of 250 t capacity.
- Ventilation air extraction system and fabric filter.
- Fire refining and anode casting plant - 45 t/h extra capacity.
- 33% increase in copper electro-refinery, evaporator to produce copper sulphate.
- Refurbishment of sulphuric acid plants to handle 280000 Nm^3/h. Mercury removal stage.
- Process instrumentation.
- Civil engineering costs.

Operational data:

Recent information is available for a specific process upgrade. In this instance the published costs are given below. Plant under construction 1999 – 100000 t/a extra production of copper.

Economics:

Total project cost - 2billion Swedish crowns (224 million **€). ** Anticipated pay back period 6.5 years.

Source – Boliden

Year	Installed Cost € per t/a production capacity.	Product made and Design Capacity t/a	Plant sections included
1990	1300 – 1500	Anode copper 50000 t/a	Material handling/storage, shaft furnace, converter, anode plant.
1990	1100 – 1300	Anode copper 80000 – 100000 t/a	Material handling/storage, electric furnace, converter, anode plant.
1991	1250 – 1400	Anode copper, 60000 t/a	Material handling/storage, TBR furnace, anode plant. *)

Note. *) The technical concept is different from the process now used at Metallo Chimique and Elmet. Cost indications are in year indicated without consideration of escalation or adjustment! Original costs were in $ and have been converted using € = 1.06$. Source Copper industry - tm 92, Copper Expert Group 1998.

Table I.3: Secondary copper smelters

Year	Installed Cost € per t/a production capacity.	Product made and Design Capacity in t/a	Plant sections included
1976	470	Cathode copper 380000 t/a	Conventional process concept with starter sheets and mechanisation
1987	550 – 600	Cathode copper 40000 t/a	ISA Process concept with permanent cathodes.
1990	400 – 450	Cathode copper 180000 t/a	ISA Process concept with permanent cathodes.
1993	450 – 480	Cathode copper 150000 t/a	ISA Process concept with permanent cathodes.
1994	650	Cathode copper 280000 t/a	Retrofit/expansion of an existing refinery based on the Kidd Creek concept with permanent cathodes
1996	400 – 450	Cathode copper 200000 t/a	ISA Process concept with permanent cathodes.
Note. Cost indications are in year indicated without consideration of escalation or adjustment! Original costs were in $ and have been converted using € = 1.06$.			

Table I.4: Electrolytic copper refineries
Source Copper industry – [tm 92, Copper Expert Group 1998]

Year	Installed Cost € per t/a production capacity.	Product made and Design Capacity in t/a	Plant sections included
1992	180 – 200	Copper wire-rod 220000 t/a	Continuous Southwire type rod line with shaft furnace for melting
1995	280 – 320	Copper wire-rod 80000 t/a	Continuous Southwire type rod line with shaft furnace for melting
1995	290 – 330	Copper wire-rod 80000 t/a	Continuous Contirod type rod line with shaft furnace for melting
Note. Cost indications are in year indicated without consideration of escalation or adjustment! Original costs were in $ and have been converted using € = 1.06$.			

Table I.5: Copper wire-rod plants
Source Copper industry – [tm 92, Copper Expert Group 1998]

I.3 Specific investment costs for primary and secondary aluminium processes

Primary Aluminium Smelters

The following ranges are given as investment costs for conversions that are identified as possible options for upgrading existing plants or a modern new plant.

Side Worked Prebaked(SWPB) to Point Feeder Prebaked(CWPB-pf): 400 –1000 € per tonne yearly production capacity
Centre Worked Prebaked to Point Feeder Prebaked: 100 – 200 € per tonne yearly production capacity
Vertical Stud Søderberg(VSS) to Point Feeder Prebaked: 2500-4000 €ε per tonne yearly production capacity
Conventional VSS to modernised VSS: 100- 250 € per tonne yearly production capacity
New Point Feeder Prebaked (green site): 4000-5000 € per tonne yearly production capacity

The conversion of SWPB or VSS to Point Feeder Prebaked can in most cases never be achieved to a standard comparable to a completely new PFPB plant.

The operating cost for a primary smelter depends entirely on the factors given above, and will according to reports from various consultants be in the range 950 – 1500 € per. tonne, excluding capital costs.

Investment costs for abatement equipment will again depend on site-specific conditions, since this will determine the extent of additional equipment and work necessary in addition to the actual equipment installation. The following ranges can be given.

Dry scrubbing unit: 150 – 250 € per year tonne production

SO_2 seawater scrubber for pot gases: 40 – 70 € per year tonne production

SO_2 alkali scrubber for pot gases: 100 – 200 € per year tonne production

Cost data for secondary smelters

Process equipment costs:

Rotary furnace: 15 – 60 € per year tonne

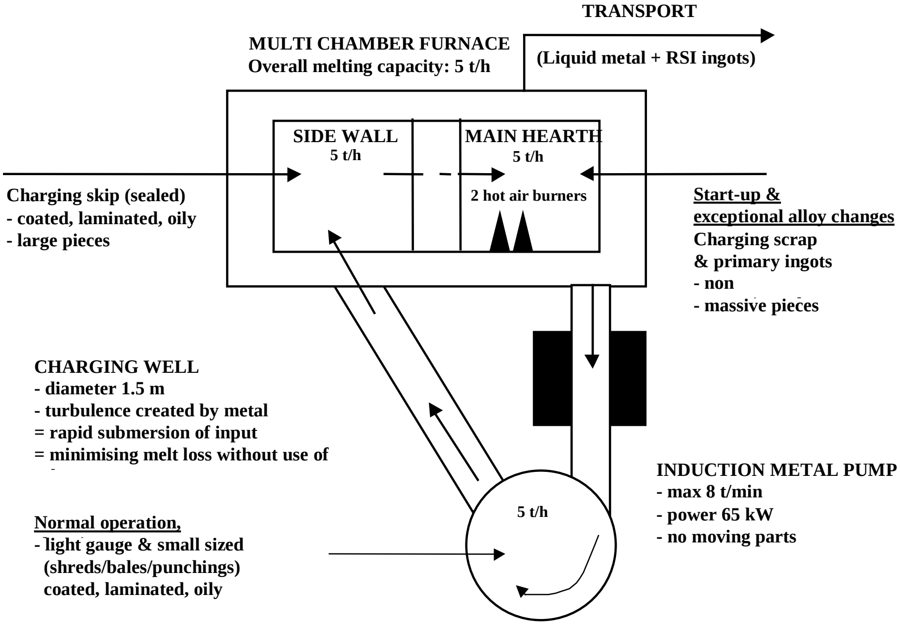
Abatement equipment costs:

Bag house filter system: 30 – 75 € per year tonne
Ceramic filter system: < 30 € per year tonne

Use of metal pumping system in a secondary smelter.

Description:

Reverberatory furnace with side well, charge well and pumped metal system.



Main environmental benefits

Potential elimination of salt flux. Greater range of raw materials than simple reverberatory furnace, improved capture of furnace gases.

Operational data:

Improvement in metal yield from 83 to 88%., reduction in energy costs

Economics:

Cost (1997)of 30 tonne furnace and EMP system £1800000 (2.73 million €),
Estimated cost savings (energy, improved yield, flux savings and treatment savings) £832000 (1.26 million €) per year.
Pay back 2.2 years.
Cost of pumping system and charge well ~ £300000 (456000 €).

Applicability:

New and upgraded furnaces.

Example plants:

Belgium and UK

Reference literature:

[tm 123, ETSU 1998. tm 122, McLelan 1998]

I.4 Specific investment costs for Pb-Zn processes

The following tables give some data for primary and secondary lead smelters, for electrolytic Zinc plants as well as Pb-Zn shaft furnaces, for a waelz kiln, a fuming plant and H_2SO_4-plants. Costs are given in US$ per t/a metal produced. Again the exchange rate US$ to local currency is very important, which is time dependant.

The data presented includes

- the year where those cost figures have been evaluated
- the volume of delivery
- the size of the smelter
- the specific investment costs per tonne of metal

In case of Pb-Zn-shaft furnaces the investment costs are related to Zn production alone as well as to total Zn + Pb production. The costs only show the order of magnitude for such investments.

Year	Installed Cost € per t/a production capacity.	Product made and Design Capacity in t/a	Plant sections included
1980	660	100000 t/a Pb	sinter machine, Shaft furnace, H_2SO_4, lead refining
1990	400	60000 t/a Pb	Secondary, Plastics separation, Smelting, lead refining
1990	635	30000 t/a Pb	Secondary, Plastics separation, Smelting, lead refining (Same order of magnitude for CX-system)
1997	625	100000 t/a Pb	QSL-plant, H_2SO_4, without lead refining (Kivcet and TBRC process should show similar investment costs)
1997	330	30000 t/a Pb	Secondary shaft furnace, lead refining
1997	145	100000 t/a Pb	Lead refining

Table I.6: Lead processes
[tm 120, TU Aachen 1999]

Year	Installed Cost € per t/a production capacity.	Product made and Design Capacity in t/a	Plant sections included
1980	1580	100000 t/a Zn	Roasting, leaching, purification, electrolysis, H_2SO_4 plant, foundry
1996	1530	100000 t/a Zn	Roasting, leaching, purification, electrolysis, H_2SO_4 plant, foundry
1997	1450	100000 t/a Zn	Roasting, leaching, purification, electrolysis, H_2SO_4 plant, foundry

Table I.7: Zinc processes
[tm 120, TU Aachen 1999]

Year	Installed Cost € per t/a production capacity.	Product made and Design Capacity in t/a	Plant sections included
1980	1550	100000 t/a Zn, 40000 t/a Pb	sinter-roasting, ISF, H_2SO_4 plant, Zn-refining
1996	1380	100000 t/a Zn, 40000 t/a Pb	sinter-roasting, ISF, H_2SO_4 plant, Zn-refining
1996	2080	100000 t/a Zn	sinter-roasting, ISF, H_2SO_4 plant, Zn-refining
1997	1790	100000 t/a Zn, 40000 t/a Pb	sinter-roasting, ISF, H_2SO_4 plant, Zn-refining
1997	2580	100000 t/a Zn	sinter-roasting, ISF, H_2SO_4 plant Zn-refining
1994	2800	85000 t/a Zn, 35000 t/a Pb	sinter-roasting, ISF, H_2SO_4 plant, Zn-refining

Table I.8: Zinc and lead processes
[tm 120, TU Aachen 1999]

Year	Installed Cost € per t/a production capacity.	Product made and Design Capacity in t/a	Plant sections included
1980	480	21000 t/a Waelz Oxide	waelz kiln, cooler, filter
1997	415	20000 t/a slag	Drying, fuming, waste heat boiler, PSA, filter

Table I.9: Zinc residues
[tm 120, TU Aachen 1999].

I.5 Cost Data for Abatement Techniques

I.5.1 Air abatement copper industry

The techniques applied for cleaning the off-gases and ventilation gases from copper operations are directed towards elimination of particulate and gaseous matter including SO_2 and SO_3. Examples for widely applied gas cleaning systems /equipment are: Dry gas cleaning: Electrostatic precipitator (EP), fabric filters (bag-houses), cassette type filters, ceramic filters, etc.

The following data is given for waste heat boiler, hot and wet EPs, gas cooling and cleaning.

The data for complete sulphuric acid plants is given later.

Application: Smelting Furnace Waste Heat Boiler	
Design basis:	
Gas temperature: Inlet: Outlet:	 1300 – 1350 °C 300 – 400 °C
Gas flow	100000 Nm³/h
Steam production	35 t/h
Total installed costs: **Million €**	**7.0 – 8.0**

Table I.10: Indirect Gas Cooling - Energy Recovery

Application: Smelter SO$_2$ gas cleaning		
	Flash furnace EP	**Flash furnace EP**
Design basis:		
Operating temperature	300 –400 °C	300 – 400 °C
Gas flow	43000 Nm^3/h	61000 Nm^3/h
Dust inlet	10 - 20 g/Nm^3	10 – 15 g/Nm^3
Dust outlet	150 - 200 mg/Nm^3	200 - 300 mg/Nm^3
Efficiency	99.9%	99.8%
EP characteristics:	4 fields, 3000 m^2 collection area, single unit	3 fields, 4800 m^2 collection area, single unit
Equipment supply costs: Total = **Million €**	**1.0 *)**	**2.0 *)**
Main consumption:		
Electricity	250 kW installed	400 kW installed

Note. *) Civil work, erection, etc. excluded; for installed costs approx. 80 – 100% will have to be added.

Table I.11: Dry EP Gas Cleaning
SOURCE: Lurgi Umwelt GmbH

Bag house, fabric filter			
Application:	**Shaft furnace, converter & anode furnace**	**TBRC**	**Cooler & fabric filter**
Design basis:			
Operating temperature	~ 100 °C	~ 100 °C	~ 100 °C
Gas flow	750000 Nm^3/h	730000 Nm^3/h	70000 Nm^3/h
Dust outlet	< 10 mg/Nm^3	< 10 mg/Nm^3	< 10 mg/Nm^3
Total installed cost: Million €	**20 *)**	**14 **)**	**2 – 2.5 ***)**
Main consumption:			
Electricity	2.5 - 3 kWh/1000 Nm^3	2 – 3 kWh/1000 Nm^3	1.5 – 4 kWh/1000 Nm^3
Others	1 g/Nm^3 lime ****)		

Note. *) Including ductwork and stack. **) Excluding duct work and stack.
) Total installed cost including gas cooler and stack. *) For anode furnace gas stream

Table I.12: Fabric filters
[tm 92, Copper Expert Group 1998]

Wet Electrostatic Precipitator for SO_2 gas treatment	
Type:	Two wet EPs in line
Application:	Final SO_2 gas cleaning for further treatment.
Design basis:	
Operating temperature	27 °C inlet
Gas flow	88.00 Nm^3/h
Precipitation efficiency for	
Dust	99%
Arsenic	99%
H_2SO_4	99%
Total equipment supply costs: **Million €**	**2.0 *)**
Main consumption: Electricity	112 kW
Note. *) Civil work, erection, etc. excluded; for installed costs approx. 60 - 80% will have to be added.	

Table I.13: Wet EP gas Cleaning
SOURCE: Lurgi Umwelt GmbH

Wet Gas Cooling and Cleaning System for Smelter SO2 gases		
System:	**Wet gas cleaning for furnace SO_2 gas**	**Wet gas cooling and cleaning section for combined SO_2 in furnace and converter gases**
System equipment:	1 radial flow scrubber, 1 ID fan, 2 in-line wet EPs with a 2000 m^2 total collection area, acid cooler and acid circulation pumps, 1 cooling tower, 900 m^3/h cooling media circulation.	2 radial flow scrubbers, 3 lines with 2 in-line wet EPs with 7000 m^2 total collection area, acid cooler and acid circulation pumps, 2 cooling towers, 2200 m^3/h cooling media circulation.
Design basis:		
Operating temperature	390 °C inlet, 35 °C outlet	370 °C inlet, 27 °C outlet
Gas flow	96000 Nm^3/h	250000 Nm^3/h
Precipitation efficiency for: -		
Dust	96 – 97%	96 – 97%
Arsenic	99.0 %	99.0 %
Mist	> 99.5%	> 99.5%
Equipment supply costs: Million €	**7.5 - 8 *)**	**16 - 17 **)**
Electricity consumption:	828 kW	1250 kW
Note. *) Civil work, erection, etc. excluded; for installed costs approx. 60 - 80% will have to be added. **) Civil work, erection, etc. excluded; for installed costs approx. 70 - 100% will have to be added.		

Table I.14: Wet EP gas cleaning
SOURCE: Lurgi Umwelt GmbH

The following cost data is given for abatement systems used in secondary copper processes and is provided by Austria. The costs are given in Austrian Schillings (ATS) and Euros **(€)**, site specific investment, operating and disposal costs are given [tm 160, Winter Cu 1999].

Regenerative afterburner installation with reactor and bag filter treating off-gases from a shaft furnace.		
Input data: - Volume of exhaust gas of 20000 Nm^3/h.	Quantity of metal produced 18000 t/a Black Copper Operating hours 6300 h/a	
Output data: - < 0.1 ng/Nm^3 PCDD/F		
Description: Regenerative afterburner installed after a fabric filter treating 20000 Nm^3/h of de-dusted gas with a reduction of 98% for dioxins.		**Costs ATS/t metal (€/t metal)**
Input factors for annual expenditure		
Investment costs (Million. ATS)	12 +/-20%	
Number of years	15	
Rate of interest (%)	6	
Annual repayment incl. Interest (Million. ATS/a)	1.24	
Proportional investment costs incl. Interest		**68.64** **(4.99 €/t)**
Maintenance + wear and tear (% of investment costs = 0.24 Million ATS/a)	2	**13.33** **(0.97 €/t)**
Proportional costs		
Support fuel MJ/t	1342	80.52
Electrical energy consumption (kWh/t) at 0.9 ATS/kWh	13.5	12.15
Total costs		**~ 175** **(12.72 €/t)**

Table I.15: Afterburner, reactor and fabric filter
Source: - Austrian cost data in [tm 160, Winter Cu 1999]

Afterburner placed between a shaft furnace and waste heat boiler.		
Input data: - Volume of exhaust gas of 20000 Nm^3/h.	Quantity of metal produced 18000 t/a Black copper Operating hours 6300 h/a	
Description: 98% removal of dioxins		**Costs ATS/t metal (€/t metal)**
Input factors for annual expenditure		
Investment costs (Million. ATS)	8 +/-20%	
Number of years	15	
Rate of interest (%)	6	
Annual repayment incl. Interest (Million. ATS/a)	0.82	
Proportional investment costs incl. Interest		**45.76** **(3.33 €/t)**
Maintenance + wear and tear (% of investment costs)	2	**8.89** **(0.65 €/t)**
Proportional costs		
Support fuel MJ/t	1304	78.24
Electrical energy consumption (kWh/t)	16.0	5.4
Total costs		**~ 138** **(10.03 €/t)**

Table I.16: Afterburner
Source: - Austrian cost data in [tm 160, Winter Cu 1999]

Wet de-sulphurisation process to remove sulphur dioxide from scrap converter off-gases.		
Input data: - Volume of exhaust gas of 35000 Nm^3/h. Average input SO_2 ~2300 mg/Nm^3, peak 4000 mg/Nm^3	Quantity of metal produced 12000 t/a raw copper Operating hours 1200 h/a	
Output data: - Annual average SO_2 < 50 mg/Nm^3 - peak < 200 mg/Nm^3		
Description		**Costs ATS/t metal (€/t metal)**
Input factors for annual expenditure		
Investment costs (Million. ATS)	25	
Number of years	15	
Rate of interest (%)	6	
Annual repayment incl. Interest (Million. ATS/a)	2.54	
Proportional investment costs incl. Interest		**214.51 (15.59 €/t)**
Maintenance + wear and tear (% of investment costs)	2	**41.67 (3.03 €/t)**
Proportional costs		
Cost of CaO kg/t at 1 ATS/kg	6.74	6.74
Disposal cost of gypsum kg/t at 0.2 ATS/kg	22.99	4.6
Electrical energy consumption (kWh/t) at 0.9 ATS/kWh	16.39	14.75
Total costs		**~ 282 (20.49 €/t)**

Table I.17: Wet de-sulphurisation
Source: - Austrian cost data in [tm 160, Winter Cu 1999]

Semi-dry de-sulphurisation process to reduce sulphur dioxide from an anode furnace.		
Input data: - Volume of exhaust gas of 80000 Nm^3/h. Pressure-drop 20 mbar. SO_2 ~500 mg/Nm^3	Quantity of metal produced 60000 t/a anode copper Operating hours 7000 h/a	
Output data: - SO_2 ~ 50 mg/Nm^3, 95% reduction of PCDD/F		
Description		**Costs ATS/t metal (€/t metal)**
Input factors for annual expenditure		
Investment costs (Million. ATS)	30 +/- 20%	
Number of years	15	
Rate of interest (%)	6	
Annual repayment incl. Interest (Million. ATS/a)	3.09	
Proportional investment costs incl. Interest		**51.48** **(3.74 €/t)**
Maintenance + wear and tear (% of investment costs)	3	**15** **(1.09 €/t)**
Proportional costs		
CaO kg/t Cu	7.35	7.35
Carbon kg/t Cu	1.87	6.53
Combustion air	23.33	3.97
Disposal kg/t Cu	13.42	26.83
Electrical energy consumption (kWh/t)	14.08	12.67
Total costs		**~ 124** **(9.01 €/t)**

Table I.18: Semi-dry scrubber
Source: - Austrian cost data in [tm 160, Winter Cu 1999]

Activated carbon final filter for black copper production.		
Input data: - Volume of exhaust gas 20000 Nm^3/h. Pressure drop 25 mbar	Quantity of metal produced 18000 t/a Black copper. Operating hours 6300 h/a	
Output data: - PCDD/F < 0.1 ng/Nm^3		
Description		**Costs ATS/t metal (€/t metal)**
Input factors for annual expenditure		
Investment costs (Million. ATS)	12	
Number of years	15	
Rate of interest (%)	6	
Annual repayment incl. Interest (Million. ATS/a)	1.24	
Proportional investment costs incl. Interest		**68.64 (4.99 €/t)**
Maintenance + wear and tear (% of investment costs)	2	**13.33 (0.97 €/t)**
Proportional costs		
Consumption and disposal of activated carbon kg/t at 6.5 ATS/kg	1.4	9.1
Electrical energy consumption (kWh/t) at 0.9 ATS/kWh	17.51	15.76
Total costs		**~ 107 (7.78 €/t)**

Table I.19: Activated carbon filter
Source: - Austrian cost data in [tm 160, Winter Cu 1999]

Selective catalytic reduction to reduce oxides of nitrogen.		
Input data: - Volume of exhaust gas of 20000 Nm^3/h.	Quantity of metal produced 18000 t/a Black copper. Operating hours 6300 h/a	
Output data: - NO_x < 100 mg/Nm^3, 98% reduction of PCDD/F		
Description		**Costs ATS/t metal (€/t metal)**
Input factors for annual expenditure		
Investment costs (Million. ATS)	10	
Number of years	15	
Rate of interest (%)	6	
Annual repayment incl. Interest (Million. ATS/a)	1.03	
Proportional investment costs incl. Interest		**57.2** **(4.16 €/t)**
Maintenance + wear and tear (% of investment costs)	2	**11.11** **(0.81 €/t)**
Proportional costs		
Cost of Ammonia kg/t at 1.8 ATS/kg	2.07	3.73
Replacement catalyst m^3/a at 200000 ATS/m^3	0.5	5.56
Energy for reheat MJ/t at 60 ATS/GJ	284	17.01
Electrical energy consumption (kWh/t) at 0.9 ATS/kWh	19.03	17.13
Total costs		**~ 112** **(8.14 €/t)**

Table I.20: SCR
Source: - Austrian cost data in [tm 160, Winter Cu 1999]

I.5.2 Air abatement – aluminium industry

The following cost data is given for abatement systems used in secondary aluminium processes and is provided by Austria. The costs are given in Austrian Schillings (ATS) and Euros (**€**), site specific investment, operating and disposal costs are given [tm 145, Winter Al 1998].

Simple flow injection process using a fabric filter.		
Input data: - Volume of exhaust gas of 40000 Nm^3/h containing ~ 600 mg/Nm^3 dust, 500 mg SO_2/Nm^3,. 300 mg HCl/Nm^3 and 50 mg HF/Nm^3.	Quantity of metal produced 40000 t/a Al Operating hours 5500 h/a	
Output data: - < 5 mg / Nm^3 dust < 300 mg SO_2/Nm^3, < 30 mg HCl/Nm^3 and < 5 mg HF/Nm^3.		
Description		**Costs ATS/t metal (€/t metal)**
Input factors for annual expenditure		
Investment costs (Million. ATS)	15	
Number of years	15	
Rate of interest (%)	6	
Annual repayment incl. Interest (Million. ATS/a)	1.54	
Proportional investment costs incl. Interest		**38.61 (2.81 €/t)**
Maintenance + wear and tear (% of investment costs)	3	**11.25 (0.82 €/t)**
Proportional costs		
Consumption of CaO (kg/t metal)	22	22
Electrical energy consumption (kWh/h)	102	14.03
Technology costs		**86 (6.25 €/t)**
Disposal of filter dust (kg/t metal)	35 - 60	**70 - 240 (5.09 - 17.44 €/)**
Total costs		**~ 156 - 326 (11.34 - 23.69 €/t)**

Table I.21: Dry scrubber and fabric filter
[tm 145, Winter Al 1998]

The range of the total costs is influenced by the variability of the disposal cost for filter dust. This factor will be a significant variable over EU.

Semi-dry reduction process using spray absorber, fabric filter and absorbent re-circulation.		
Input data: - Volume of exhaust gas of 40000 Nm^3/h,. ~ 600 mg/Nm^3 dust, 1000 mg SO_2/Nm^3, 300 mg HCl/Nm^3 and 50 mg HF/Nm^3	Quantity of metal produced 40000 t/a Al Operating hours 5500 h/a	
Output data: - < 5 mg $/Nm^3$ dust < 200 mg SO_2/Nm^3, < 10 mg HCl/Nm^3, < 1 mg HF/Nm^3 and < 0.1 ng $PCDD/F/Nm^3$.		
Description		**Costs ATS/t metal (€/t metal)**
Input factors for annual expenditure		
Investment costs (Million. ATS)	20	
Number of years	15	
Rate of interest (%)	6	
Annual repayment incl. Interest (Million. ATS/a)	2.06	
Proportional investment costs incl. Interest		**51.48 (3.74 €/t)**
Maintenance + wear and tear (% of investment costs)	3	**15 (1.09 €/t)**
Proportional costs		
Consumption of CaO (kg/t metal)	22	22
Consumption of activated carbon (kg/t metal)	1	3.5
Electrical energy consumption (kWh/h)	110	15.13
Technology costs		**107.11 (7.78 €/t)**
Disposal of filter dust (kg/t metal)	35 - 60	**70 - 240 (5.09 - 17.44 €/t)**
Total costs		**~ 180 - 350 (13.08 - 25.44 €/t)**

Table I.22: Semi-dry scrubber and fabric filter
[tm 145, Winter Al 1998]

The range of the total costs is influenced by the variability of the disposal cost for filter dust. This factor will be a significant variable over EU.

Semi-dry reduction process using spray absorber, fabric filter and absorbent re-circulation for sulphur dioxide free gas.		
Input data: - Volume of exhaust gas of 40000 Nm^3/h,. ~ 600 mg/Nm^3 dust.	Quantity of metal produced 40000 t/a Al Operating hours 5500 h/a	
Output data: - < 5 mg /Nm^3 dust, < 0.1 ng PCDD/F/Nm^3.		
Description		**Costs ATS/t metal (€/t metal)**
Input factors for annual expenditure		
Investment costs (Million. ATS)	14	
Number of years	15	
Rate of interest (%)	6	
Annual repayment incl. Interest (Million. ATS/a)	1.44	
Proportional investment costs incl. Interest		**36.04 (2.62 €/t)**
Maintenance + wear and tear (% of investment costs)	3	**10.5 (0.76 €/t)**
Proportional costs		
Consumption of $NaHCO_3$ (kg/t metal) at 3ATS/kg	12	36
Electrical energy consumption (kWh/h) at 1 ATS/kWh	110	15.13
Technology costs		**97.67 (7.1 €/t)**
Disposal of filter dust (kg/t metal)	15 - 30	**15 - 30 (1.09 - 2.18 €/t)**
Total costs		**~ 110 - 130 (7.99 - 9.45 €/t)**

Table I.23: Semi-dry scrubber and fabric filter
[tm 145, Winter Al 1998]

The range of the total costs is influenced by the variability of the disposal cost for filter dust. This factor will be a significant variable over EU. In this particular example the filter dust is based on sodium bicarbonate and sodium chloride and is suitable for processing in a salt recovery process.

Wet processes using electrostatic precipitator and scrubber.		
Input data: - Volume of exhaust gas of 40000 Nm^3/h ~ 600 mg $dust/Nm^3$, 1000 mg $/Nm^3$ SO_2, 300 mg HCl/Nm^3 and 50 mg HF/Nm^3	Volume of metal produced 40000 t/a Al Operating hours 5500 h/a	
Output data: - ~5 - 15 mg $dust/Nm^3$, < 50 mg SO_2/Nm^3, < 5 mg HCl/Nm^3 and < 1 mg HF/Nm^3		
		Costs ATS/t metal (€/t metal)
Input factors for annual expenditure		
Investment costs (Million. ATS)	17	
Number of years	15	
Rate of interest (%)	6	
Annual repayment incl. Interest (Million. ATS/a)	1.75	
Proportional investment costs incl. interest		43.76 **(3.18 €/t)**
Maintenance + wear and tear (% of investment costs)	2	**8.5** **(0.62 €/t)**
Proportional costs		
Water consumption (m^3/t metal) and wastewater disposal	0.3	1.5 - 9
Consumption of CaO (kg/t metal)	11	11
Electrical energy consumption (kWh/h)	90	12.38
Technology costs		**77.14 - 84.64** **(5.61 - 6.15 €/t)**
Disposal of filter dust (kg/t metal)	10 - 35	20 - 140 **(1.45 –10.17 €/t)**
Disposal of neutralisation sludge (kg/t metal)	15	22.5 - 45 **(1.64 - 3.28 €/t)**
Total costs		**~ 120 - 270** **(8.72 - 19.62 €/t)**

Table I.24: Wet scrubber and EP
[tm 145, Winter Al 1998]

The range of the total costs is influenced by the variability of the disposal cost for filter dust and sludge. This factor will be a significant variable over EU.

Combination of semi-dry process with series scrubber using a spray absorber and fabric filter.		
Input data: - Volume of exhaust gas of 40000 Nm^3/h, 600 mg/Nm^3 dust, 1000 SO_2/Nm^3, 300 mg HCl/Nm^3 and 50 mg HF/Nm^3.	Quantity of metal produced 40000 t/a Al Operating hours 5500 h/a	
Output data: - < 5 mg $dust/Nm^3$, < 50 mg SO_2/Nm^3, < 5 mg HCl/Nm^3, < 1 mg HF/Nm^3 and the reduction of dioxin to under 0.1 ng/Nm^3.		
		Costs **ATS/t metal** (€/t metal)
Input factors for annual expenditure		
Investment costs (Million. ATS)	22	
Number of years	15	
Rate of interest (%)	6	
Annual repayment incl. Interest (Million. ATS/a)	2.27	
Proportional investment costs incl. Interest		**56.63** **(4.16 €/t)**
Maintenance + wear and tear (% of investment costs)	3	**16.5** **(1.2 €/t)**
Proportional costs		
Consumption of CaO (kg/t metal)	11	11
Consumption of activated carbon (kg/t metal)	1	3.5
Electrical energy consumption (kWh/h)	160	22
Technology costs		**109.63** (7.97 €/t)
Disposal of filter dust (kg/t metal)	25 - 50	**50 - 200** **(3.63 - 14.53 €/t)**
Total costs		~160 - 310 (11.63 - 22.53 €/t)

Table I.25: Semi-dry scrubber and fabric filter
[tm 145, Winter Al 1998]

The range of the total costs is influenced by the variability of the disposal cost for filter dust. This factor will be a significant variable over EU.

I.5.3 Sulphuric acid plants

Gas Cooling and Cleaning Section, Double Contact Sulphuric Acid Plant. Applied to copper smelter		
Gas cooling and cleaning system:	Wet gas cooling and cleaning section for combined SO_2 gas of furnace and converter gases	Wet gas cooling and cleaning section for combined SO_2 gas of furnace and converter gases
Equipment supplied:	2 radial flow scrubber, 3 lines with 2 in-line wet EPs, acid cooler and acid circulation pumps, 2 cooling tower, 2200 m^3/h cooling media circulation	1 reversed jet scrubber, 1 cooling tower, 3 lines first stage wet EPs, 2 lines second stage wet EPs, acid cooler, SO2 stripper, acid circulation pumps, 2 cooling towers, 6 – 24 m^3/h weak acid effluent
Contact acid plant:	Double catalysis sulphuric acid plant	Double catalysis sulphuric acid plant
Equipment supplied:	Single strand, 4 pass converter with inter-pass absorption after the 2nd pass	Single strand, 5 pass converter with inter-pass absorption after the 3rd pass
Design basis gas cleaning:		
Operating temperature	370 °C inlet, 27 °C outlet	370 °C inlet, 27 °C outlet
Gas flow	91000 – 123000 Nm^3/h	45000 – 115000 Nm^3/h
Precipitation efficiency for dust	96.7%	96.7%
Design basis contact plant:		
Gas flow	91000 – 123000 Nm^3/h	45000 – 115000 Nm^3/h
SO_2	10 – 15.1% (av. 13%)	6 – 11.3%
Conversion SO_2/SO_3	> 99.5%	> 99.5%
H_2SO_4 production	1700 t/d	1350 t/d
Installed costs: **Million €**	**44 – 45**	**51 – 52**
Main consumption:	*)	*)
Electricity	75 – 80 kWh/t acid	55 – 60 kWh/t acid
Fuel oil		2 – 3 kg/t acid
Natural gas	3 - 4 Nm^3/t acid	
Catalyst	0.02 –0.04 l/t acid	0.02 –0.04 l/t acid
Labour	0.1 h/t acid	0.1 h/t acid

*) reference t acid = nominal design production

Table I.26: Copper smelter sulphuric acid plants
Source Copper industry - tm 92, Copper Expert Group 1998

Sulphuric acid plants **Lead / Zinc smelters**			
Year	**Components**	**Cost** **€ per t/a of acid**	**Acid production**
1995	Double contact plant	40	800000 t/a acid
1996	Double contact plant + Hg removal	155 120	100000 t/a acid 200000 t acid
1997	Double contact plant + Hg removal	130 100	100000 t/a acid 200000 t acid

Table I.27: Sulphuric acid plants
Source lead/zinc industry - Tm 120, TU Aachen 1999

I.5.4 Effluent treatment systems

Neutralisation of weak acid from a sulphuric acid plant and other acidic process water	
System equipment:	Thickeners, tanks, pumps, filter press
Application:	Weak acid resulting from an SO_2 gas flow of 200000 Nm³/h
Design basis: Flow	 32 m³/h weak acid
Installed cost: **Million €**	 **2.5*)**
Main consumption: Electricity Lime milk (10%) H_2SO_4 (10% $FeSO_4.7\ H_2O$	 200 kW 15 m³/h 0.8 m³/h 80 kg/h
Note. *) Civil work, erection, etc. excluded; for installed costs approx. 90 - 110% will have to be added. SOURCE: Lurgi Umwelt GmbH	

Table I.28: Weak acid neutralisation

ANNEX II INTERNATIONAL REGULATIONS (OVERVIEW)

In this section, a rough overview of important regulations on an international level effecting the copper production industry is given. International regulations and agreements have been worked out on different levels. Besides the European level, the different international committees of the United Nations like UNEP, UNCED, UNECE, WHO, IFCS have to be mentioned and the implications of the Kyoto and Montreal Protocols taken into account. In addition, the OECD is working in the field of environmental protection. Important international regulations, effecting the pollution of the different environmental media are [tm 124, DFIU Cu 1999]: -

II.1 Long Range Treaty on Air Pollution (LRTAP)

International efforts to reduce the adverse effects of the transboundary acidification on forests, aquatic ecosystems, and human health, by way of internationally co-ordinated emission reductions, were undertaken in the 1979 Convention on Long Range Trans-boundary Air Pollution (LRTAP). After coming into force in 1983, the LRTAP Convention was augmented by: -

(1) The 1984 Protocol on long-term financing;
(2) The 1985 Helsinki Protocol reducing sulphur emissions or their transboundary fluxes by at least 30%;
(3) The 1988 Sofia Protocol on the freezing of the emission of nitrogen oxides;
(4) The 1991 Geneva Protocol on the control of the emission of volatile organic compounds; and
(5) The 1994 Oslo Protocol on the further reduction of the emission of sulphur dioxide.
(6) The 1998 Aarhus Protocols on Persistent Organic Compounds (POPs) and on Heavy Metals.

II.2 Basel Conventions

The Basel Conventions declare the responsibility of OECD states regarding the control of transboundary movements of hazardous wastes and their disposal. It was adopted in March 1989 and entered into force in May 1992. In 1996, more than 100 countries plus the EC are parties to the Convention. The conventions comprise Technical Guidelines for waste management activities. In this guidelines materials are divided into substances with a ban for export (list A) and substances, which still can be exported to non-OECD countries. A decision adopted by the parties in 1994 prohibits with immediate effect the export from OECD countries of hazardous wastes destined for final disposal in non-OECD countries. The decision also phased out similar exports destined for recycling or recovery operations before banning them completely on 31 December 1997.

II.3 OECD-Council decision on Trans-frontier Movements of Hazardous Wastes

As a reaction of the "Basel Convention" of the United Nations, the council of the OECD ratified the council decision C 88(90). A three-tiered system was proposed to delineate controls to be applied to transfrontier movements: Wastes destined for recovery operations included on the green list would move among OECD Member countries toward recovery operations subject to all existing controls normally applied in commercial transactions. A notification procedure would exist for wastes destined for recovery operations included in the yellow list and wastes destined for recovery operations included in the amber list or red list would be subject to stricter or more rigorous controls.

II.4 Protection of the aquatic environment

There are several international activities concerning the protection of the aquatic environment. The most important ones are the Oslo Paris Commission (OSPARCOM) for the protection of the maritime environment of the North Sea and the Northeast Atlantic and the Helsinki commission of the countries bordering the East Sea (HELCOM) for the protection of their maritime environment.

In addition, there exist several international agreements on the pollution prevention of the main European seas (Nordseeschutzkonferenz), lakes (Bodensee) and rivers (e.g. Rhine (IKSR), Elbe(IKSE), Donau (IKSD), Oder (IKSO)). For example, there are two international agreements dating from 1978 concerning the pollution prevention of the River Rhine referring to chemical contamination and chlorides.

II.5 Global Environment Monitoring System (WHO/UNEP)

UNEP and WHO operate the GEMS (Global Environment Monitoring System) environmental pollution monitoring programmes for urban air quality (AIR), food, human exposure assessment location (HEAL), and water. The objectives of GEMS as defined at its inception are:

- to strengthen monitoring and assessment capabilities in the participating countries,
- to increase the validity and comparability of environmental data and information,
- top produce global/regional assessments in selected fields and compile environmental information at a global level.

II.6 Member State emission Limit Values

Contaminant	Country	Industry	Unit	Limit value[5]
Dust	Belgium	Pb	mg/Nm^3	10
		Other non-ferrous	mg/Nm^3	20
	France	Zn/Pb pyro	mg/Nm^3	10
		Zn/Pb pyro	kg/h	2.5
	Germany	Non-Ferrous	mg/Nm^3	20
		Pb	mg/Nm^3	10
	Netherlands	Zn	mg/Nm^3	30.0
		Sn	mg/Nm^3	5
		General Ind.	mg/Nm^3	25
	Norway	Zn	kg/h	50.0
		Cu, Ni	kg/h	2.0
	Spain	Zn	mg/Nm^3	50
		Pb (general)	mg/Nm^3	50
		Pb (refining)	mg/Nm^3	10
		General Ind.	mg/Nm^3	150
		Cu smelting	mg/Nm^3	150
		Cu refining	mg/Nm^3	300
		Cu hydrometallurgy	mg/Nm^3	300
	Sweden	Cu, Pb,Zn	mg/Nm^3	20
		Cu, Pb,Zn	t/y	250
		Cr-Ni-Pb-Zn	kg/t feedmat	0.1
		Cr-Ni, Pb-Zn	t/y	7
Arsenic	France	Zn/Pb pyro	kg/h	0.01
	Germany	All	mg/Nm^3	1[1]
	Sweden	Cu, Pb,Zn	t/y	8
Cadmium	France	Zn/Pb pyro	kg/h	0.2
	Germany	All	mg/Nm^3	0.1[6]
	Netherlands	Non-Ferrous	mMg/Nm^3	0.2
	Norway	Cu	kg/h	2.0
	Spain	Non-Ferrous	mg/Nm^3	17.0
	Sweden	Zn, Cu, Pb	t/y	0.8
Cobalt	Germany	All	mg/Nm^3	1[1]
Chromium	Germany	All	mg/Nm^3	5[1]
Copper	Germany	All	mg/Nm^3	5[3] [4]
	Spain	Non-Ferrous	mg/Nm^3	5
	Sweden	Cu smelting	mg/Nm^3	150
		Cu refining	mg/Nm^3	300
		Cu hydromet.	mg/Nm^3	300
		Zn, Cu, Pb	t/y	10

Table continued on following page.

Contaminant	Country	Industry	Unit	Limit value[5]
Mercury	France	Zn/Pb pyro	kg/h	0.01
	Germany	All	mg/Nm^3	0.2[2]
	Sweden	Zn, Cu, Pb	t/y	0.35
		Cr, Ni, Pb, Zn	g/t feed mat	0.4
Manganese	Germany	All	mg/Nm^3	5[3]
Nickel	Germany	All	mg/Nm^3	1[1]
Lead	France	Zn/Pb pyro	kg/h	0.5[3]
		Zn/Pb pyro	t/y	50
	Germany	All	mg/Nm^3	5
	Spain	Pb (flow < 300 m/min)	mg/Nm^3	80
		Pb(flow > 300 m^3/min)	mg/Nm^3	10
	Sweden	Zn, Cu, Pb	t/y	30
Antimony	Germany	All	mg/Nm^3	5[3]
	Sweden	Zn, Cu, Pb	t/y	8
Selenium	Germany	All	mg/Nm^3	1[1]
Tin	Germany	All	mg/Nm^3	5[3]
	Netherlands	Non-Ferrous	mg/Nm^3	5
Tellurium	Germany	All	mg/Nm^3	1[1]
Thallium	Germany	All		0.2[2]
Zinc	France	Zn/Pb pyro	kg/h	0.15
	Sweden	Zn, Cu, Pb	t/y	40

Table II.1: Atmospheric pollution - Emission limits for dust and metallic contaminants [tm 026, OSPARCOM 1998]

H In Germany: -

[1] The sum of Arsenic, Cobalt, Nickel, Selenium, Chrome(VI) and Tellurium (if the mass flow is 5 g/h or more) shall not exceed 1 mg/Nm^3.

[2] The sum of Cadmium, Mercury and Thallium (if the mass flow is 1 g/h or more) shall not exceed 0.2 mg/Nm^3.

[3] The sum of Lead, Chromium (total), Mangnese, Copper, Antimony, Tin, (and some more), (if the mass flow is 25 g/h or more) shall not exceed 5 mg/Nm^3.

[4] Smelting of cathode copper in a shaft furnace: emission of copper shall not exceed 10 mg/Nm^3.

[5] For compliance with the limit values the following rules apply:
a) No daily average shall exceed the limit value.
b) 97% of the half-hour averages shall not exceed 120% of the limit value.
c) No half-hourly average shall exceed 200% of the limit value.

[6] The emission limit value for cadmium and its compounds was tightened to 0.1 mg/Nm^3 (if the mass flow is 0.5 g/h or more) on 37th conference of the federal ministers of the environment 21/22 November 1991

Contaminant	Industry	Abated release concentration (mg/Nm^3)
Total particulate matter	Zn, Pb	10
	Ni (carbonyl process)	30
	Ni (other processes)	10
Pb	Zn, Pb	2
As + Se + Te	Zn, Pb	1
Sb + Cu + Sn	Zn, Pb	2
Cd + Hg + T1	Zn, Pb	0.5

(Addendum): Atmospheric pollution - Achievable release levels for new plant using BAT (UK) [tm 026, OSPARCOM 1998]

Component		NE-Metallverordung BGBI.II 1/1998 Concentration mg/Nm^3
Dust		20
Total C_{org} of which Benzo(α) pyrene		50 0.1
SO_2		300 (1,2) 500 (3)
CO		100 (1) 175 (2) 250 (3)
NO_2		250 (1) 350 (2) 500 (3)
Emission in vapour or particulate form	Pb, Zn, Cr (except Cr VI), Cu, Mn, V, Sn	5 in total
	Cu	10 (7)
	As, Co, Ni, CrVI, Se, Te	I in total
	Cd, Be, Hg, Tl of which: - Cd Be + Hg	0.2 in total 0.05 0.1

Addendum 2 - Austrian Emission Limit Values

Compound	Country	Industry	Unit	Limit value[4)]
Sulphuric acid mist	Norway	Cu, Ni	kg/h	0.75
	Spain	Non-ferrous	mg/Nm^3	150
	Sweden	Zn, Cu, Pb	t/y	40
Sulphur dioxide	Belgium	Non-ferrous	mg/Nm^3	800
	France	Zn/Pb pyro Zn/Pb pyro	t/y kg/t H_2SO_4	10000 10
	Netherlands	Zn	mg/Nm^3	1200
	Norway	Cu, Ni	kg/h	32.5
	Spain	Cu Non-Ferrous	mg/Nm^3 mg/Nm^3	1500 1425
	Sweden	Zn, Cu, Pb	t/y	5000
Sulphur trioxide	Netherlands	Zn	mg/Nm^3	100
Sulphur dioxide +	Germany*	Non-Ferrous Raw Metal Production All others	mg/Nm^3 mg/Nm^3	800 1) 500 1)
	Norway	Zn	kg/h	10
Chloride	Norway	Cu, Ni	kg/h	1.5
Chlorine	Germany*	Al-smelters All others	mg/Nm^3 mg/Nm^3	3 5 2)
Hydrochloric acid	Germany*	General	mg/Nm^3	30 3)
	Norway	Cu, Ni	kg/h	2.5
	Spain	Cu Non-Ferrous	mg/Nm^3 mg/Nm^3	300 460
Nitrogen oxides	Germany*	All	mg/Nm^3	500 1)
Carcinogenic substances	Germany*	All 5) Class I Class II Class III	 mg/Nm^3 mg/Nm^3 mg/Nm^3	 0.1 6) 1 7) 5 8)
Organic substances	Germany*	All 5) Class I Class II Class III	 mg/Nm^3 mg/Nm^3 mg/Nm^3	 20 9) 100 10) 150 11)

Table II.2: Atmospheric pollution - Emission limits for non-metallic contaminants [tm 026, OSPARCOM 1998]

* for Germany: - 1)If the mass flow is 5 kg/h or more.

2) The sum of Bromine, Chlorine, Fluorine, (and their compounds), (if the mass flow is 50 g/h or more) shall not exceed 5 mg/Nm.

3) If the mass flow is 0.3 kg/h or more.

4)For compliance with the limit values the following rules apply:

a) No daily average shall exceed the limit value.
b) 97% of the half-hour averages shall not exceed 120% of the limit value.
c) No half-hourly average shall exceed 200% of the limit value.

5) Dependent of harmfulness

6) If the mass flow is 0.5 g/h or more.

7) If the mass flow is 5 g/h or more.

8) If the mass flow is 25 g/h or more.

9) If the mass flow is 0.1 kg/h or more.

10)If the mass flow is 2 kg/h or more.

11)If the mass flow is 3 kg/h or more.

Contaminant	Industry	Abated release concentration
Oxides of sulphur (as SO_2)	Zn, Pb	800
Oxides of nitrogen (as NO_2)	Ni	300
Fluorides (as HF)	Ni	5

Table 2 (Addendum): Atmospheric pollution. Non-metallic contaminants - Achievable release levels for new plant using BAT (UK)
[tm 026, OSPARCOM 1998]

Contaminant	Country	Conditions	Industry	Unit	Limit value
Silver	Belgium	Total	All	mg/l	0.1
	Germany	Qualified random sample or 2 hour mixed sample	Pb, Cu, Zn	mg/l	0.1 2)
Aluminium	Germany	Qualified random sample or 2 hour mixed sample	Al_2O_3 Al smelters	kg/t kg/t	0.009 0.02
Arsenic	Belgium	Total	All	mg/l	1
	Germany	Qualified random sample or 2 hour mixed sample	All	mg/l g/t(*)	0.1 2) 2 1) 2)
	Norway	Monthly average	Cu, Ni	kg/d	4
	Sweden		Zn, Cu, Pb Cr-Ni-Pb-Zn	t/y t/y	20 0.001
	Spain		All Dissolved metal	mg/l	0.5
Cadmium	Belgium	Total existing plants Monthly average, existing Plants Total, new plants Monthly average, new plants Total	Zn, Pb Zn, Pb Zn, Pb Zn, Pb Cu, Ni, Sn	mg/l mg/l mg/l mg/l mg/l	0.9 0.3 0.5 0.2 1
	France		Zn	mg/l	0.5
	Germany	Qualified random sample or 2 hour mixed sample	All	mg/l g/t	0.2 2) 3 1) 2)
	Norway	Monthly average	Cu, Ni Zn roasting & H_2SO_4 production Zn leaching plant	kg/d mg/l kg/d mg/l kg/d	0.01 0.2 0.03 0.2 0.3
	Sweden		Zn, Cu, Pb Cr-Ni-Pb-Zn	t/y t/y	0.4 0.001
	Spain	Monthly average Daily average	All Dissolved metal	mg/l mg/l	0.2 0.4
Cobalt	Belgium	Dissolved	All	mg/l	3
	Germany	Qualified random sample or 2 hour mixed sample	All	mg/l	1 2)
	Norway	Monthly average	Cu, Ni	kg/d	2.5

I Data from Sweden are per plant.

Table continued on following page

Contaminant	Country	Conditions	Industry	Unit	Limit value
Chromium	Belgium	dissolved total	All All	mg/l mg/l	2 5
	Germany	total	Pb, Cu, Zn	mg/l g/t	0.5 2) 10 1) 2)
	Spain	Cr (III)	All Dissolved metal	mg/l	2
	Belgium	Cr (VI)	All	mg/l	0.2
	Germany	Cr (VI) random sample	Pb, Cu, Zn	mg/l	0.1 3)
	Norway	Cr (VI) monthly average	Cu, Ni	kg/d	0.01
	Spain	Cr (VI)	All Dissolved metal	mg/l	0.2
	Sweden		Cr-Ni-Pb-Zn	t/y	0.025
Copper	Belgium	dissolved dissolved total total	Zn Pb Ni Cu Zn Pb Ni Cu	mg/l mg/l mg/l mg/l	2 3 4 6
	Germany	qualified random sample or 2 hour mixed sample	All	mg/l g/t	0.5 2) 10 1) 2)
	Norway	monthly average	Cu, Ni Zn roasting & H_2SO_4 production Zn leaching plant	kg/d mg/l kg/d mg/l kg/d	10 0.2 0.03 0.2 0.3
	Sweden		Zn, Cu, Pb Cr-Ni-Pb-Zn	t/y t/y	2 0.04
	Spain		All Dissolved metal	mg/l	0.2
Unbound Cyanide	Germany	qualified random sample or 2 hour mixed sample	All	mg/l	0.1 3)
Hydrocarbons	Germany	qualified random sample or2 hour mixed sample	Al-smelting Al-casting & semi finished products process	kg/t kg/t	0.02 0.05
Iron	Belgium	dissolved total	All All	mg/l mg/l	2 20
	Germany	qualified random sample or 2 hour mixed sample	All	kg/t	0.1
	Norway	monthly average	Cu, Ni	kg/d	40
	Spain		All Dissolved metal	mg/l	2

(*) kg/t in Germany means kilograms of contaminant per tonne of metal produced

Table continued on following page

Contaminant	Country	Conditions	Industry	Unit	Limit value
Mercury	Belgium	total	All	mg/l	0.1
	Germany	qualified random sample or2 hour mixed sample	All	mg/l g/t	0.05[2)] 1.0[1) 2)]
	Norway	monthly average	Cu, Ni Zn roasting & $H2SO_4$ prodn Zn leaching plant	kg/d mg/l kg/d mg/l kg/d	0.01 0.1 0.02 0.03 0.05
	Sweden		Zn, Cu, Pb Cr-Ni-Pb-Zn	t/y t/y	0.1 0.01
	Spain	monthly average daily average	All Dissolved metal All	mg/l mg/l	0.05 0.10
Nickel	Belgium	dissolved	All	mg/i	3
	Germany	qualified random sample or 2 hour mixed sample	Pb, Cu, Zn	mg/i g/t	0.5[2)] 15[1) 2)]
	Norway	monthly average	Cu, Ni	kg/d	15
	Spain		All Dissolved metal	mg/l	2
	Sweden		Cr-Ni-Pb-Zn	t/y	0.01
Lead	Belgium	total	All	mg/l	2
	Germany	qualified random sample or2 hour mixed sample	All	mg/l g/t	0.5[2)] 15[1) 2)]
	Norway	monthly average	Cu, Ni	kg/d	1.0
	Sweden		Zn, Cu, Pb Cr-Ni-Pb-Zn	t/y t/y	2 0.01
	Spain		All Dissolved metal	mg/l	0.2
Free chlorine	Germany	random sample	Al (wastewater from off-gas treatment after chlorine refining	mg/l	0.5[3)]
Fluoride	France		Zn	mg/l	10
Fluoride	Germany	qualified random sample or 2 hour mixed sample	Al smelters Al casting & semi prodn	kg/t kg/t	0.3 0.3
Sulphide (dissolved)	Germany	qualified random sample or 2 hour mixed sample	Pb, Cu, Zn	mg/l	1[2)]
Tin	Belgium	dissolved	All	mg/l	2[2)]
	Germany	qualified random sample or 2 hour mixed sample	Pb, Cu, Zn	mg/l	2
	Spain		All Dissolved metal	mg/l	10
Thallium	Germany	qualified random sample or 2 hour mixed sample	Pb, Cu, Zn	mg/l	1

Table continued on following page

Contaminant	Country	Conditions	Industry	Unit	Limit value
Zinc	Belgium	dissolved total	All All	mg/l mg/l	3 7
	France	total	Zn	mg/l	1
	Germany	qualified random sample or 2 hour mixed sample	Pb, Cu, Zn	mg/l g/t	1[2] 30[1] [2]
	Norway	monthly average	Cu, Ni	kg/d	4
			Zn roasting & H_2SO_4 production	mg/l kg/d	5 0.75
			Zn leaching plant	mg/l kg/d	5 7.5
			Zn electrolysis and discarding	kg/d	30
	Sweden		Zn, Cu, Pb Cr-Ni-Pb-Zn	t/y t/y	8 0.1
	Spain		All Dissolved metal	mg/l	3
Cd+Zn+Cu+Fe+ Cr+Ni	France		Zn	mg/l	10
Ni+Cr+Cu+As+ Pb	Belgium	dissolved	All	mg/l	8
pH	Norway		Zn leaching	pH	9 - 11
	Spain			pH	5.5 - 9.5
Suspended solids	France		Zn	mg/l	30
	Spain		All	mg/l	80
Hexachloro benzene	Germany	qualified random sample or 2 hour mixed sample	Al (wastewater from off-gas treatment after chlorine refining	mg/l	0.003
Toxicity to fish, as dilution factor T_F	Germany	qualified random sample or 2 hour mixed sample	Pb, Cu, Zn		4
AOX	Germany	qualified random sample or 2 hour mixed sample	Al, Pb, Cu, Zn	mg/l	1
COD	France		Zn	mg/l	40
	Germany	qualified random sample or 2 hour mixed sample	Pb, Cu, Zn Al_2O_3 Al smelters Al casting & semi finished	kg/t	1.5 0.5 0.3 0.5
	Spain			mg/l	160

Table II.3: Water pollution - Limit values for discharges into water [tm 026, OSPARCOM 1998]

For Germany: - [1] additional requirement at a production capacity > 10 t/d
[2] before mixing with other wastewater,
[3] at the place of wastewater generation

Contaminant	Industry	Abated release concentration (µg/litre)
Cadmium	Zn, Pb	100
Mercury	Zn, Pb	20

Table 3 (Addendum) - Water pollution. Achievable release levels for new plant using BAT (UK)
[tm 026, OSPARCOM 1998]

	daily average	half hourly average	average of sampling
total dust	10 mg/Nm³	30 mg/Nm³	
organic matter	10 mg C/m³	20 mg C/m³	
CO	50 mg CO/m³	100 mg CO/m³	
gaseous inorganic compounds of chlorine	10 mg HCl/m³	60 mg HCl/m³	
gaseous inorganic compounds of fluorine	1 mg HF/m³	4 mg HF/m³	
SO_2 and SO_3	50 mg SO_2/m³	200 mg SO_2/m³	
NO and NO_2	200 mg NO_2/m³	400 mg NO_2/m³	
∑ Cd, Tl compounds			0.05 mg metal/m³
Hg compounds	0.03 mg Hg/m³	0.05 mg Hg/m³	
∑ Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Sn compounds			0.5 mg metal/m³
∑ PCDD/F			0.1 ng TE/m³

Table II.4: German emission limit values for incineration processes

In general, these values are applicable to all installations or parts of installations where waste is being burned. Hence these limit values are partly being applied for thermal treatment of input material in several branches of secondary production of non-ferrous metals (e.g. lead, precious metals, nickel). If only parts of the input to the installation is classifies as waste, the limit value will be calculated taking into account the present limit values, the limit values for the originate metal production, and the input percentage of waste.