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 2.1: 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 2.2: Metal content of some dusts from various lead and zinc production processes [tm 25, DFIU 1996]

1.1.3 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 2.3: Summary of associated emissions to water for some processes

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.

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.

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.

2 PROCESSES TO PRODUCE PRECIOUS METALS

2.1 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 2.1: 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.

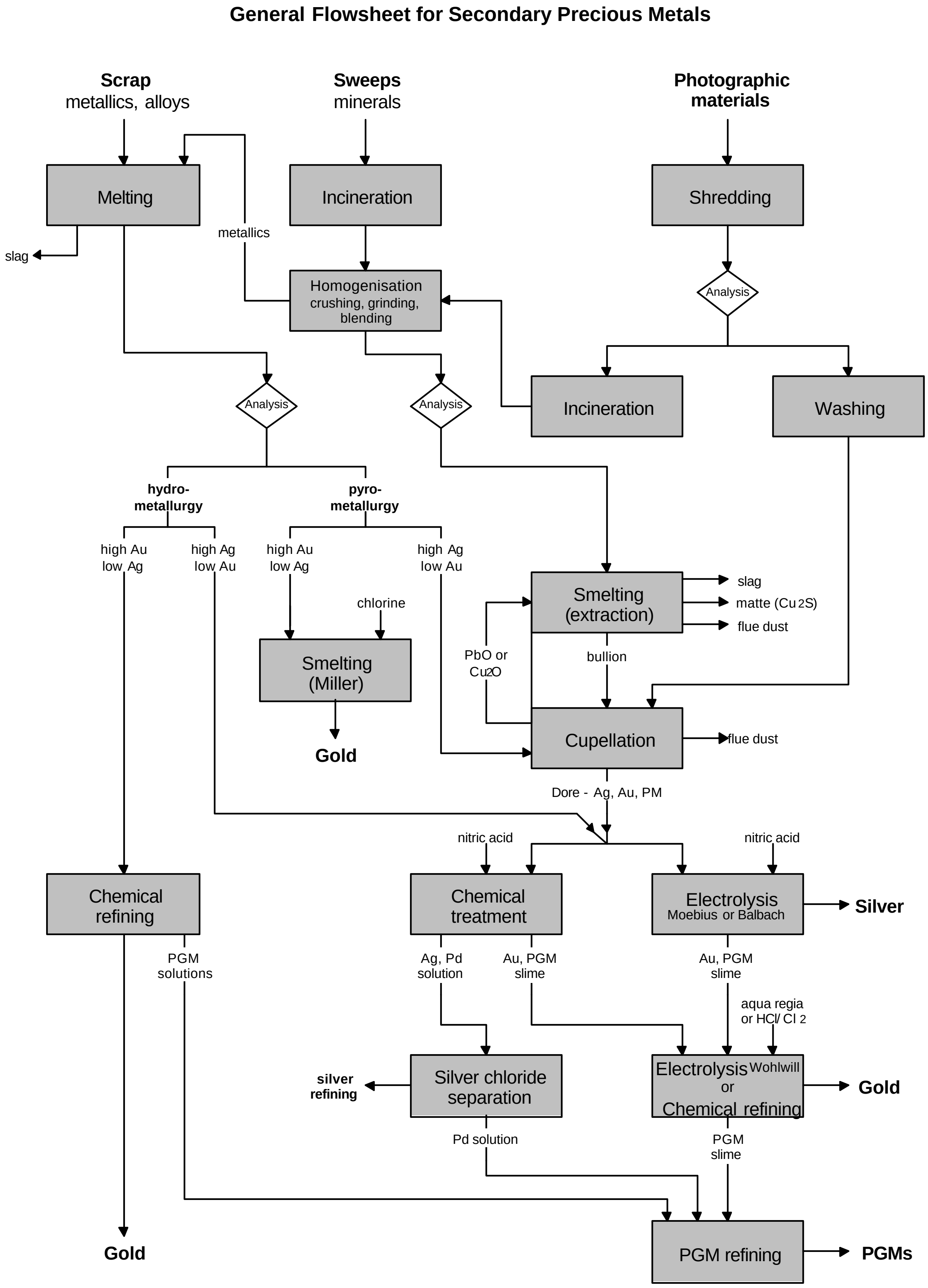


Figure 2.1: General flow-sheet for precious metal recovery

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.

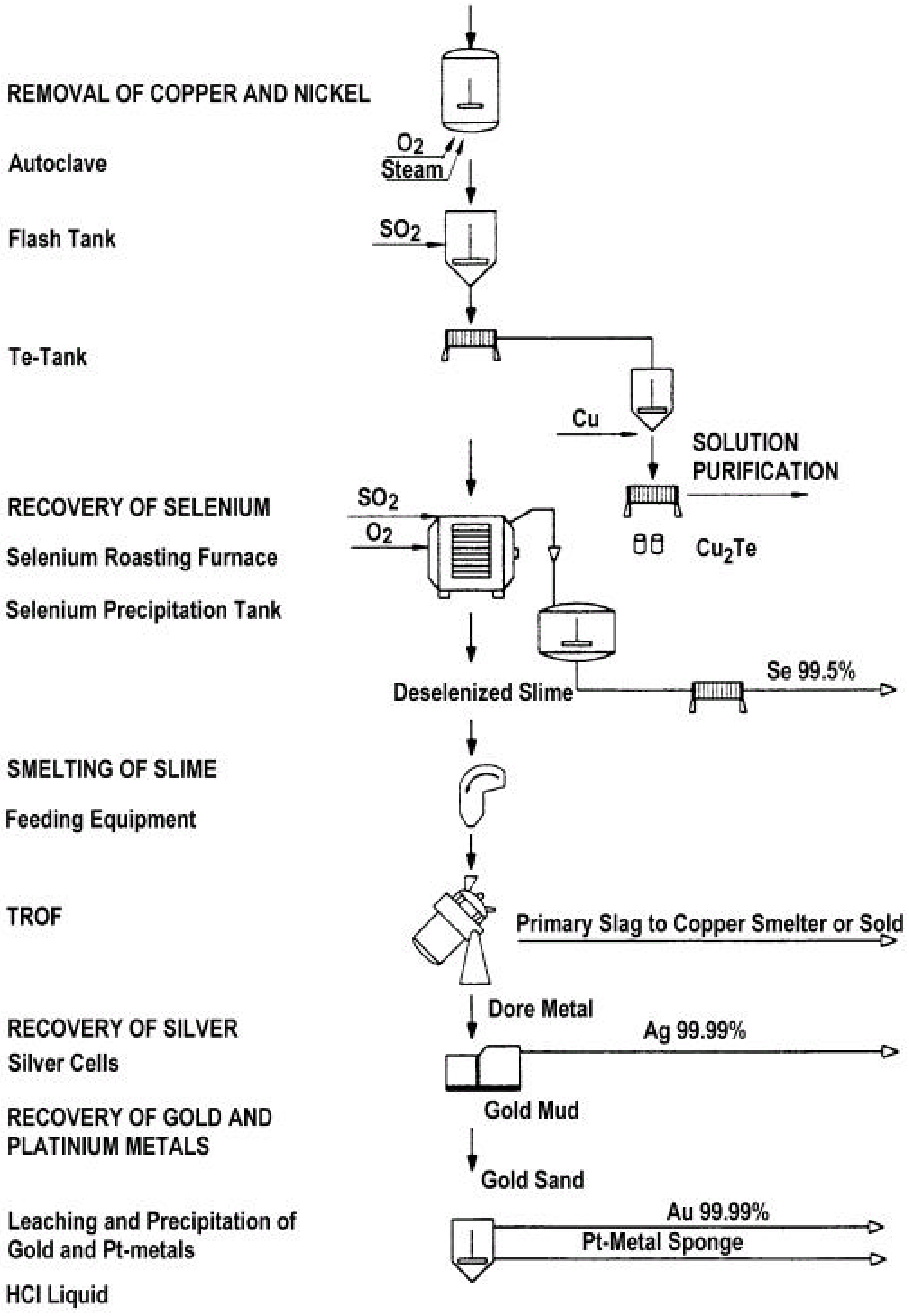


Figure 2.2: Example flow-sheet for anode slime treatment

2.1.1 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].

2.1.1.1 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).

2.1.1.2 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.

2.1.1.3 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.

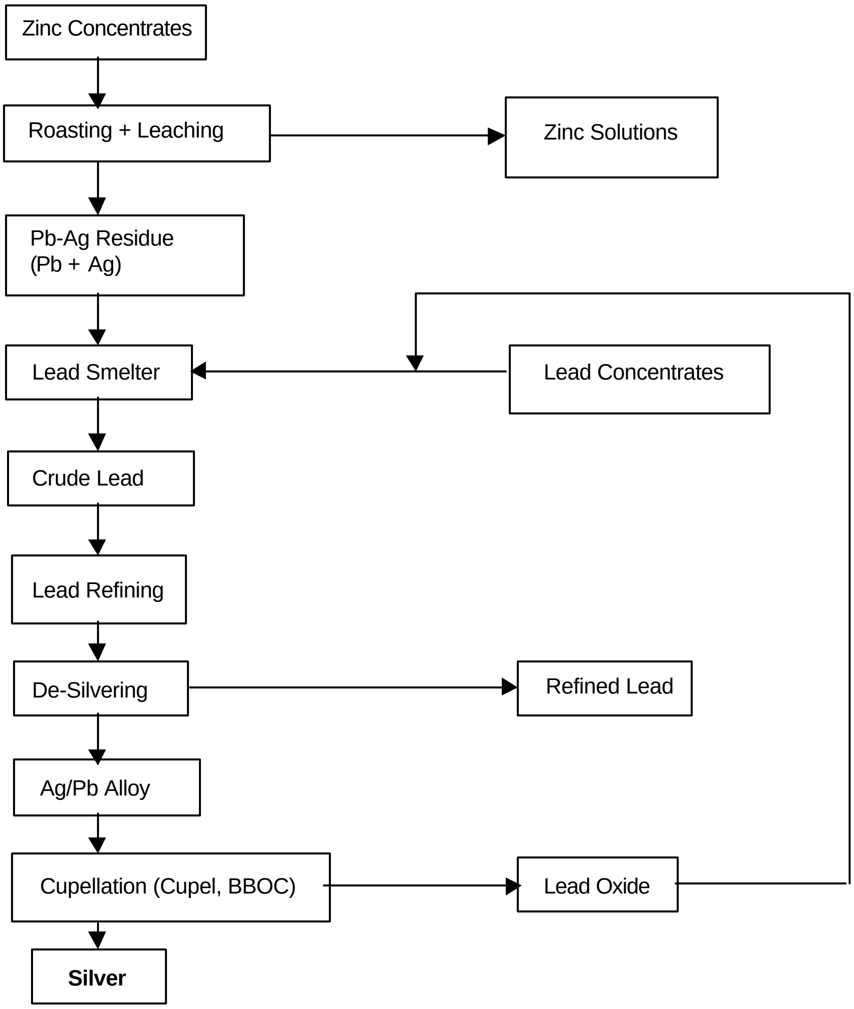


Figure 2.3: Recovery of silver from zinc and lead production

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.

2.1.1.4 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.

2.1.2 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.

2.1.2.1 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.

2.1.2.2 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.

2.1.2.3 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.

2.1.3 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.

2.2 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.

2.2.1 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.

2.2.1.1 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.

2.2.1.2 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.

2.2.2 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 2.2: 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 2.3: Emissions to air from a range of large processes

2.2.2.1 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].

2.2.2.2 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.

2.2.2.3 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.

2.2.2.4 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.

2.2.2.5 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 2.4: Emissions to air from a range of small processes
[tm 164, Bobeth 1999]

2.2.3 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 2.5: 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 2.6: 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.

2.2.4 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 2.7: Example of waste quantities

2.2.5 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.

2.3 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.

2.3.1 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 2.8: Material handling and pre-treatment

2.3.2 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 2.9: 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.

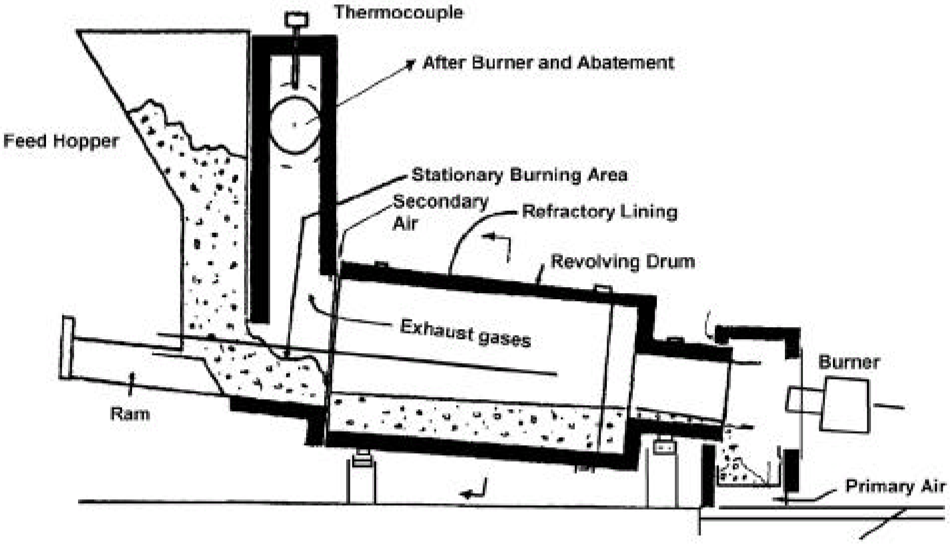


Figure 2.4: Incinerator for photographic film

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 2.10: Smelting and cupelling furnaces

2.3.3 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.

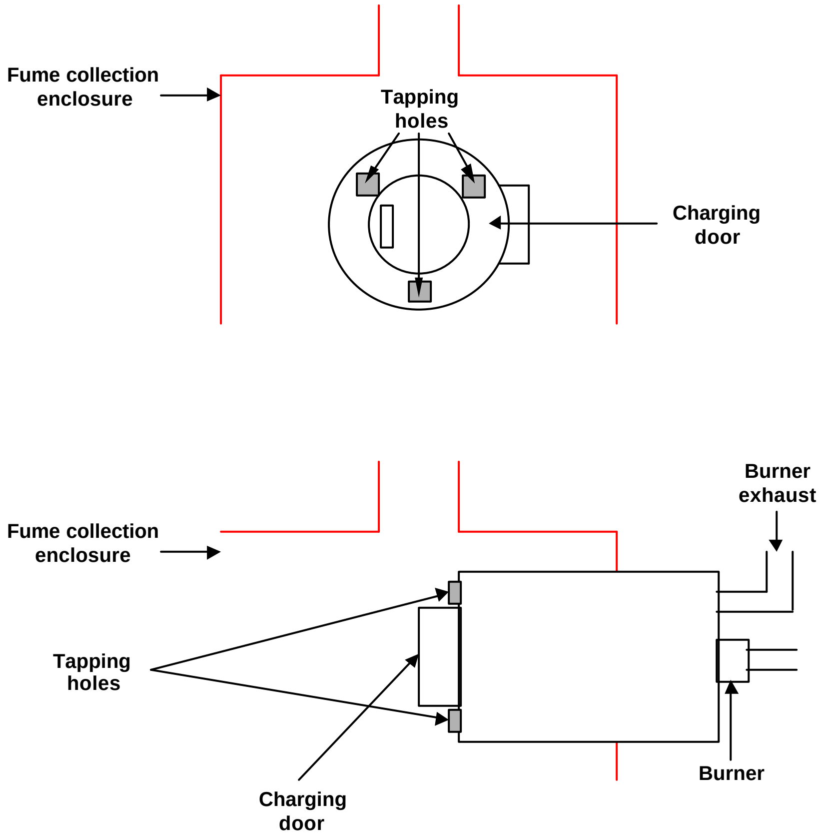


Figure 2.5: Co-incident fume capture system

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.		

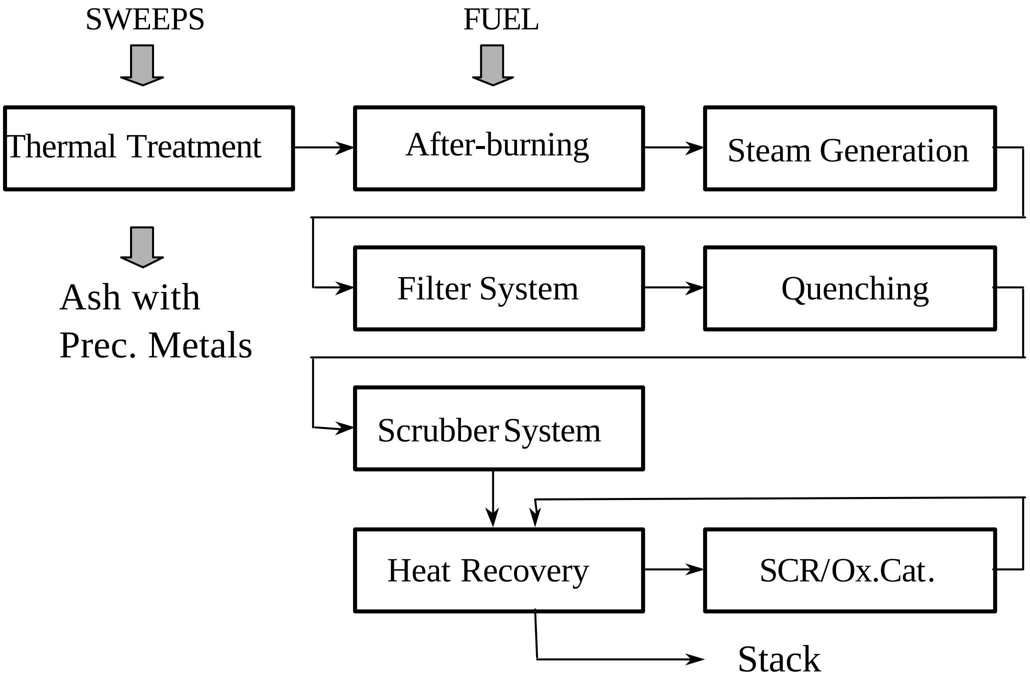
Table 2.11: Chemical treatment methods for some gaseous components

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.

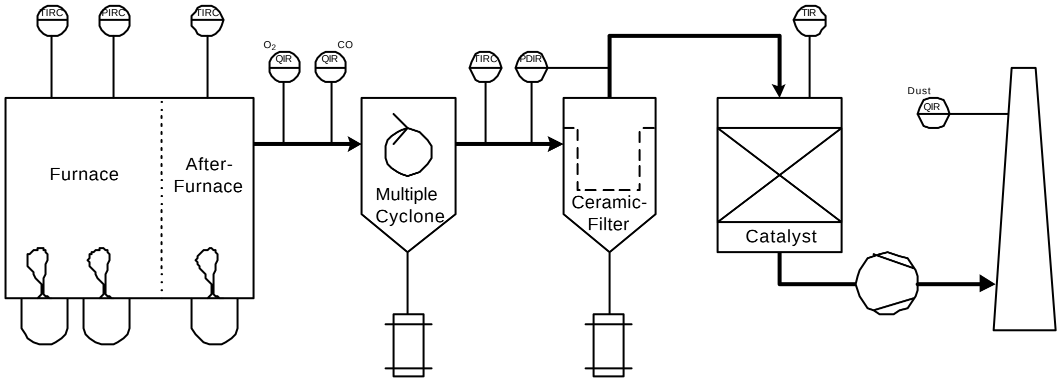
Applicability: - Not reported.

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]

2.3.4 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]

2.3.5 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.

2.3.6 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.

2.3.7 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.

2.4 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].

2.4.1 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.

2.4.2 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.

2.4.2.1 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

2.4.2.2 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 2.12: Furnace options for precious metals

2.4.2.3 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.

2.4.3 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 2.13: 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.

2.4.3.1 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 2.14: 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 2.15: 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 2.16: 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.

2.4.4 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 2.17: Emissions to water associated with the use of BAT

2.4.5 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.

2.4.6 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.

2.5 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 ìm) 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.

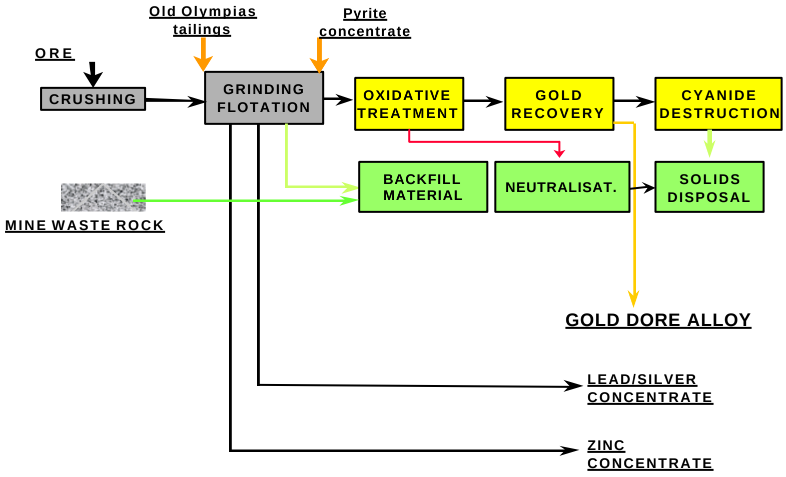


Figure 2.6: Ore treatment flow-sheet

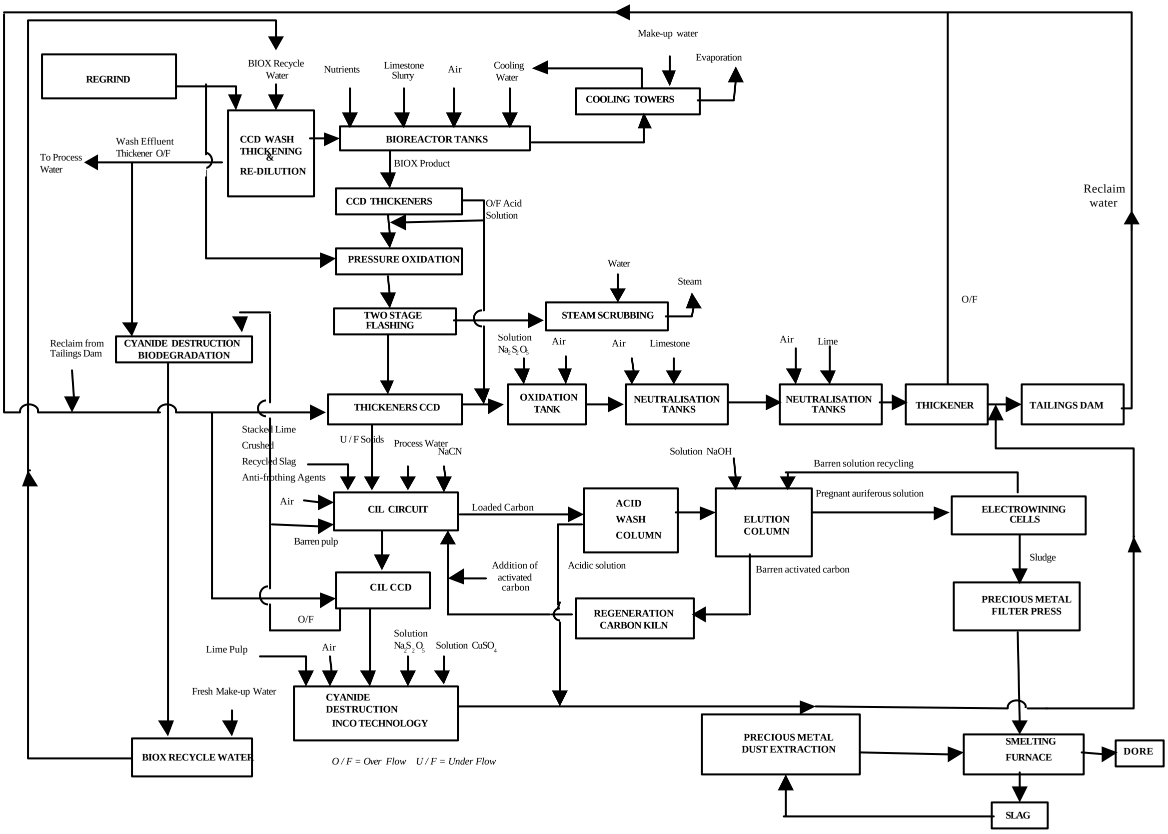


Figure 2.7: Metallurgical process flow-sheet

3 PROCESSES TO PRODUCE MERCURY

3.1 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.

3.1.1 Primary production

3.1.1.1 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].

3.1.1.2 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].

3.1.2 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.

3.2 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].

3.2.1 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 3.1: 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 3.2: Emissions to water from primary production

3.2.2 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 3.3: Emissions to air from secondary production

Year	Hg to water ppb.	Volume m^3
1997	0.3 g/tonne	

Table 3.4: Emissions to water from secondary production

3.2.3 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.

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 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.

3.3.1 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:

$$HgCl_2 + Hg \Rightarrow Hg_2Cl_2$$

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]

3.3.2 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.

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 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.

3.4.1 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.

3.4.2 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.

3.4.3 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 3.5: Summary of abatement methods for components in the off-gas

3.4.3.1 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 3.6: 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 3.7: 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).

3.4.4 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.

3.4.5 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.

3.5 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.

4 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.

4.1 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.

4.1.1 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.

4.1.1.1 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 ºC. 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.

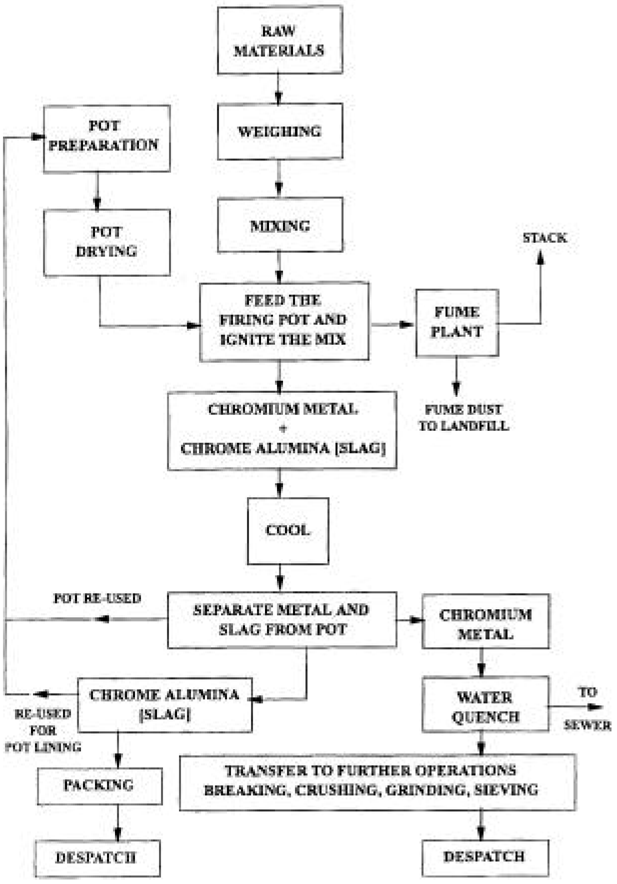


Figure 4.1: Production of chromium metal by the metallo-thermic process

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.

4.1.1.2 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 ºC. 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.

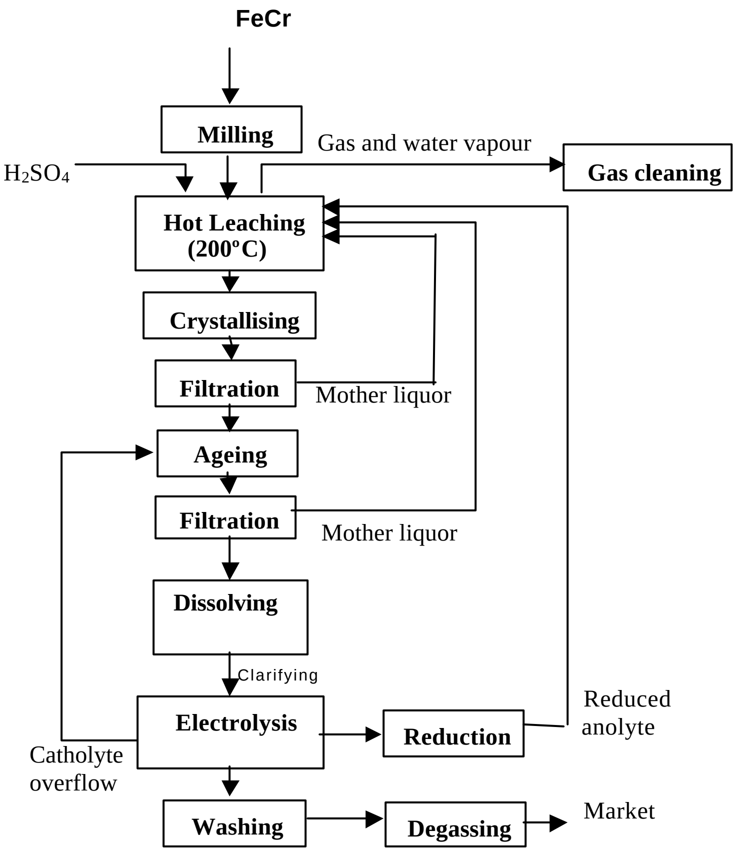


Figure 4.2: Production of chromium metal by electrolysis

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.

4.1.2 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.

4.1.2.1 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.

4.1.2.2 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.

4.1.3 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.

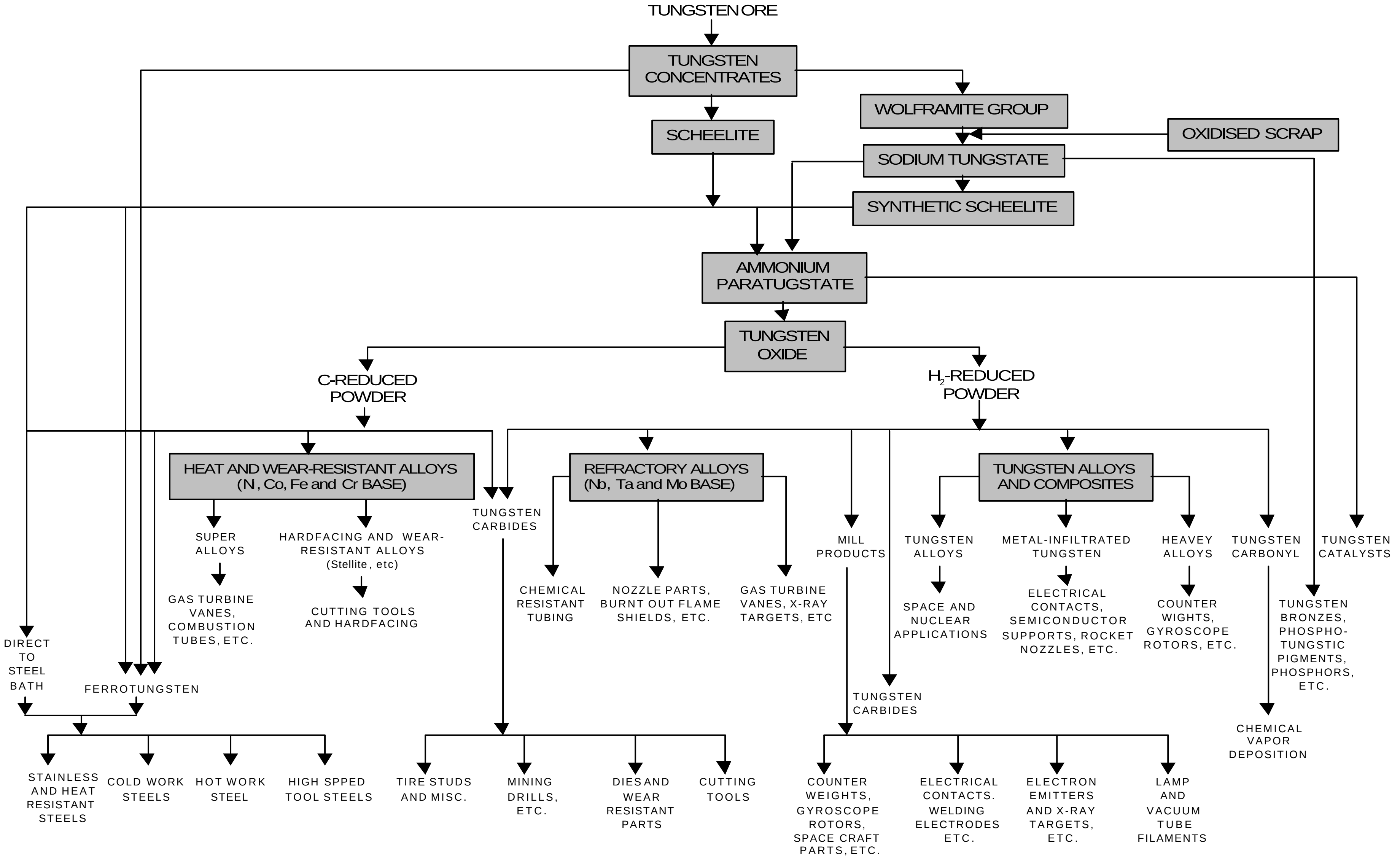


Figure 4.3: Tungsten flow-sheet
[tm 008, HMIP 1993]

4.1.3.1 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.

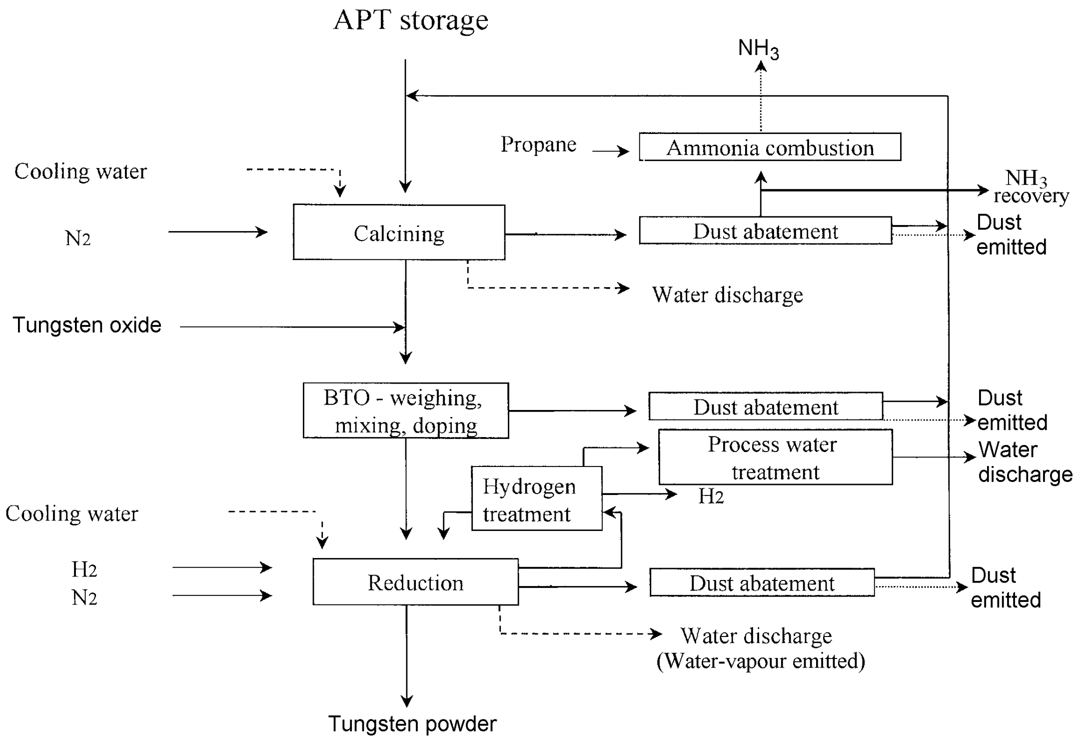


Figure 4.4: Production of tungsten metal powder
[tm 182, ITIA 1999]

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 ºC.
- **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 ºC.

The process of carburisation tungsten metal powder is shown in the following flowsheet.

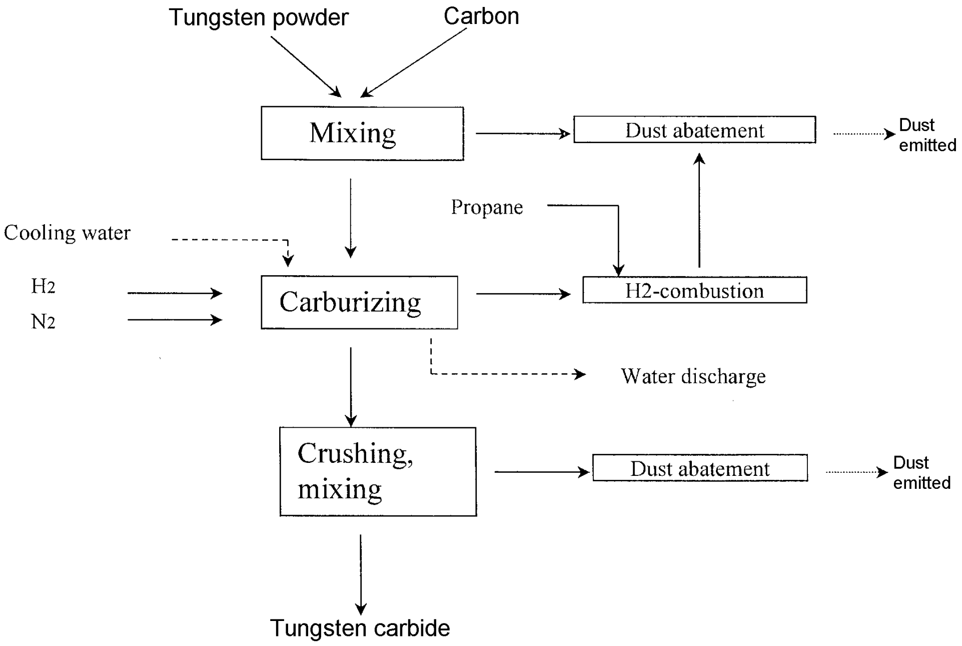


Figure 4.5: Production of tungsten carbide
[tm 182, ITIA 1999]

4.1.3.2 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.

4.1.4 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.

4.1.4.1 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.

4.1.4.2 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.

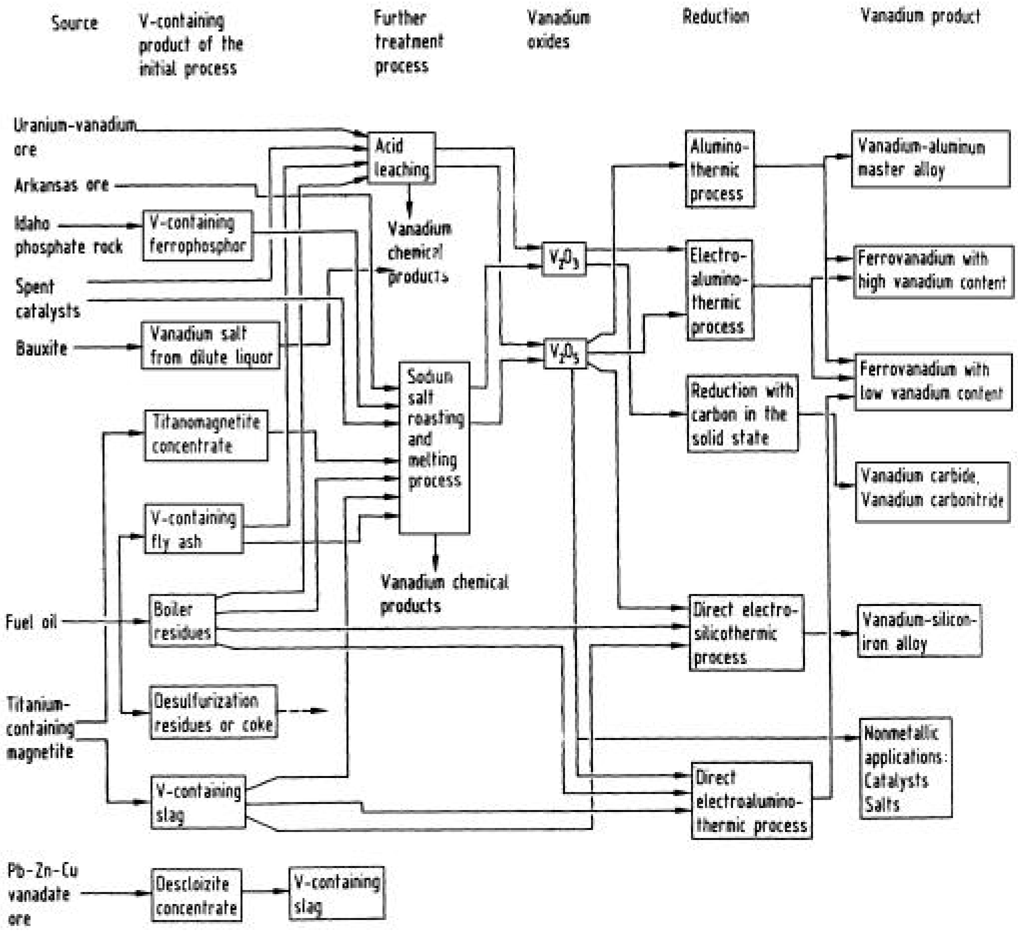


Figure 4.6: Production of vanadium pentoxide and vanadium metal
[tm 008, HMIP 1993]

4.1.5 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.

4.1.5.1 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.

4.1.5.2 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.

4.1.6 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%.

4.1.6.1 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.

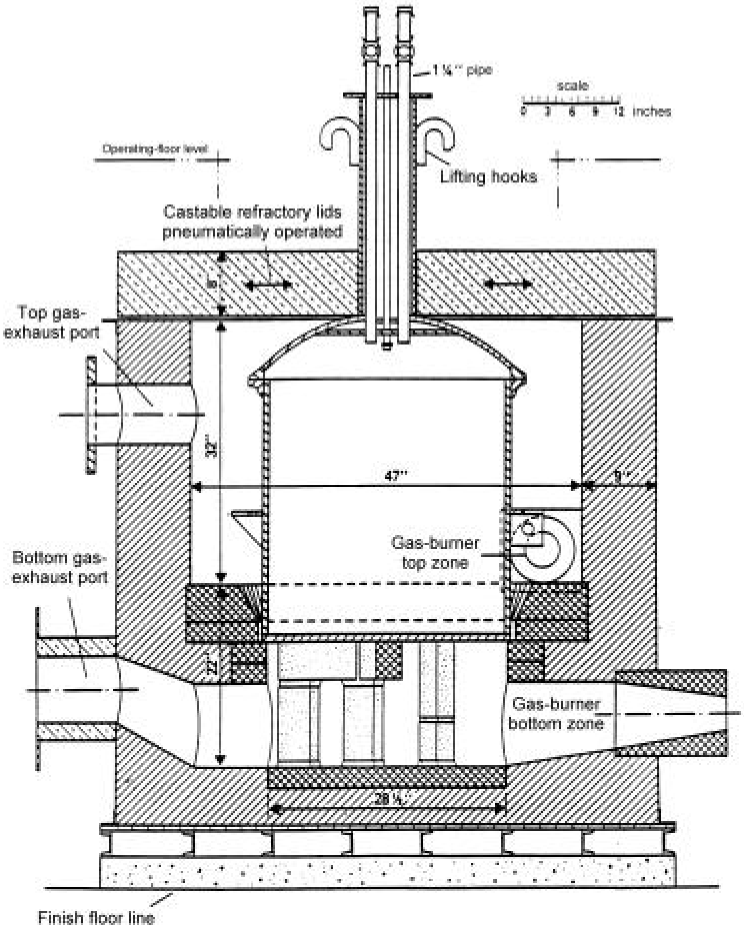


Figure 4.7: Reaction vessel of the titanium production using the Kroll process [tm 008, HMIP 1993]

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 ºC, 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.

4.1.6.2 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.

4.1.7 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.

4.1.7.1 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.

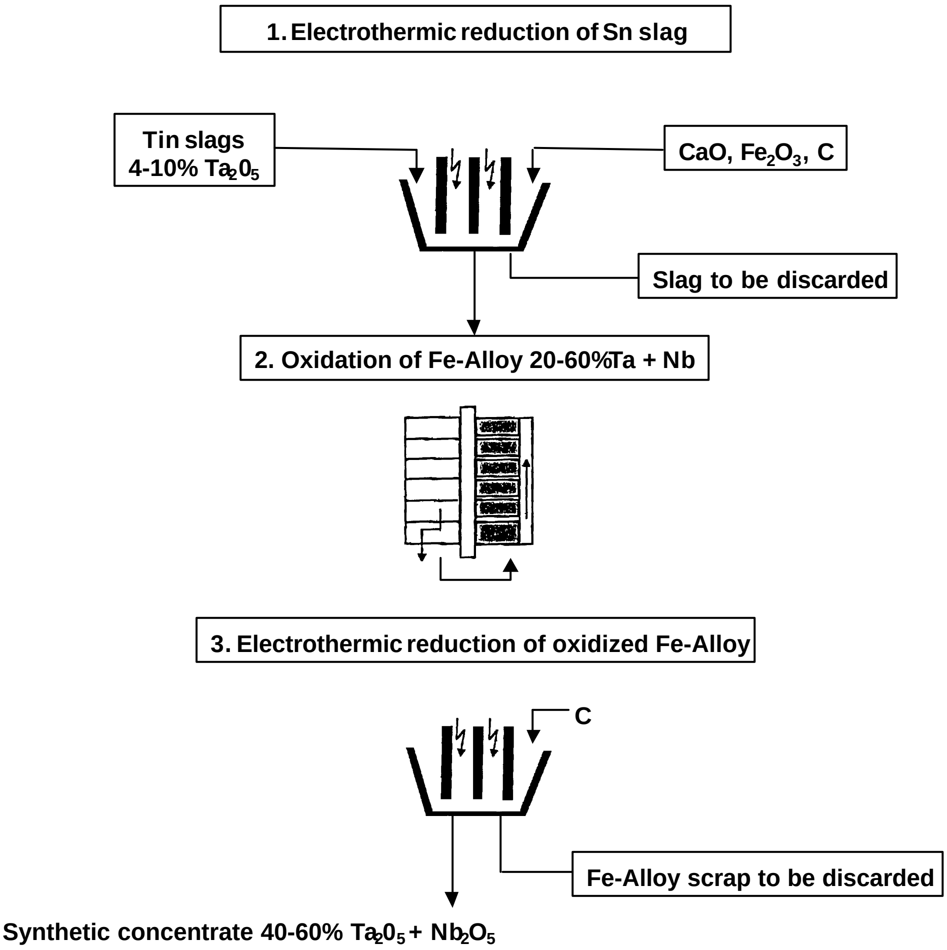


Figure 4.8: The production of tantalum and niobium oxides from tin slag

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.

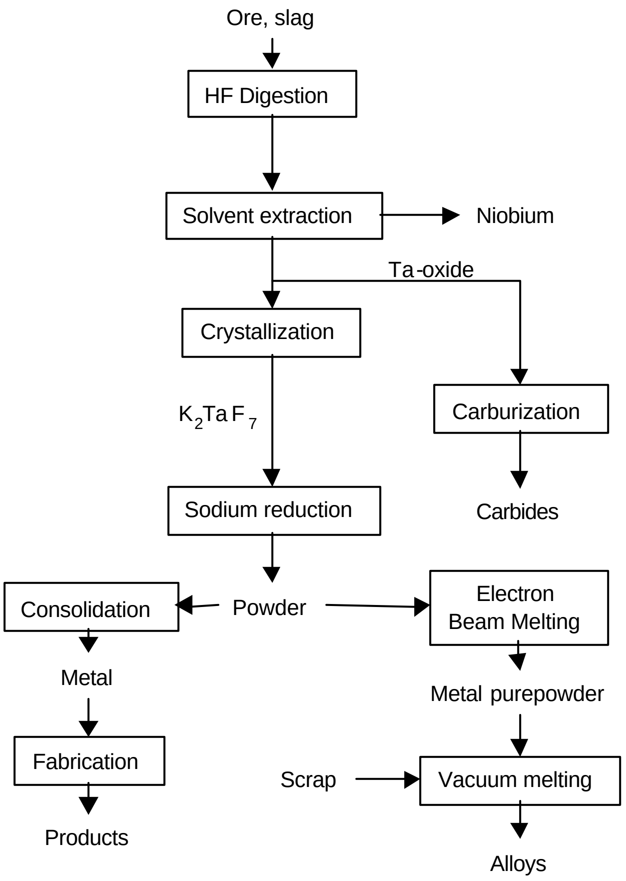


Figure 4.9: Production of pure tantalum metal powder

4.1.7.2 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.

4.1.8 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.

4.1.8.1 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.

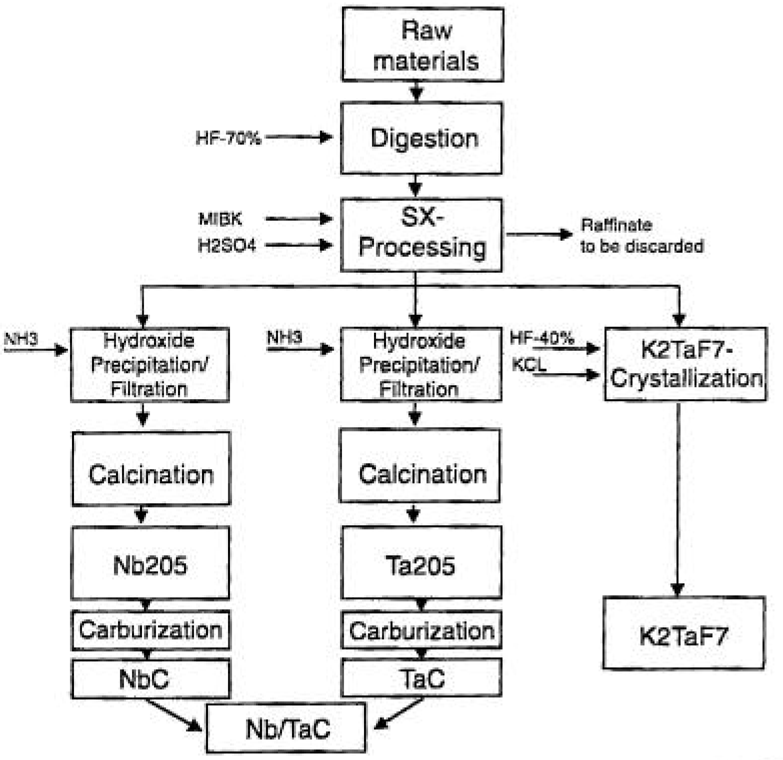


Figure 4.10: Processing of niobium and tantalum compounds

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 ºC 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.

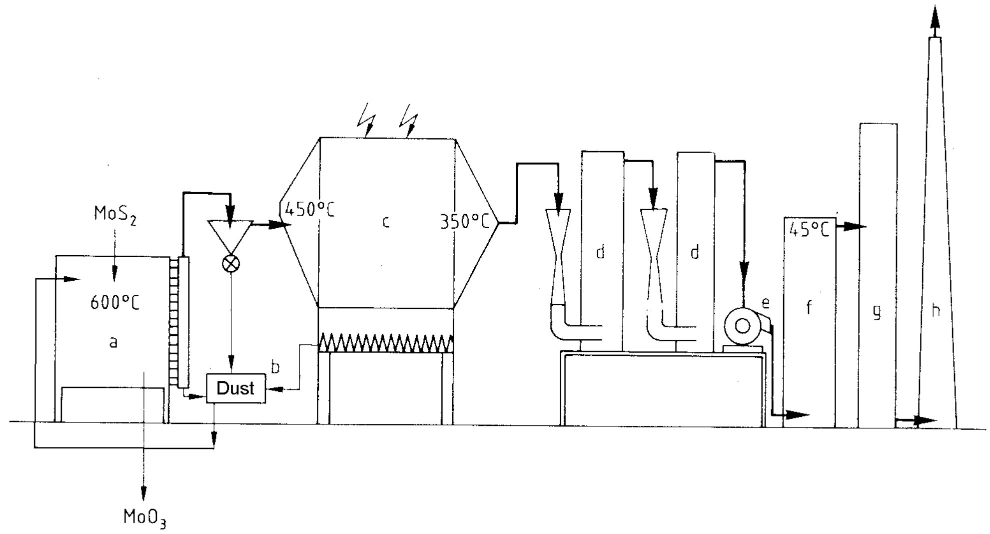
4.1.9 Rhenium

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.

4.1.9.1 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 4.11: 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.

4.1.9.2 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 °C rhenium dioxide will be produced. The second stage reduces the rhenium dioxide at 800 °C 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.

4.1.10 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.

4.2 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

4.2.1 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 4.1: 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 4.2: Process data for smelting refractory metals in an electron beam furnace
[tm 107, Ullmanns 1996]

4.2.2 Emissions

4.2.2.1 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].

4.2.2.2 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.

4.2.2.3 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.

4.2.2.4 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 4.3: 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 4.4: 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 4.5: 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 4.6: 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 4.7: 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 4.8: 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 4.9: Emissions by producing rhenium, zirconium and hafnium metal

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.

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]

4.3.1 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.

4.3.2 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 4.10: 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.

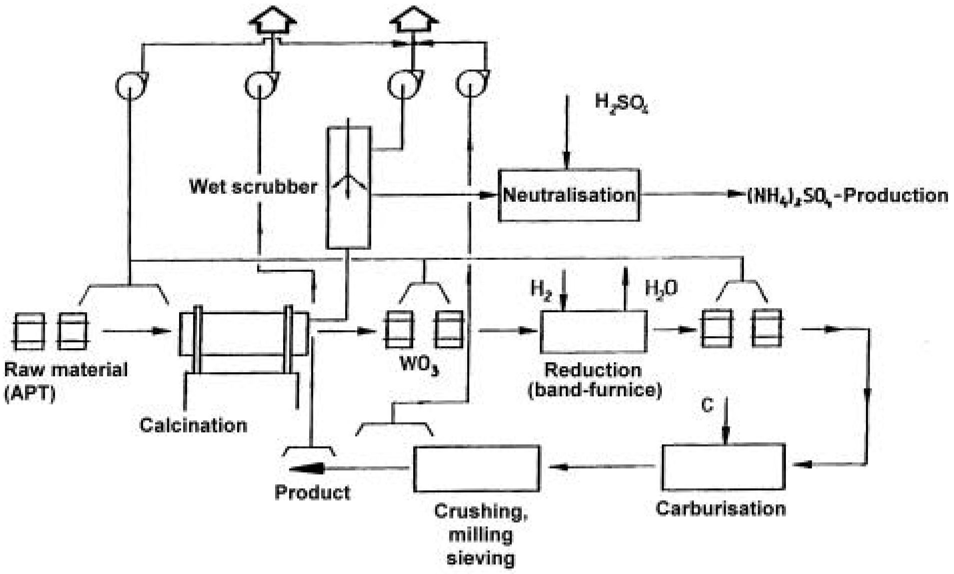


Figure 4.12: Production of tungsten powder and tungsten carbide

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 4.11 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]

4.3.3 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.

4.3.4 Process control

The principles of process control discussed in Chapter 2 are applicable to the production processes used in this Group.

4.3.5 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.

4.3.6 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.

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 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.

4.4.1 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.

4.4.2 Process selection

4.4.2.1 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 4.12: Furnaces considered as BAT for the production of refractory metals

4.4.2.2 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.

4.4.3 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 4.13: **Emission levels to air associated with the use of BAT**

4.4.4 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.

4.4.5 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 4.14: Recycling and reuse of residues from the production of refractory metals

4.5 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.

5 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.

<u>Primary Processes:</u>

Oxidic metal ore + iron ore/scrap + reductant ® ferro-alloy + reductant oxide + slag

<u>Secondary Processes:</u>

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**

5.1 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.

5.1.1 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*”)

5.1.1.1 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.

5.1.1.2 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.

5.1.1.3 Production of ferro-chrome and silico-chromium

5.1.1.3.1 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.

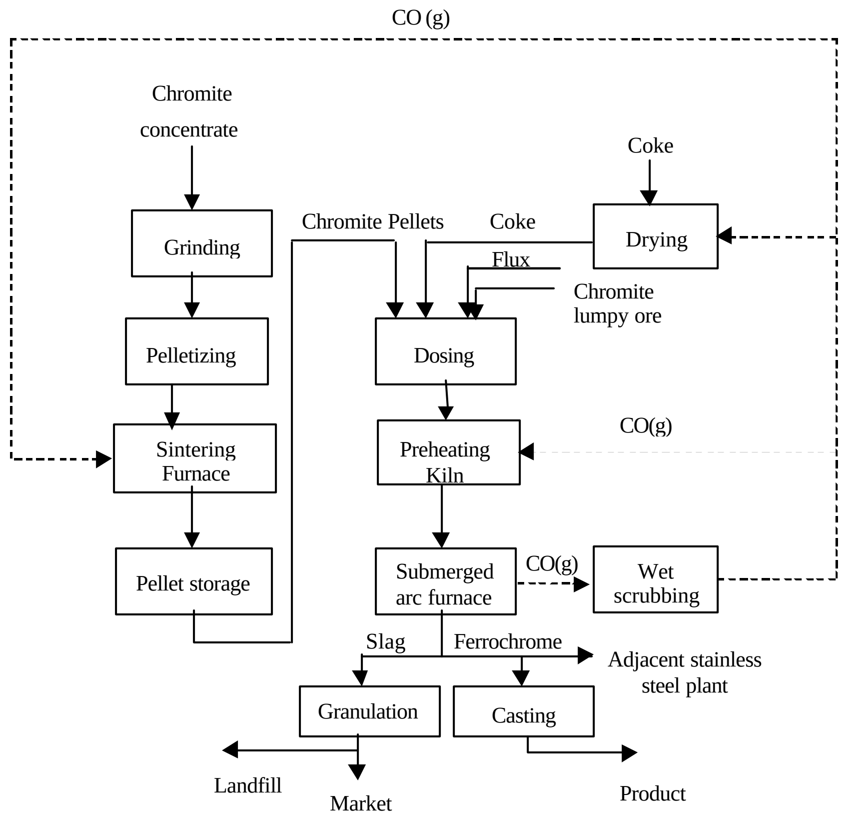


Figure 5.1: High-carbon ferro-chrome production by using a closed furnace

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.

5.1.1.3.2 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.

5.1.1.3.3 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.

5.1.1.3.4 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.

5.1.2 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%

5.1.2.1 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 5.1: 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.

5.1.2.2 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.

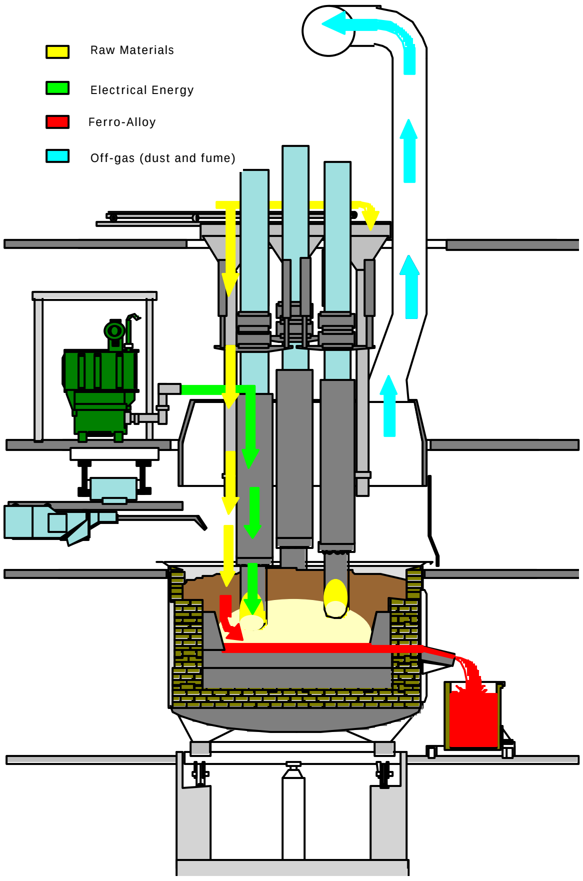


Figure 5.2: Electric arc furnace for the production of Si-metal, ferro-silicon and CaSi

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.

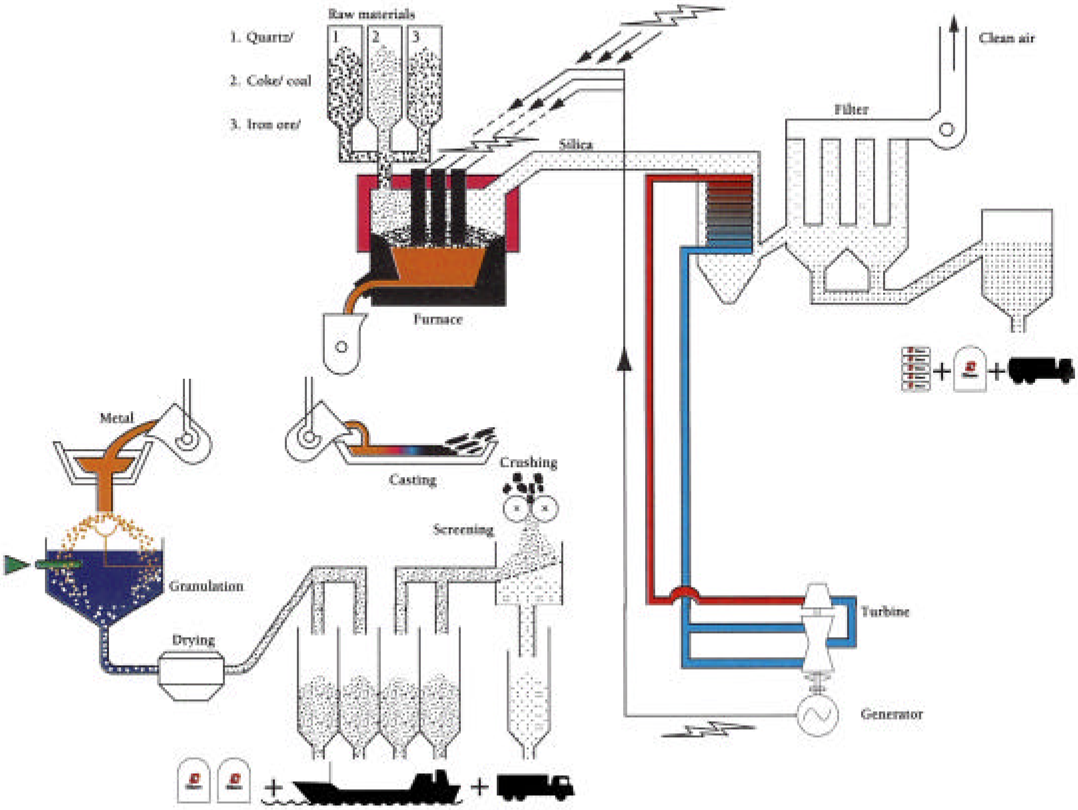


Figure 5.3: Process flow diagram for a modern production of ferro-silicon and silicon metal [tm 152, A. Schei, J.Kr. Tuset, H.Tveit 1998]

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.

5.1.3 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

5.1.3.1 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.

5.1.3.2 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.

5.1.3.3 Production of ferro-manganese and silico-manganese

5.1.3.3.1 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 ºC 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.

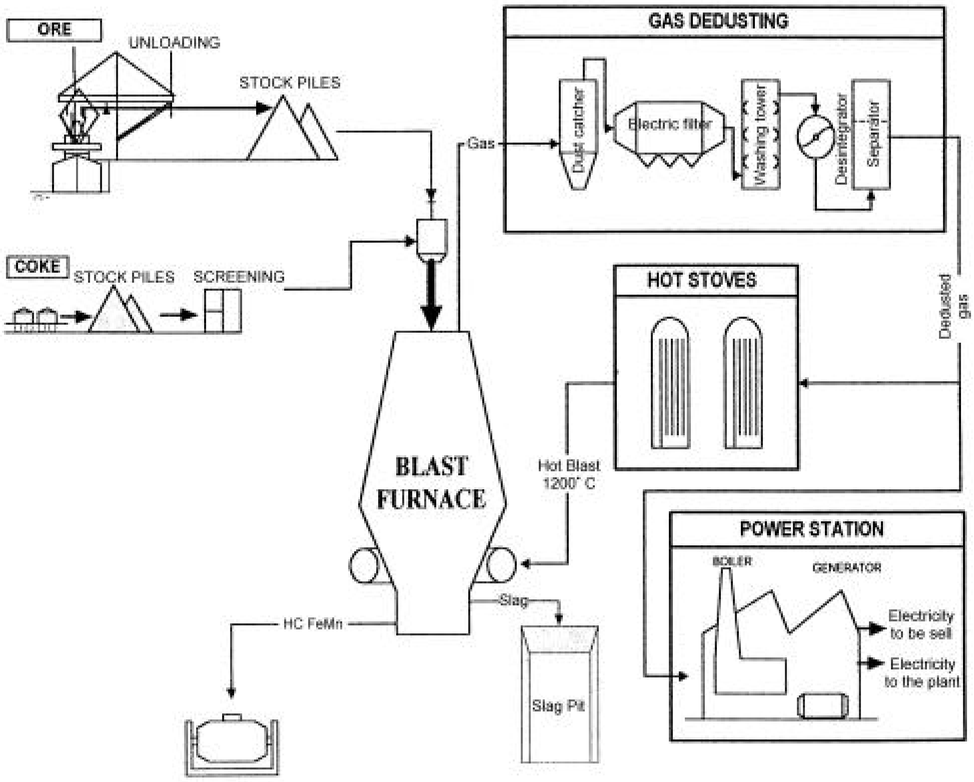


Figure 5.4: Production of HC FeMn in a blast furnace

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.

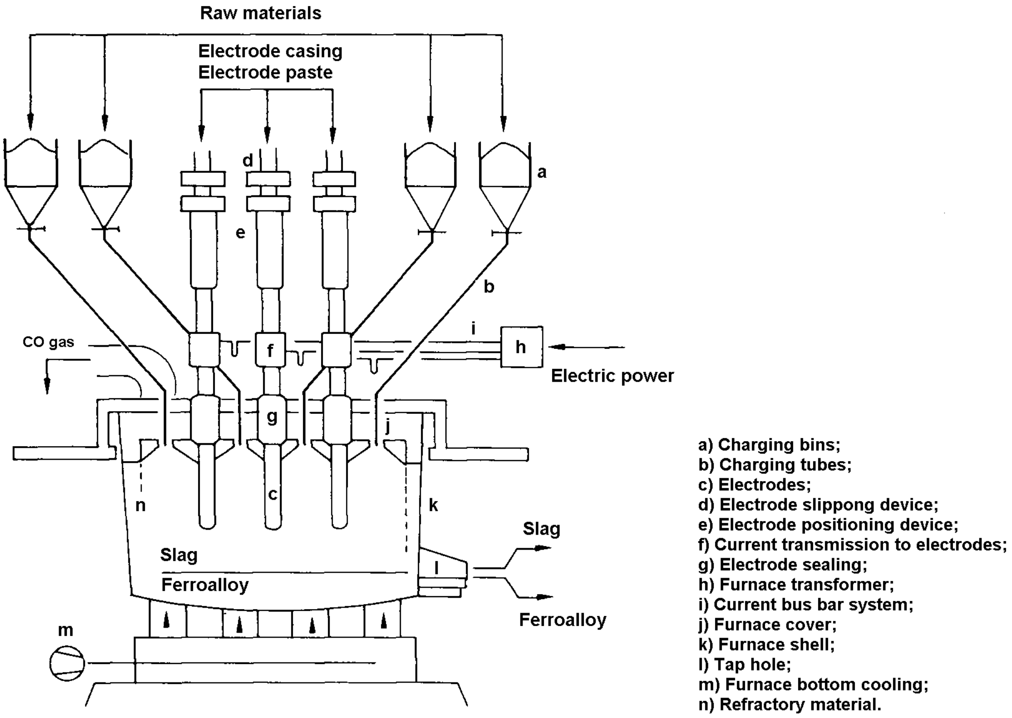


Figure 5.5: Closed electric arc ferro-manganese furnace operating Søderberg electrodes [tm 107, Ullmanns 1996]

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.

5.1.3.3.2 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.

5.1.3.3.3 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.

5.1.3.3.4 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.

5.1.4 Ferro-nickel

5.1.4.1 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.

5.1.4.2 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.

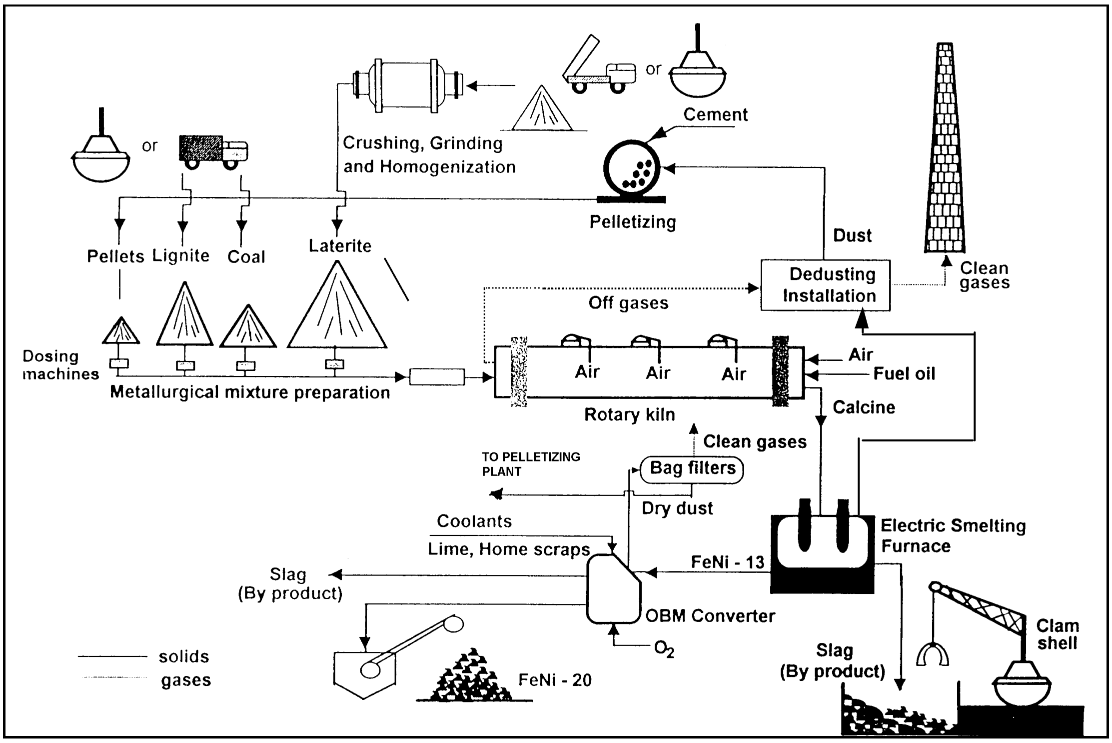


Figure 5.6: Rotary kiln-electric arc furnace process for the ferro-nickel production

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.

5.1.4.3 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.

5.1.5 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.

5.1.6 Molybdenite roasting and the production of ferro molybdenum

5.1.6.1 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.

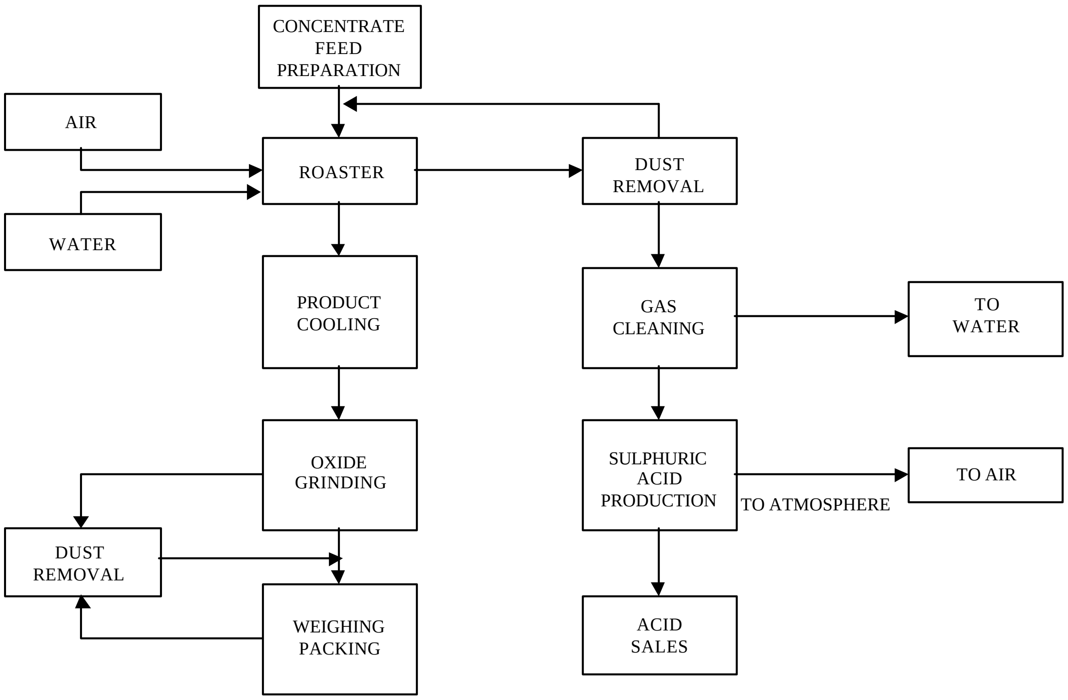


Figure 5.7: Molybdenite roasting flow sheet

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,

5.1.6.2 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.

5.1.6.2.1 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.

5.1.6.2.2 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.

5.1.6.2.3 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.

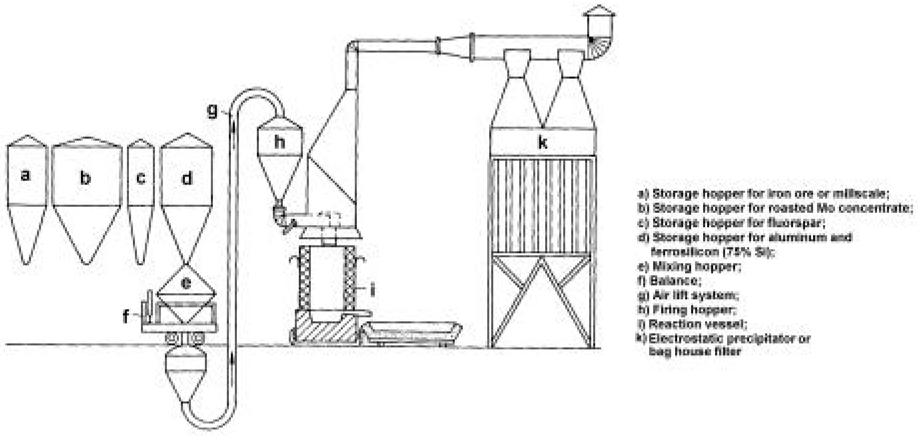


Figure 5.8: Metallo-thermic firming arrangement
[tm 107, Ullmanns 1996]

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.

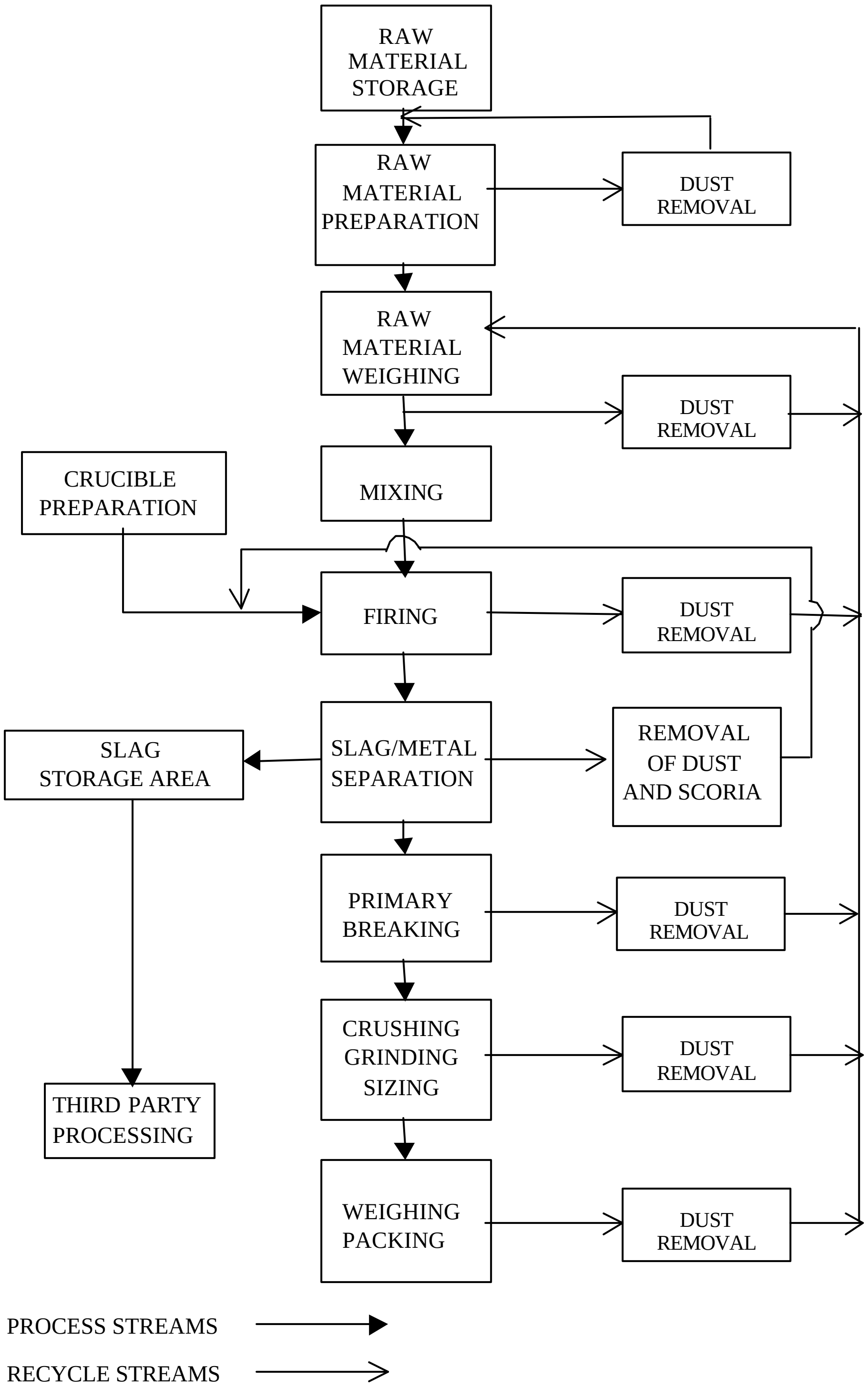


Figure 5.9: Production of ferro-molybdenum by a metallo-thermic reduction

5.1.7 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 °C. Besides this tungsten will increase a number of other properties like the hardness, yield strength and the ultimate tensile strength [tm 107, Ullmanns 1996].

5.1.7.1 Production of ferro-tungsten and tungsten melting base

5.1.7.1.1 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.

5.1.7.1.1.1 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.

5.1.8 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.

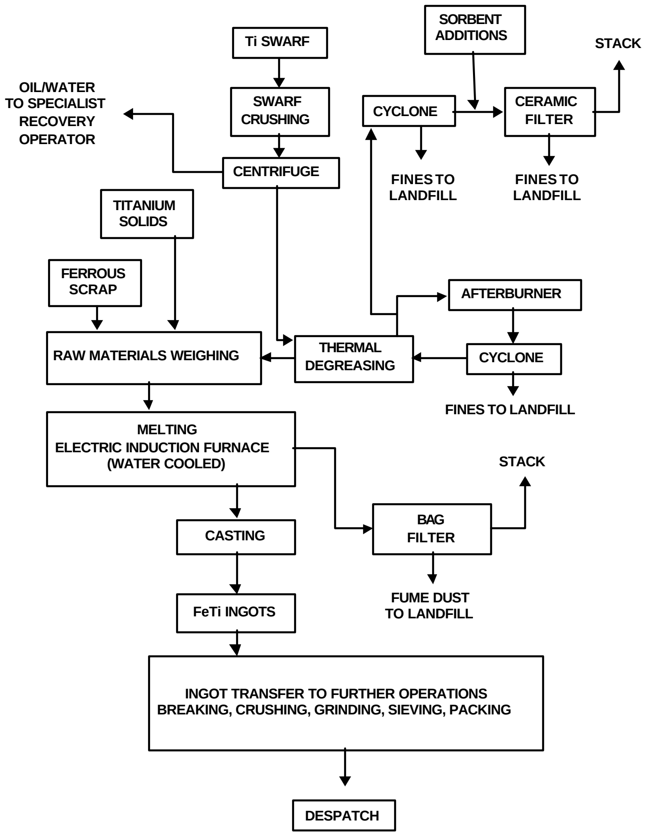


Figure 5.10: Flow diagram of the ferro-titanium production

5.1.9 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.

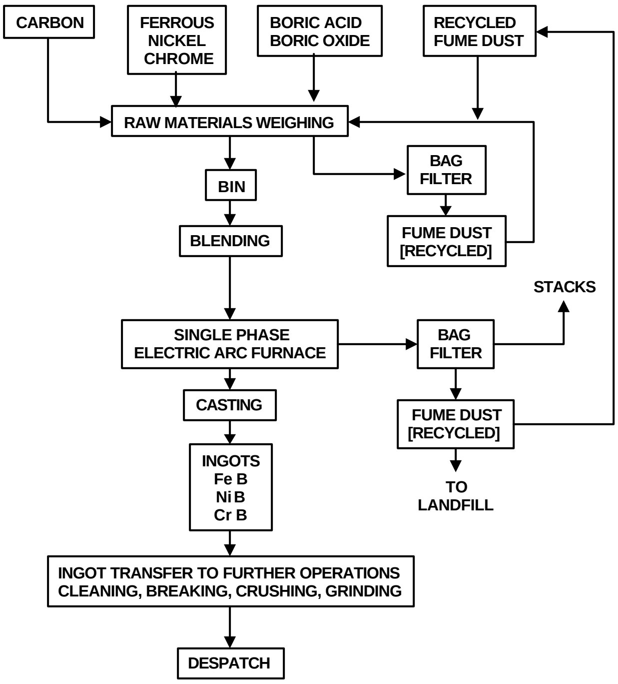


Figure 5.11: Process for ferro-boron and boron –alloy production

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.

5.1.10 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.

5.1.11 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.

5.1.11.1 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 5.2: 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

5.1.11.2 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.

5.1.11.2.1 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.

5.1.11.3 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.

5.1.11.4 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.

5.2 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

5.2.1 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 5.3: 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 5.4: 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 5.5: 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 FurnaceEAF = Electric Arc Furnacen.a. =data not available n.r. = not relevant

Table 5.6: 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 5.7: 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.

5.2.2 Emissions

5.2.2.1 Emissions to air

5.2.2.1.1 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.

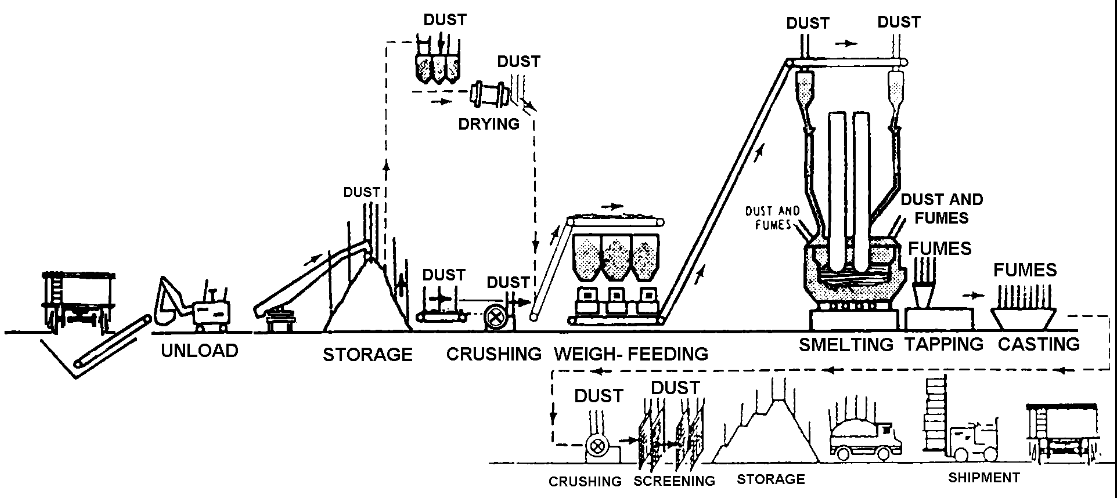


Figure 5.12: Ferroalloy production flow diagram showing potential points of air emissions [tm 35, ECE 1995]

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 relevantn.m. = not measured f = fugitive dust emissions
r = dust is recycled back into the process

Table: 5.8 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 5.9: 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 FurnaceEAF = 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 5.10: 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 5.11: Dust emissions to air (after abatement) by producing ferro-alloys

5.2.2.1.2 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.	5ìg/t (N 8)	n.a.	3ìg/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 ìgHg/Nm^3 (N 8)	n.a.	0.131 ìgHg/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 5.12: 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 5.13: 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 5.14: Emission concentration figures by producing secondary ferro-alloys

5.2.2.2 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.

5.2.2.3 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 5.15: 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 5.16: Emissions to water by roasting molybdenite

5.2.2.4 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_2O_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 5.17: 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 5.18: Generation, recycling, reuse and discharge of dust and sludge from the air abatement system

5.2.3 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.

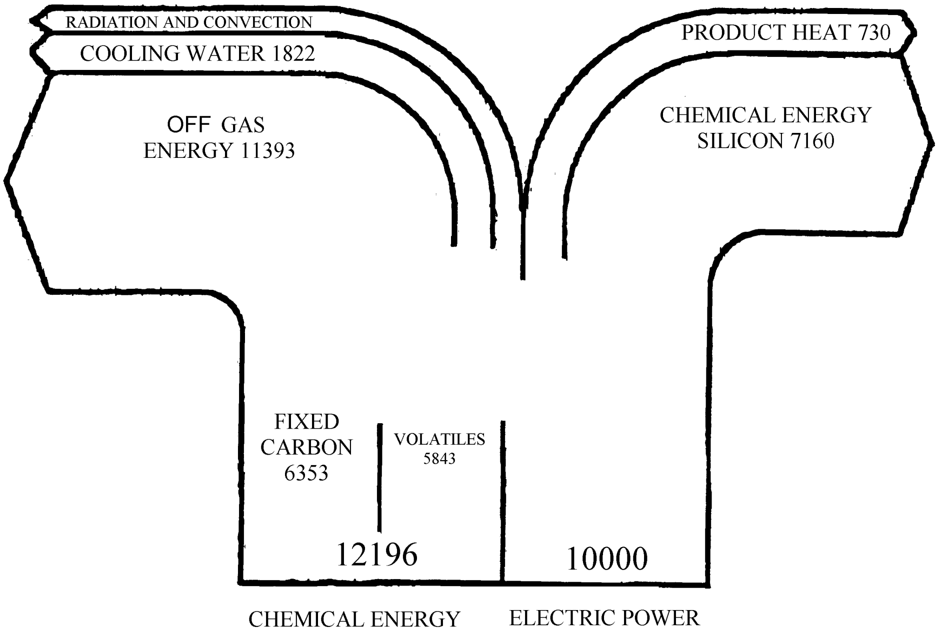


Figure 5.13: Energy flow in a 10 MW silicon furnace
[tm 152, A. Schei, J.K.Tuset, H. Tveit 1998]

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 5.19: 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 5.20: Energy reuse by producing bulk ferro-alloys

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.

5.3.1 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.

5.3.2 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.

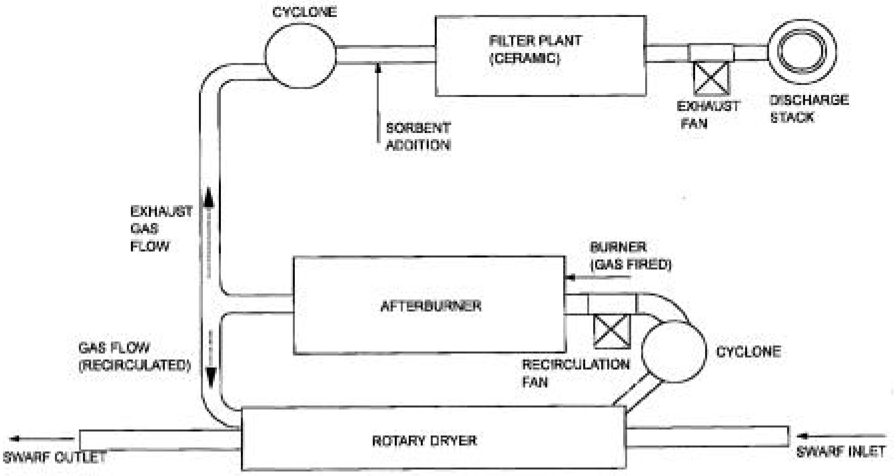


Figure 5.14: Gas cleaning system for a de-greasing plant

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]

5.3.3 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.

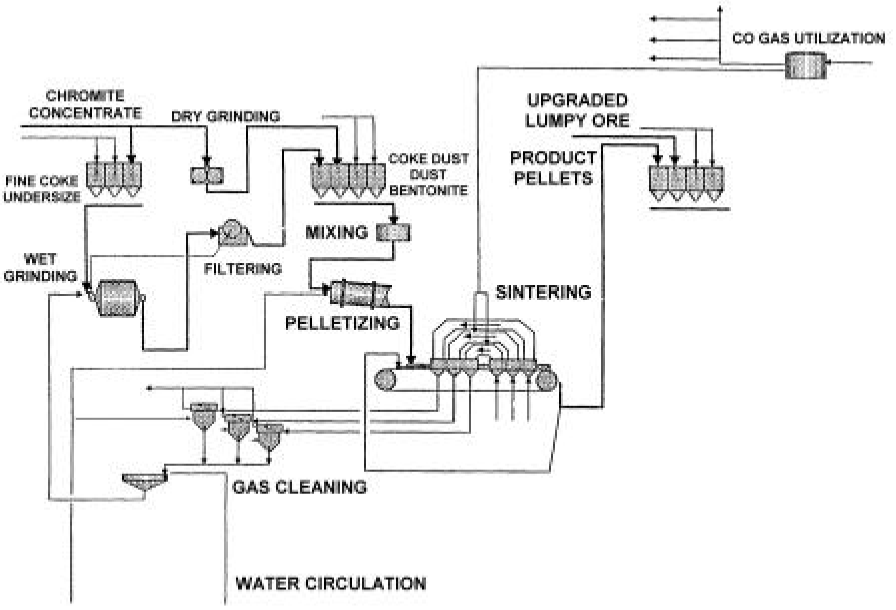


Figure 5.15: Steel belt sinter furnace

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]

5.3.4 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 °C 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]

5.3.5 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 5.21: 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.

5.3.6 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.

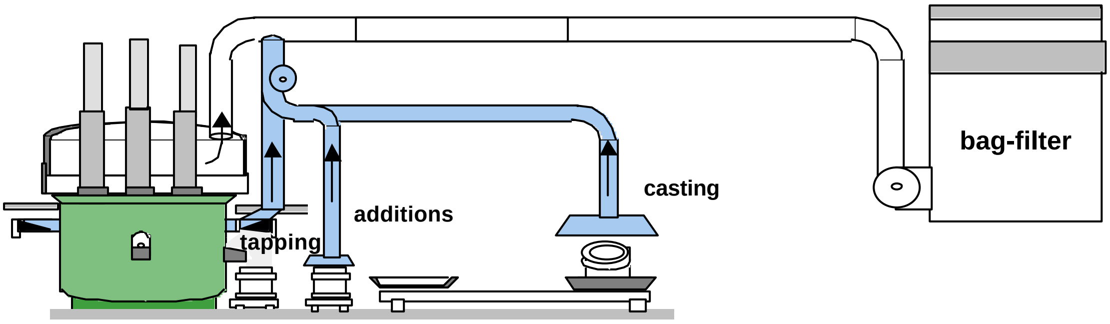


Figure 5.16: Collection of tapping and casting fume

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.

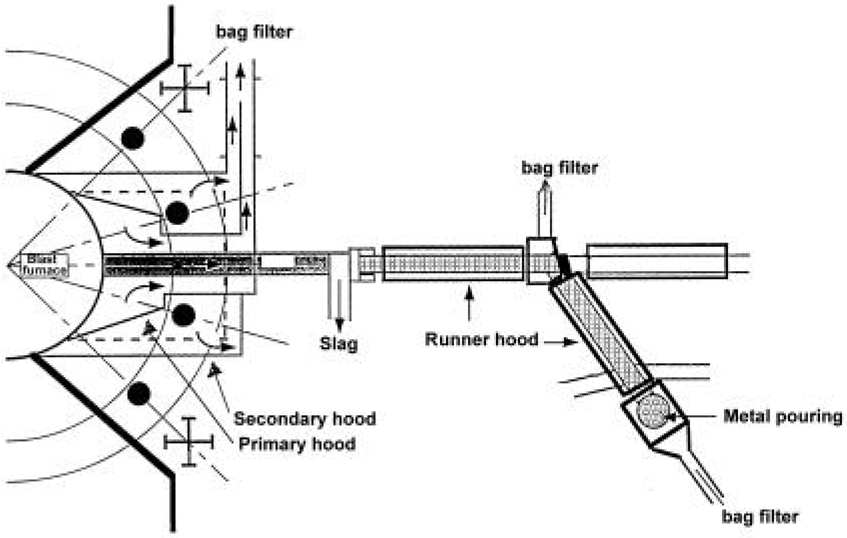


Figure 5.17: Hooding system for a blast furnace

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]

5.3.7 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.

5.3.8 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].

5.3.9 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.

5.3.10 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.

5.3.11 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 5.22: 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 5.23: 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 ºC

Table 5.24: 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.

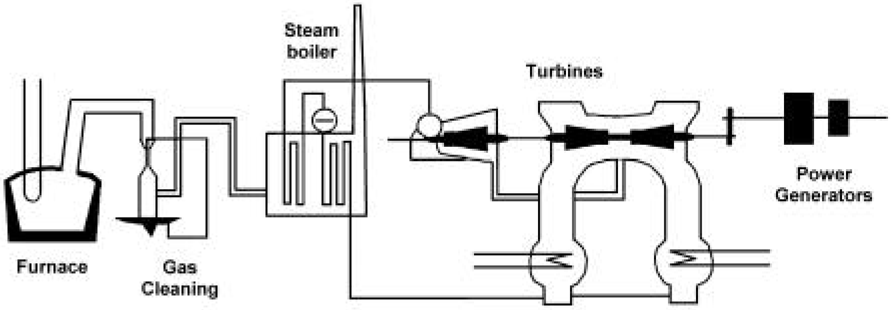


Figure 5.18: Direct use of the CO gas for the production of electrical energy

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.

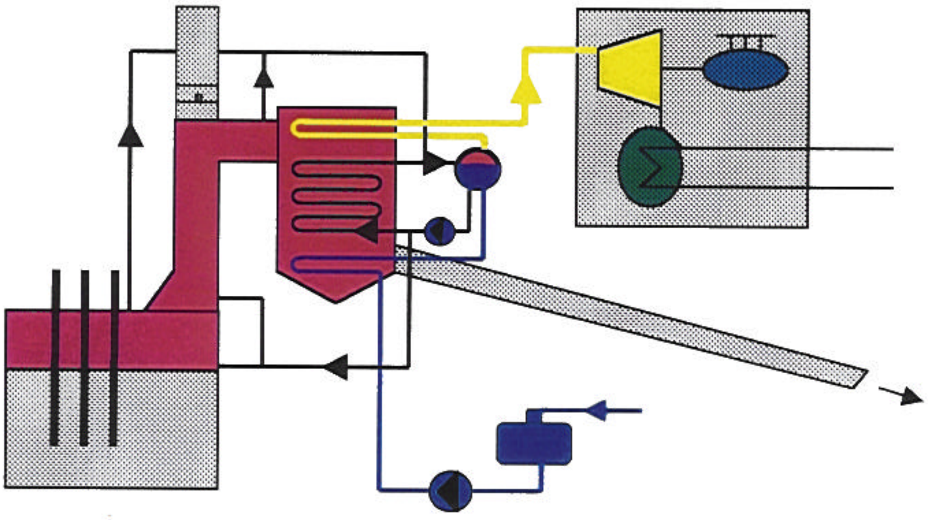


Figure 5.19: Energy recovery from a semi-closed furnace

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.

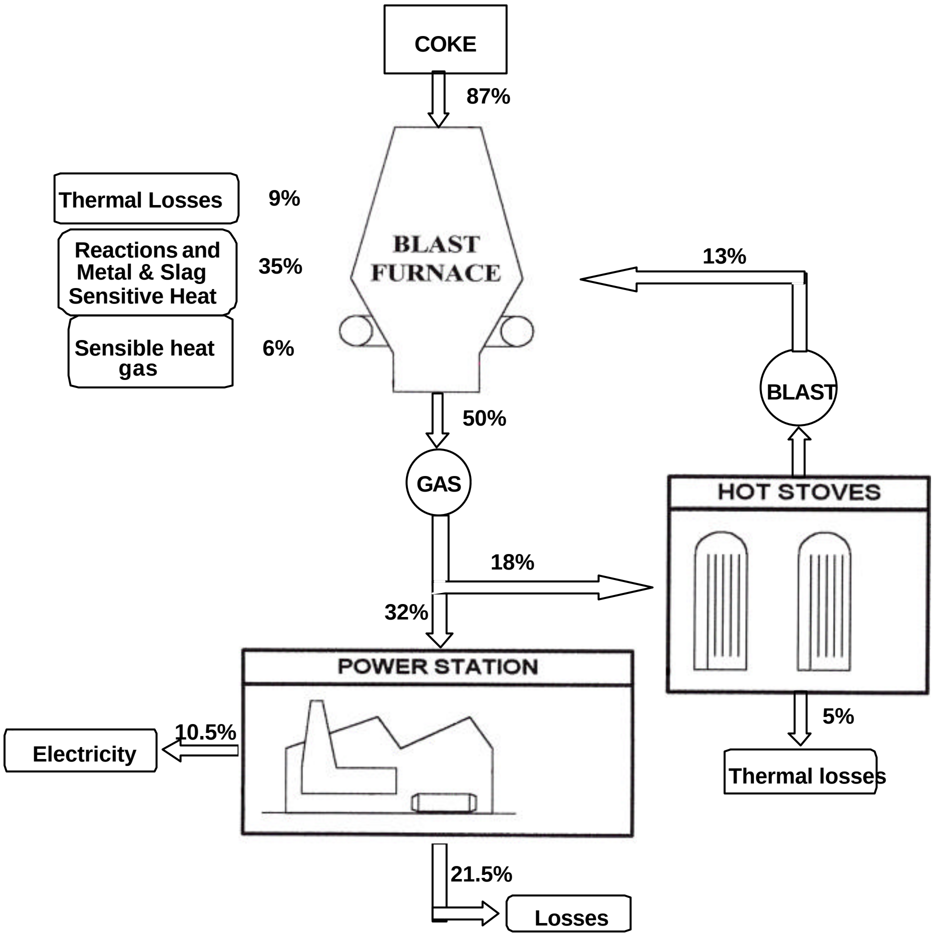


Figure 5.20: Energy recovery system for a blast furnace

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.

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 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.

5.4.1 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.

5.4.2 Process selection

5.4.2.1 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.

5.4.2.2 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.

5.4.2.3 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.

5.4.2.4 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 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 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
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 5.25: 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	Energy recovery using the CO-	• Due to the high coke consumption the blast furnace has to

		scrubber or Dry cleaning system	rich off gas for heating the hot stoves and electricity production	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 5.26: Smelting furnaces considered as BAT for the production of ferro-alloys

5.4.2.5 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.

5.4.2.6 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.

5.4.3 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 5.27: Emission levels to air associated with the use of BAT

5.4.4 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.

5.4.5 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 5.28: 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 5.29: Recycle and reuse of the collected filter dust and sludge from the production of ferro-alloys

5.4.6 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 **FeMo** **FeW** **FeTi** **FeB** **FeNb**	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.		
Notes: Combining the different recovery techniques can increase the overall efficiency of an energy recovery system.			

Table 5.30: 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.

5.5 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.

6 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.

6.1 Applied Processes and Techniques

6.1.1 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.

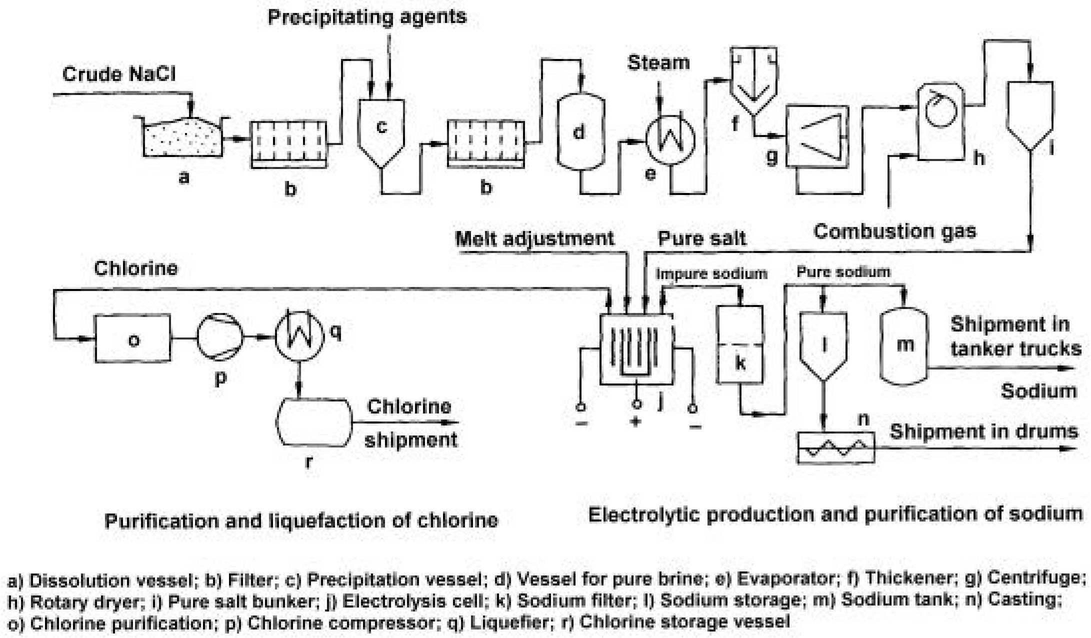


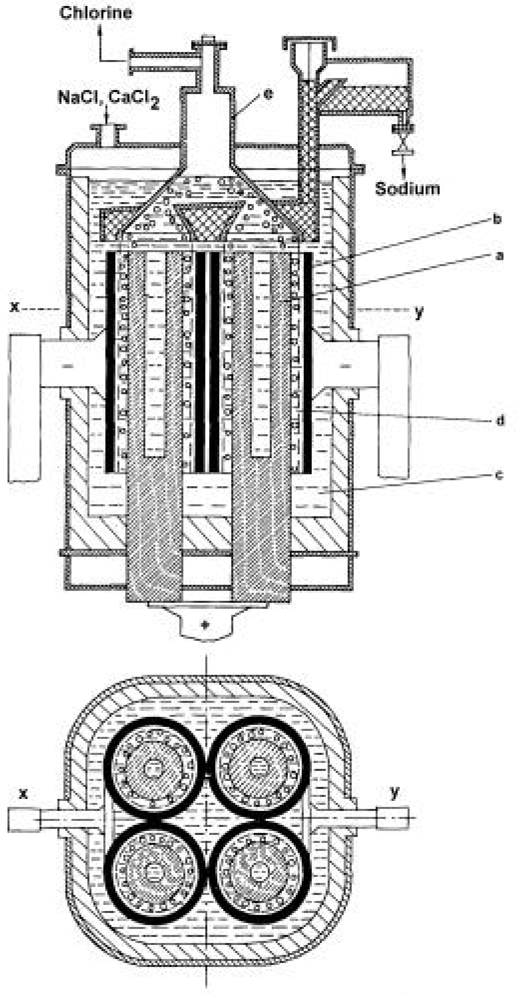
Figure 6.1: Flow sheet of sodium production
[tm 107, Ullmanns 1996]

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 6.2: The Downs Cell
[tm 107, Ullmanns 1996]

6.1.2 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.

6.1.3 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].

6.1.4 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.

6.1.4.1 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.

6.1.4.1.1 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.

6.1.4.1.2 The metallo-thermic process

The production of calcium metal depends on a small finite equilibrium of calcium vapour in the range of 1000–1200 °C. 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 °C. 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.

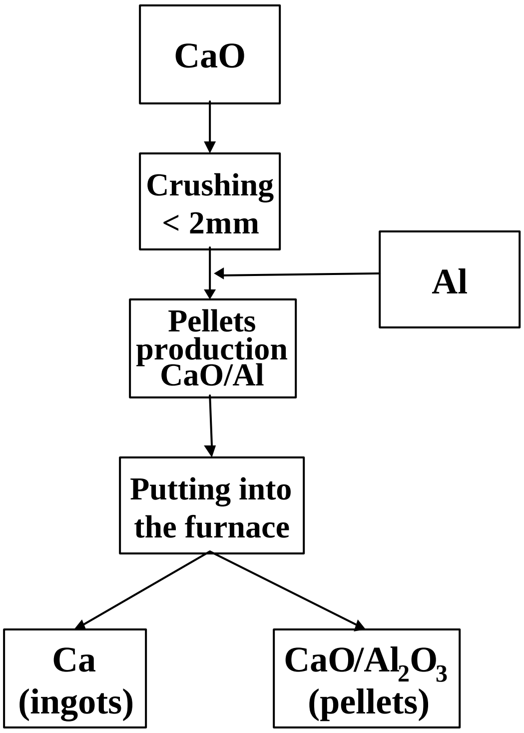


Figure 6.3: Flow diagram of the production of calcium metal

6.1.4.2 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.

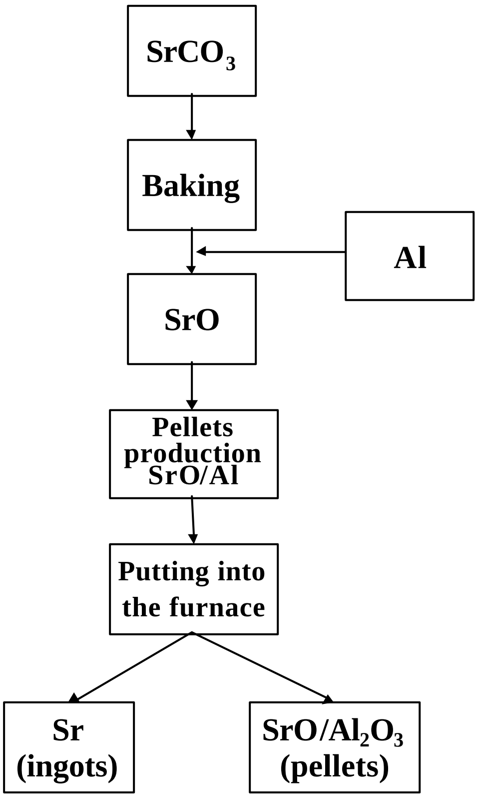


Figure 6.4: Flow diagram of the production of strontium metal

6.1.5 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.

6.1.5.1 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.

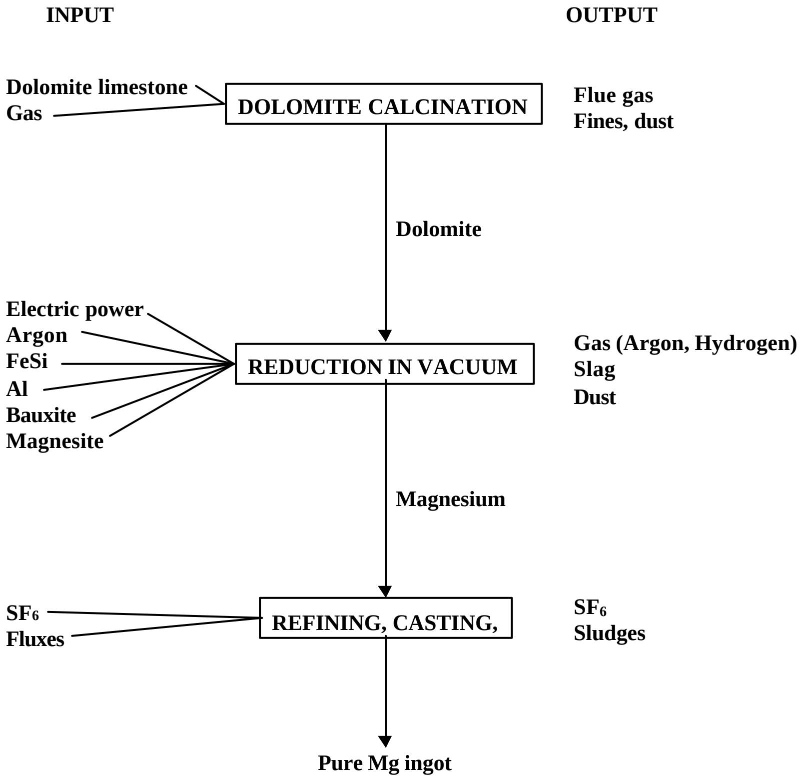


Figure 6.5: Schematic flow sheet of the thermal reduction process to produce magnesium metal

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.

6.1.5.2 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.

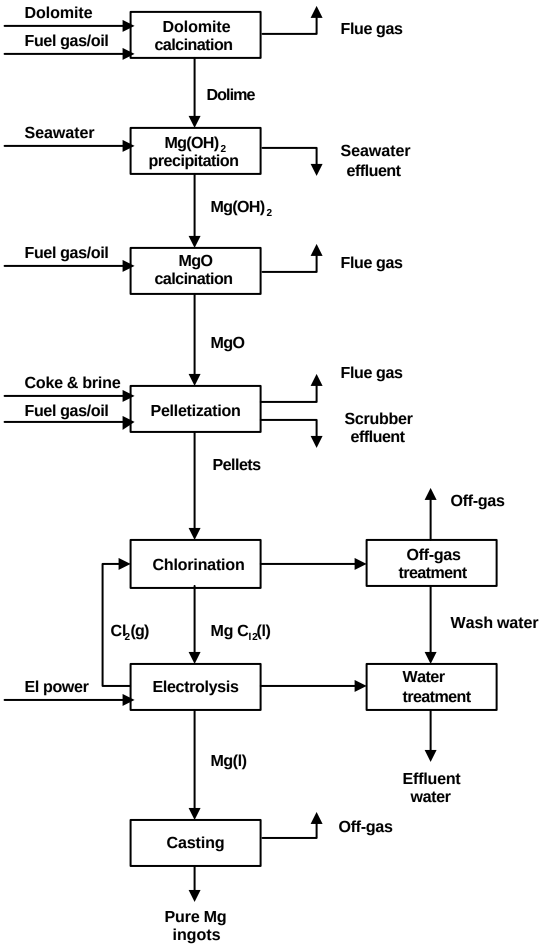


Figure 6.6: Process flow diagram of magnesium production by electrolysis

6.1.5.3 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 6.1: Definition of magnesium containing scrap and materials for recycling

A typical secondary magnesium production is shown in the next figure.

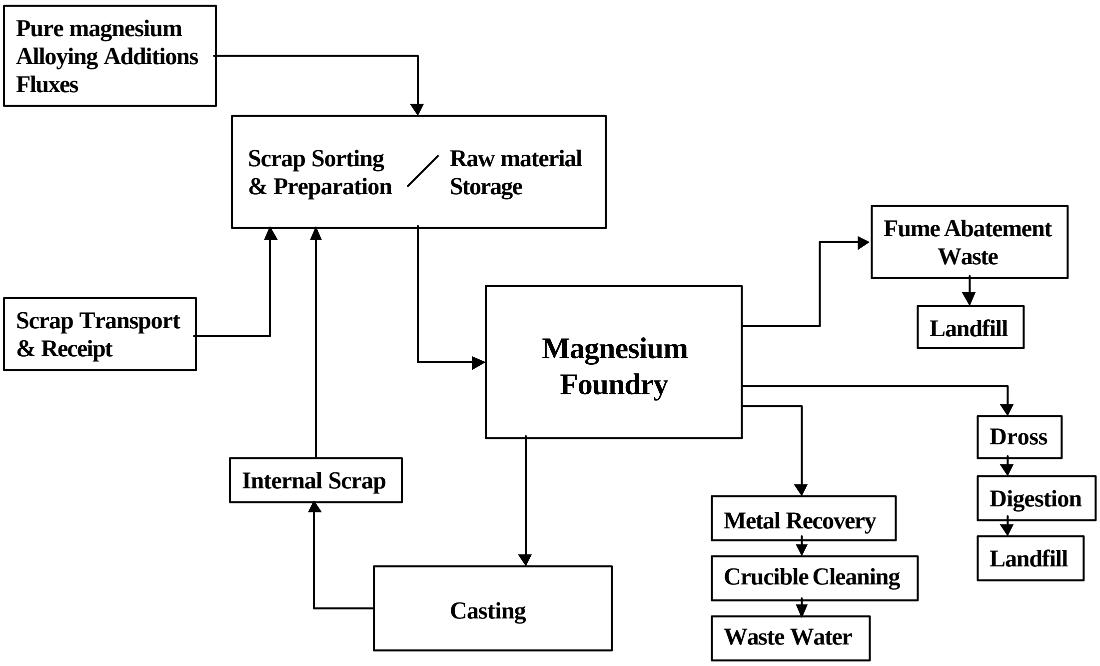


Figure 6.7: Flow sheet of a production process for secondary magnesium

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.

6.2 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

6.2.1 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.

6.2.2 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 6.2: 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	4 kg/t

	treatment 3 From chlorination (vent. gas) 16	(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 From chlorination (vent. gas) 0.8 ng/Nm^3 From electrolysis/chlorination (hall/ gas)	12 ìg/t TEQ 28 ìg/t TEQ 13 ìg/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 6.3: 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 ìg/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 6.4: Emission to air by producing magnesium metal by using the thermal reduction process

6.2.3 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 6.5: 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 ìg/t Mg-metal Total 33 ìg/t Mg-metal (TCDD equivalents)

Notes:
(N 1) Sum of hexachlorobenzene, pentachlorbenzene and octochlorostyrene
n.a. = data not available

Table 6.6: 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.

6.2.4 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 wet slag slag	refining stage	0.5 - 0.7 t/t metal 0.3 - 0.5 t/t metal 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 6.7: Residues by producing alkali and alkaline metals

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.

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.

6.3.1 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.

6.3.2 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.

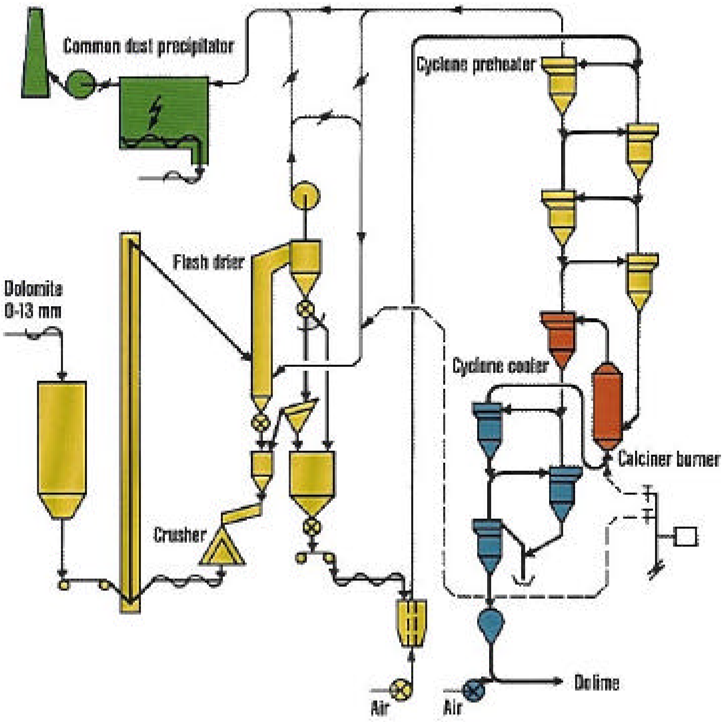


Figure 6.8: Gas Suspension calciner

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]

6.3.3 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.

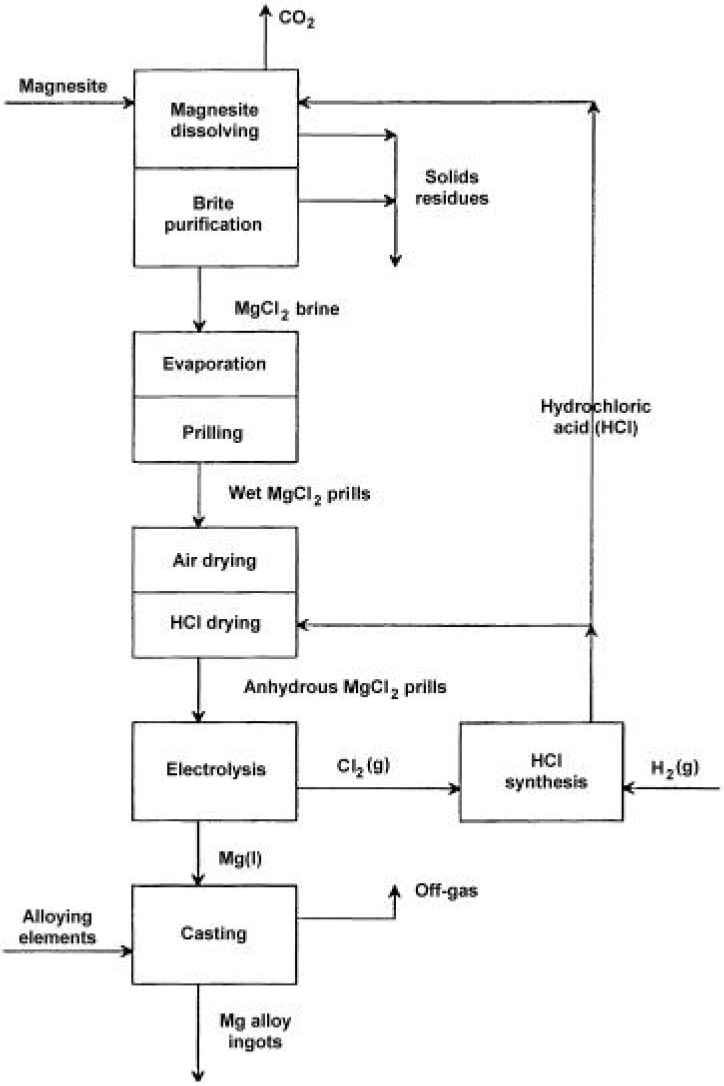


Figure 6.9: Block diagram for the dehydration process for primary magnesium production

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]	< 10	ìg/t Mg

Water emissions:

Chlorinated Hydrocarbons[2]	< 0.01	g/t Mg
Dioxins[1]	< 0.1	ìg/t Mg

[1] Sum of PCDDs and PCDFs expressed as TCDD-equivalents.

[2] Sum of hexa - and penta-chlorobenzene and octachlorostyrene.

Applicability: New plants

6.3.4 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]

6.3.5 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.

6.3.6 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.

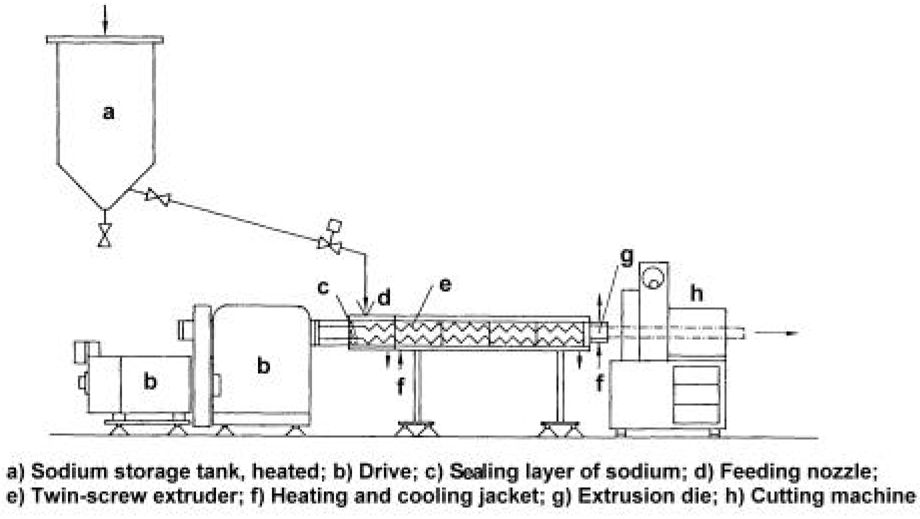


Figure 6.10: Schematic of an extrusion plant for the production of alkali-metal billets

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]

6.3.7 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

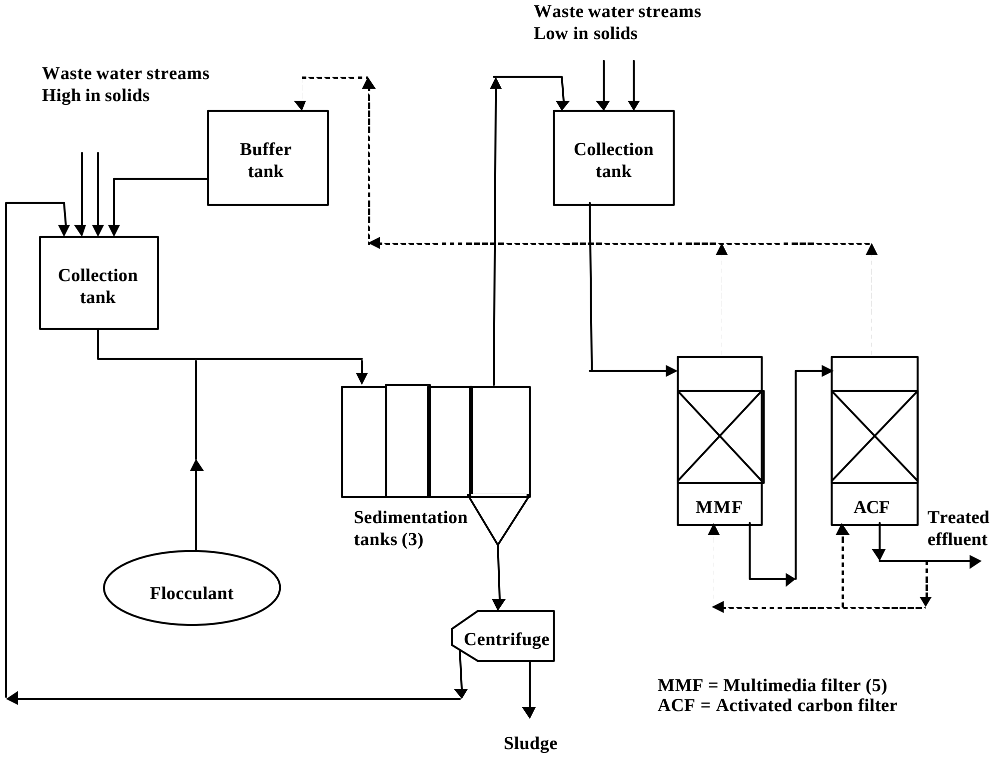


Figure 6.11: Treatment plant for cleaning dioxin and chlorinated hydrocarbon contaminated wastewater

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.

6.3.8 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.

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 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.

6.4.1 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.

6.4.2 Process selection

6.4.2.1 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.

6.4.2.2 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 ìg/t TEQ instead of 53 ìg/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 6.8: Production units considered as BAT for the production of alkali and alkaline metals

6.4.2.3 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.

6.4.2.4 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.

6.4.3 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 ìg/t TEQ for the $MgCl_2$ brine dehydration process instead of 53 ìg/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 6.9: Emission levels to air associated with the use of BAT

6.4.4 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.

6.4.5 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 6.10: Utilisation, recycling and reuse of residues by producing alkali and alkaline metals

6.5 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.

7 PROCESSES TO PRODUCE NICKEL AND COBALT

7.1 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 7.1: 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].

7.1.1 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.

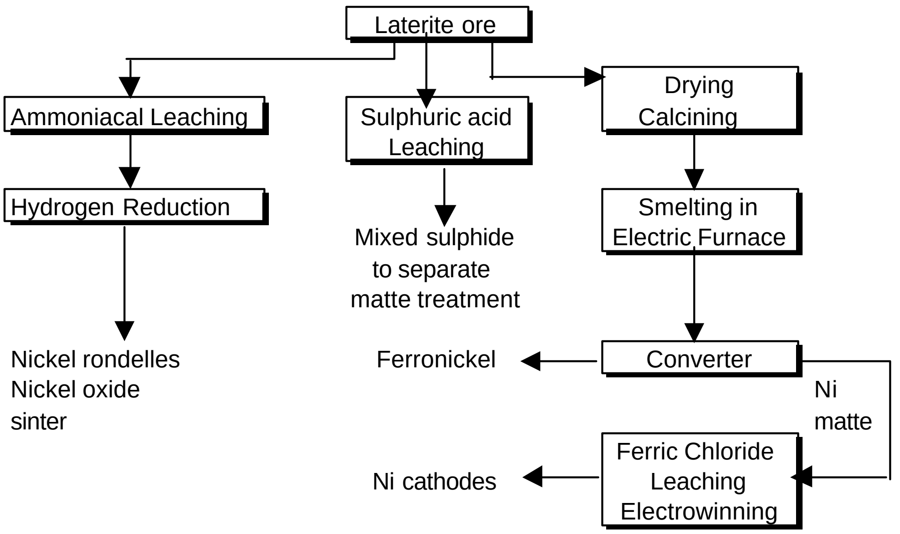


Figure 7.1: Generic flow sheet for nickel production from Laterite ores

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.

7.1.2 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 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.

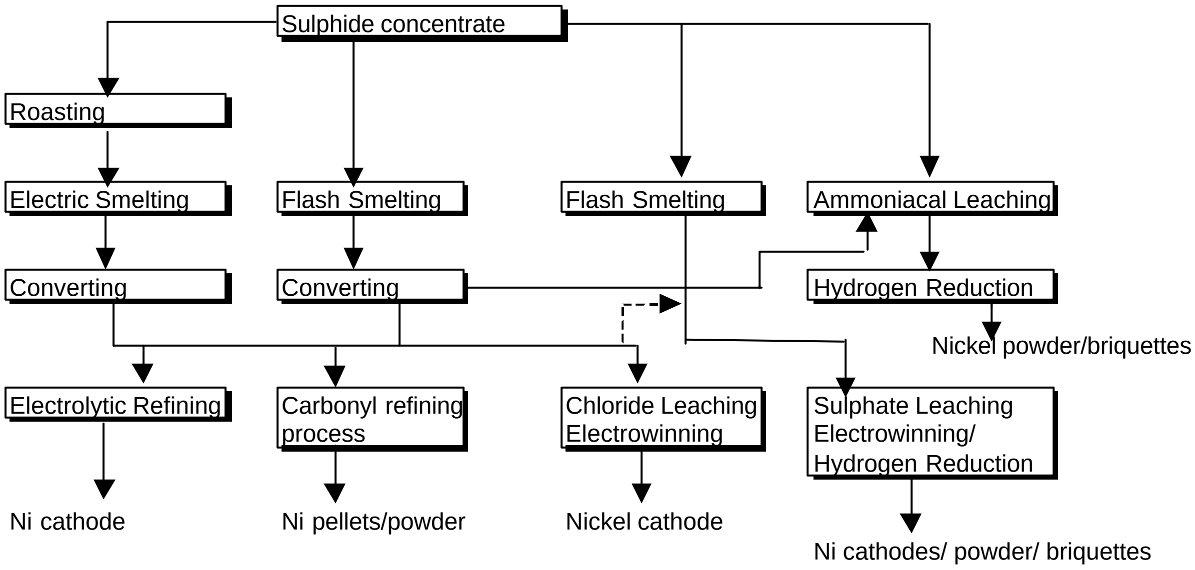


Figure 7.2: Generic flow sheet for the production of nickel from sulphide concentrates

7.1.2.1 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.

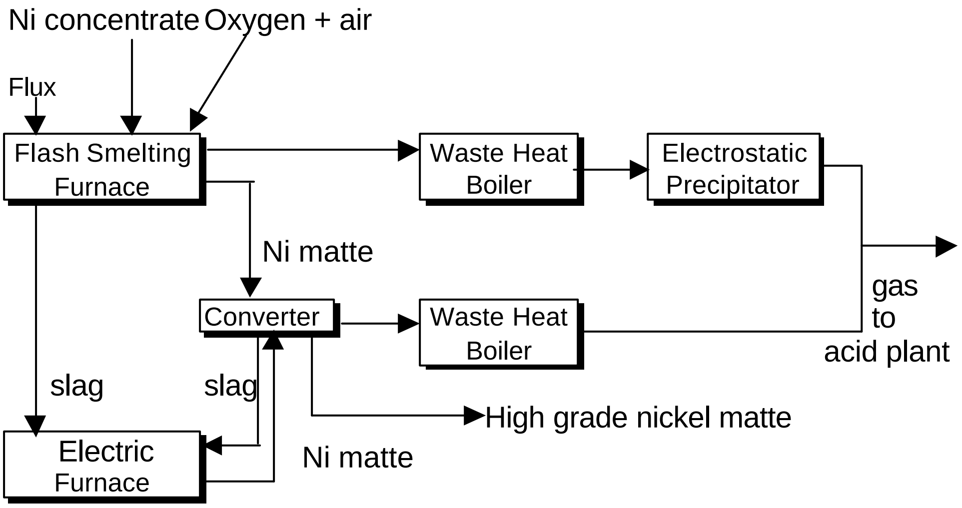


Figure 7.3: Conventional flash smelting

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.

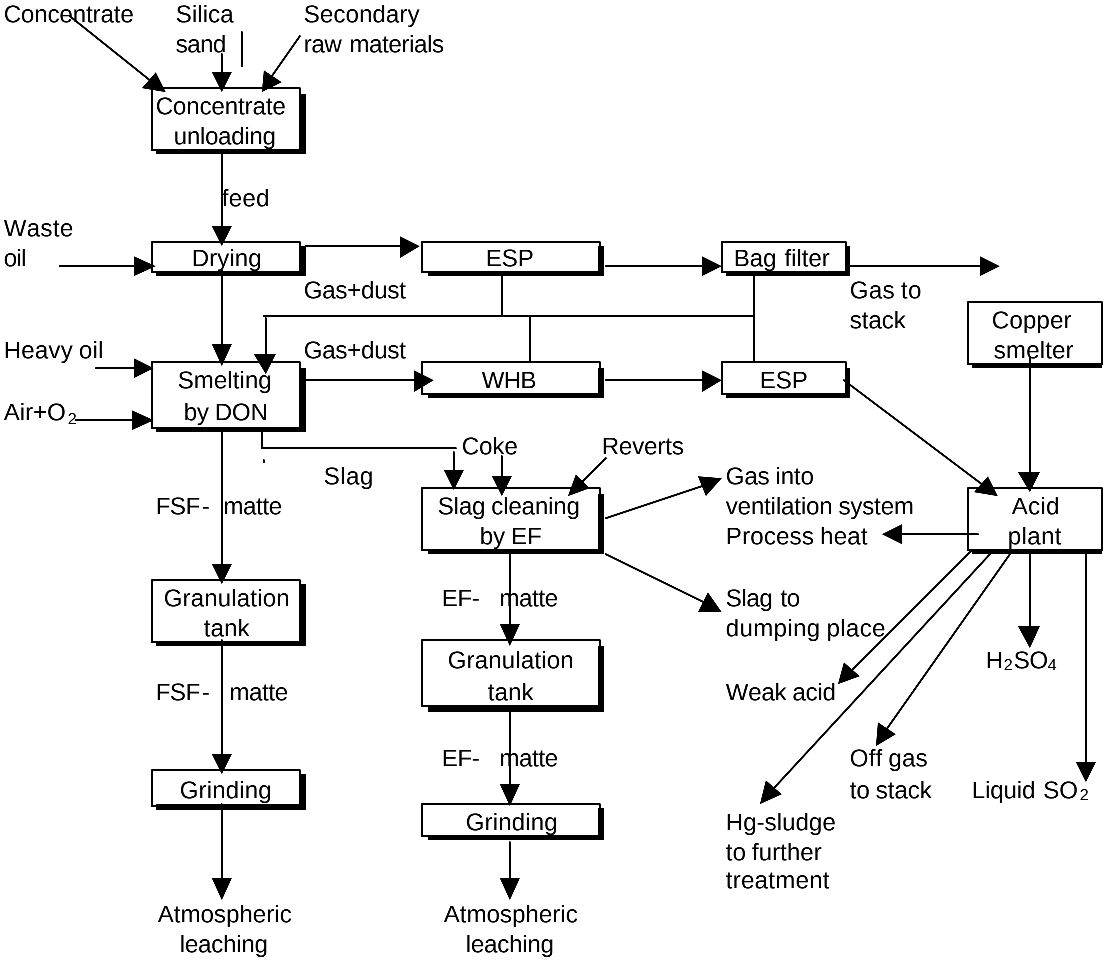


Figure 7.4: The DON process

7.1.3 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.

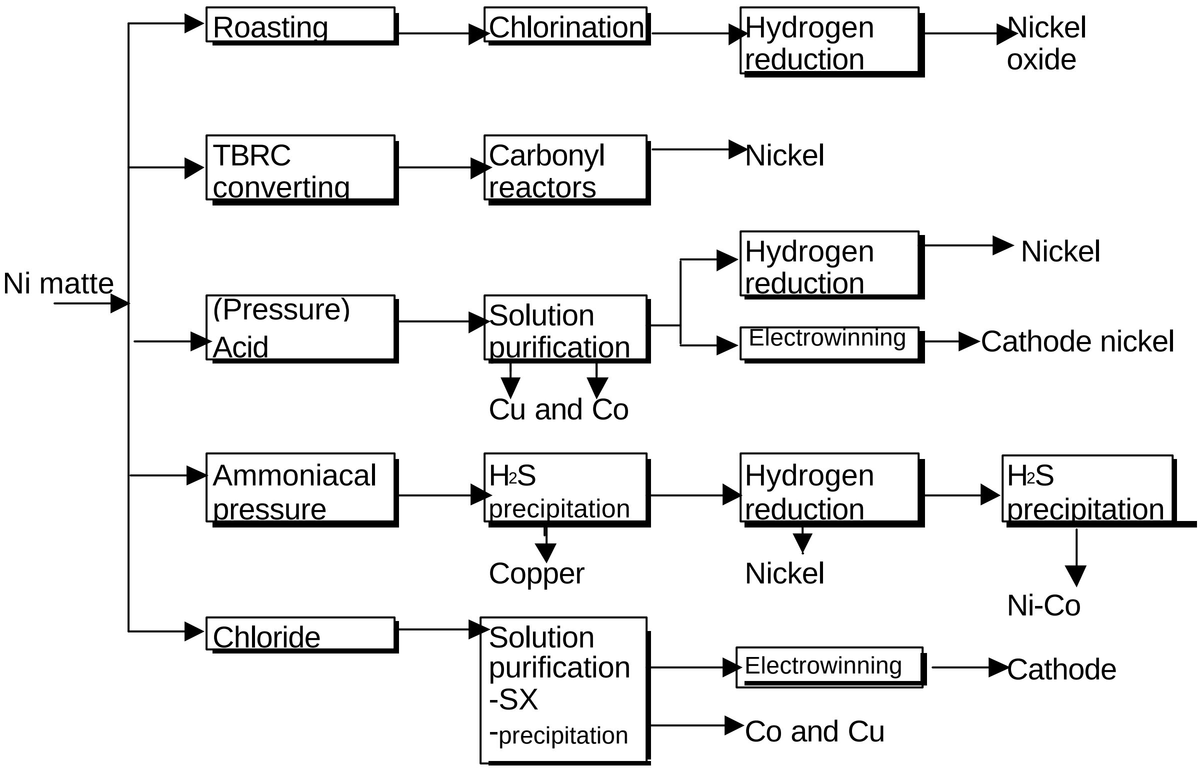


Figure 7.5: Generic flow sheet for nickel matte refining processes

7.1.3.1 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.

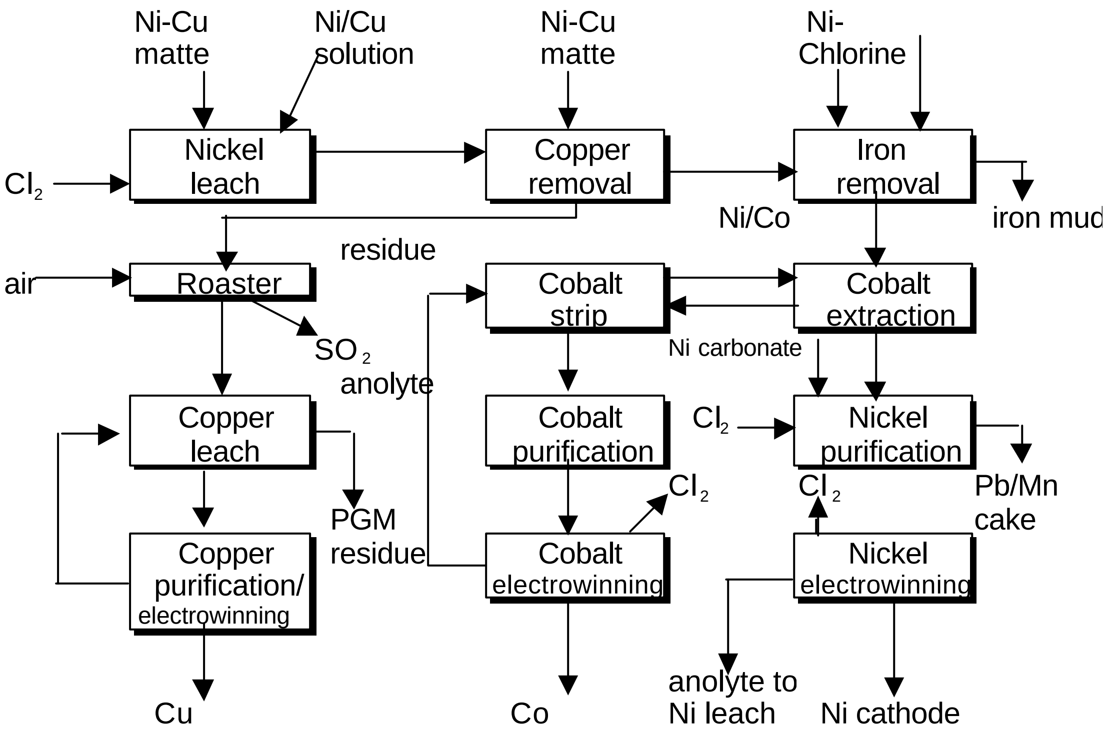


Figure 7.6: Falconbridge process
Chlorine from electrolysis is returned to the leach and purification stages

7.1.3.2 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.

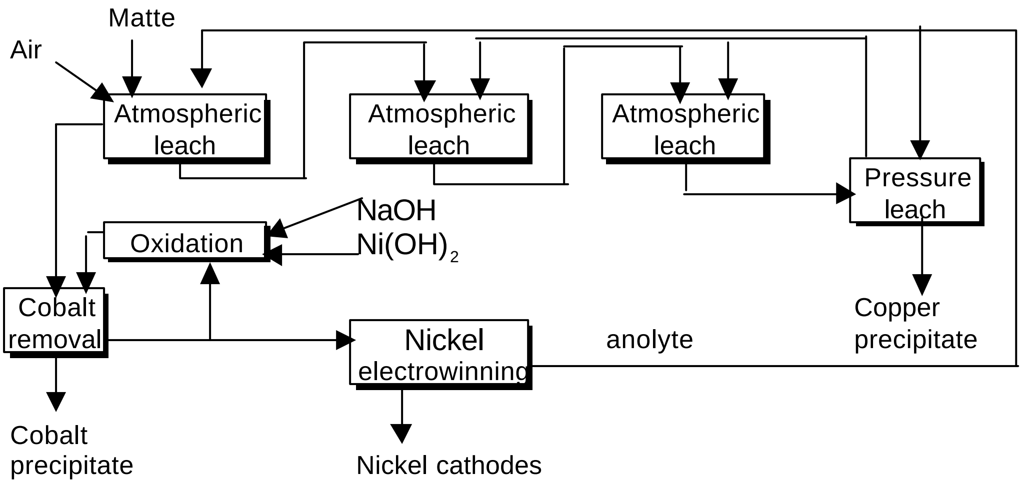
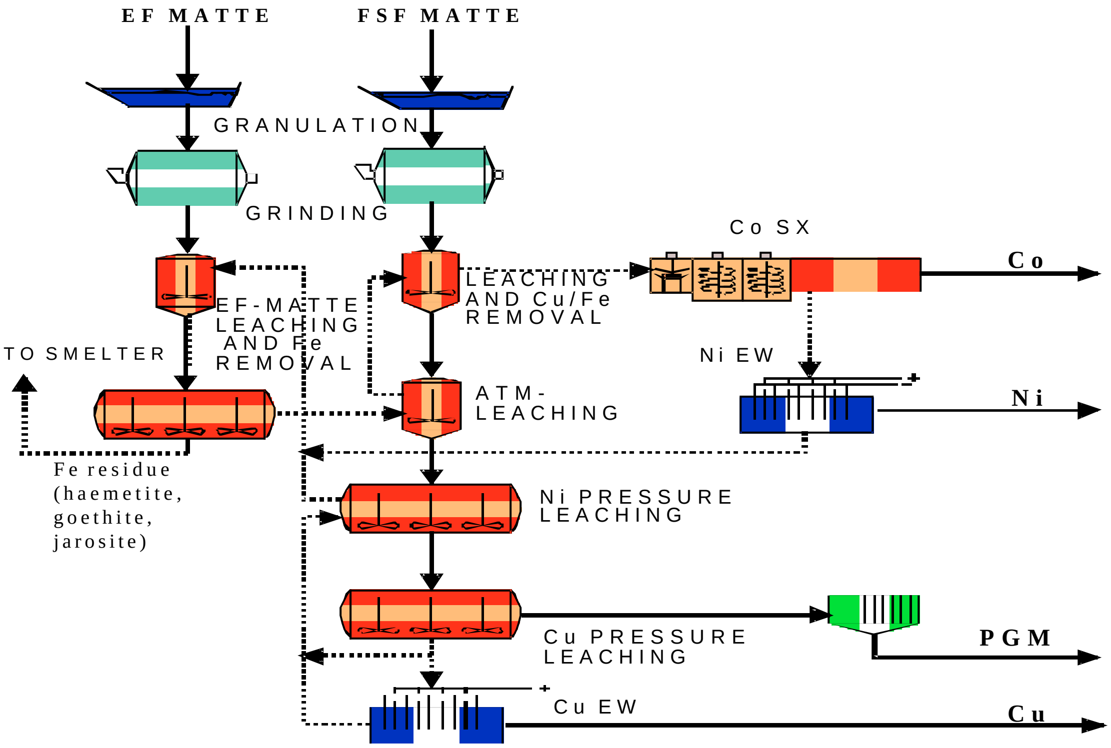


Figure 7.7: Sulphate based leaching process

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 7.8: 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.

7.1.3.3 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].

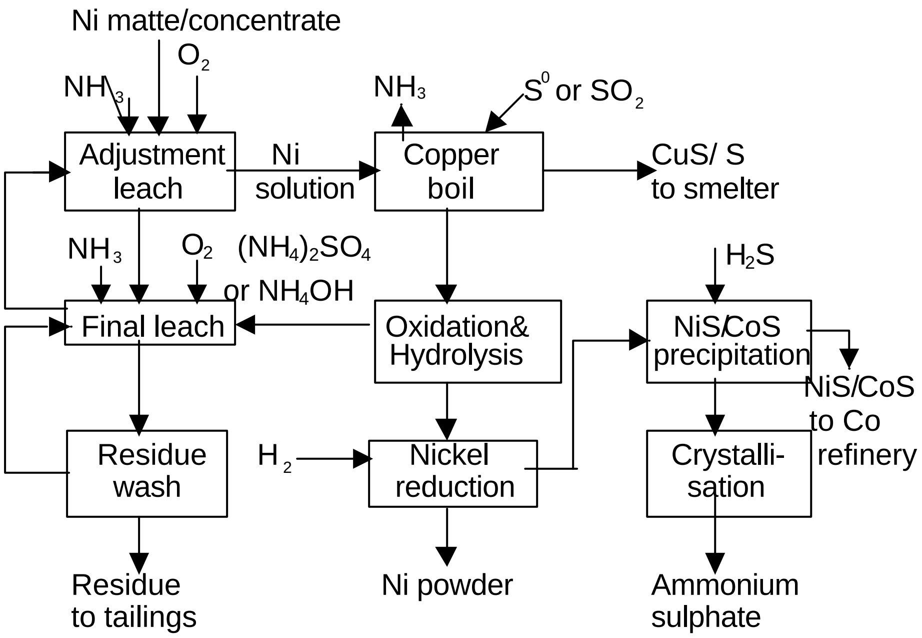


Figure 7.9: Sherritt ammoniacal leaching

7.1.3.4 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.

7.1.3.5 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.

7.1.3.6 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].

7.1.3.7 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.

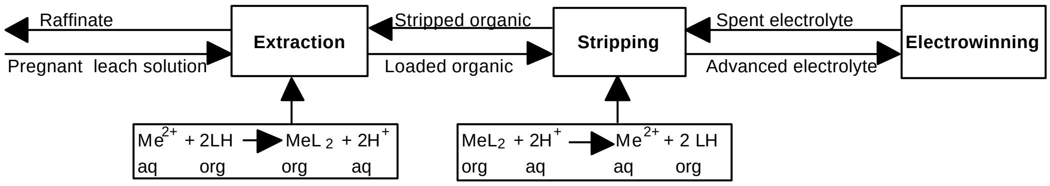


Figure 7.10: Solvent extraction (SX) process outline

7.1.4 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.

7.1.5 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.

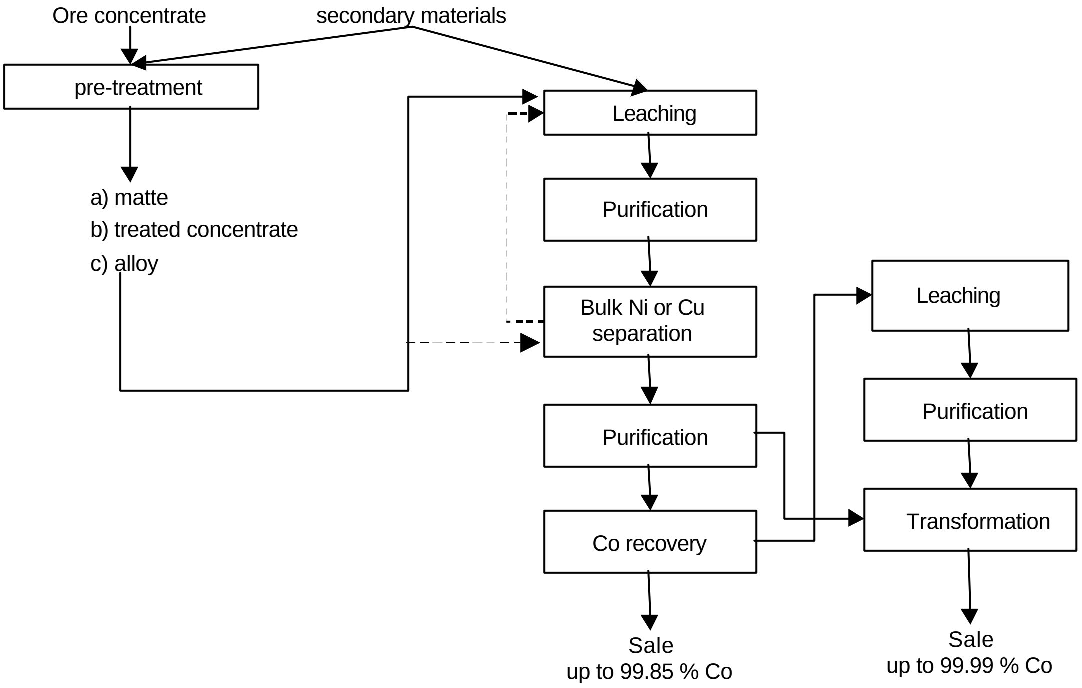


Figure 7.11: Generic flow sheet showing possible process steps for cobalt production

7.2 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 7.2: Example input and output data for worldwide nickel production

7.2.1 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.

7.2.2 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 7.3: 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.

7.2.2.1 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 7.4: Sulphur dioxide production from some nickel and cobalt processes

7.2.2.2 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.

7.2.2.3 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 7.5: Mass release of metals from some European processes

7.2.2.4 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.

7.2.2.5 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.

7.2.2.6 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.

7.2.2.7 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 7.6: 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.

7.2.3 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.

7.2.3.1 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 Chloride Fluoride	13 – 25 g/l 1.3 - 1.8 g/l 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 7.7: Typical gas cleaning effluents

7.2.3.2 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 7.8: Summary table of potential wastewater sources and options

Process	Effluent [m^3/t]	Flow [m^3/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 7.9: Examples of wastewater analyses

7.2.4 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.

7.2.4.1 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 7.10: 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.

7.2.4.2 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 7.11: 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 7.12: Solid residues from Ni and Co processes

7.2.4.3 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.

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 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.

7.3.1 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.

7.3.2 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.

7.3.3 Refining and transformation processes

7.3.3.1 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]

7.3.3.2 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.

7.3.3.3 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.

7.3.3.4 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.

7.3.4 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 7.13: 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.

7.3.5 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.

7.3.6 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.

7.3.7 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.

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 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.

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.

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 7.14: Storage, handling and pre-treatment methods for nickel and cobalt

7.4.2 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.

7.4.2.1 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.

7.4.2.2 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.

7.4.3 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 7.15: Summary of the abatement options considered as Best Available Techniques

7.4.3.1 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 7.16: 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 7.17: 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 7.18: 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.

7.4.4 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.

7.4.5 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.

7.4.6 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.

7.5 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.

8 PROCESSES TO PRODUCE CARBON AND GRAPHITE ELECTRODES ETC.

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: -

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 8.1: Overview of process steps

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.

Prebaked anodes, electrodes and carbon shapes

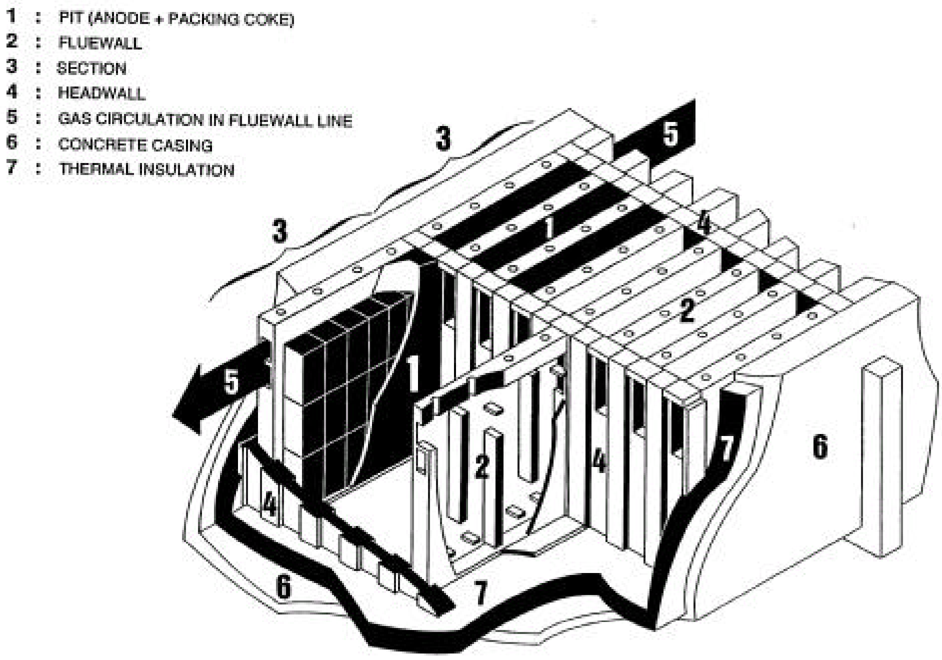
The primary aluminium prebake process uses prebaked anodes, which are manufactured by anode production plants. These anode production plants can be associated within the site of the aluminium smelter and several of these plants produce anodes that are sold to other plants and processes. Other dedicated 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 SECTIONS
OF AN OPEN TYPE BAKING FURNACE



VIEW OF AN OPEN TYPE BAKING FURNACE

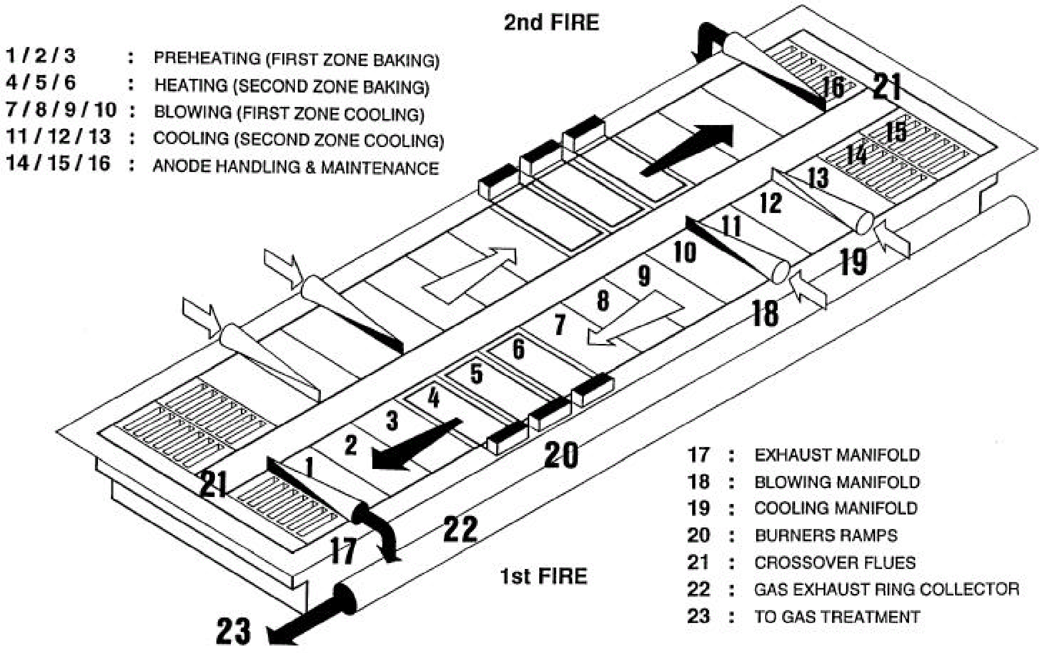


Figure 8.2: General views of an open baking furnace for anodes

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.

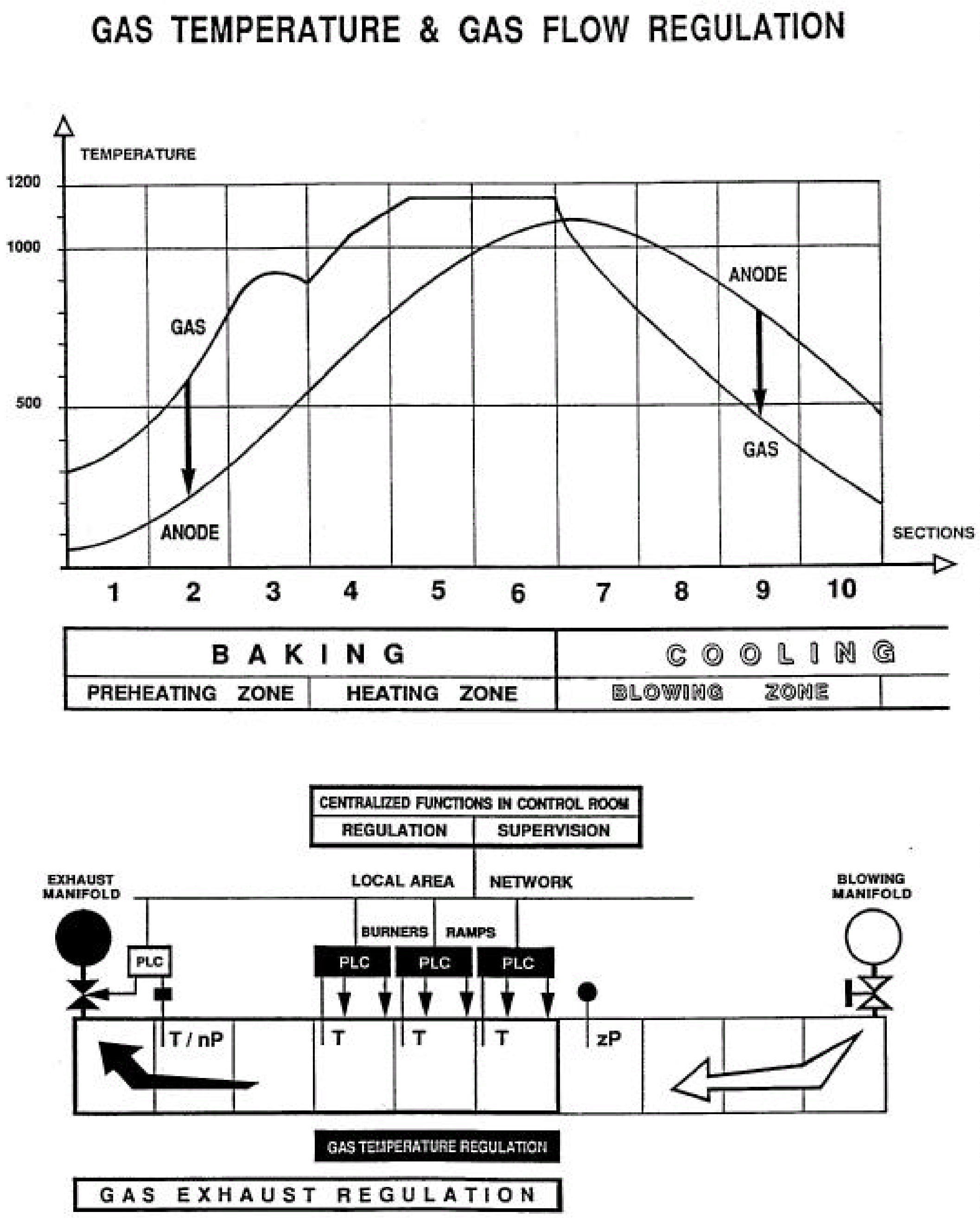


Figure 8.3: Temperature profile during the baking of anodes

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.

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.

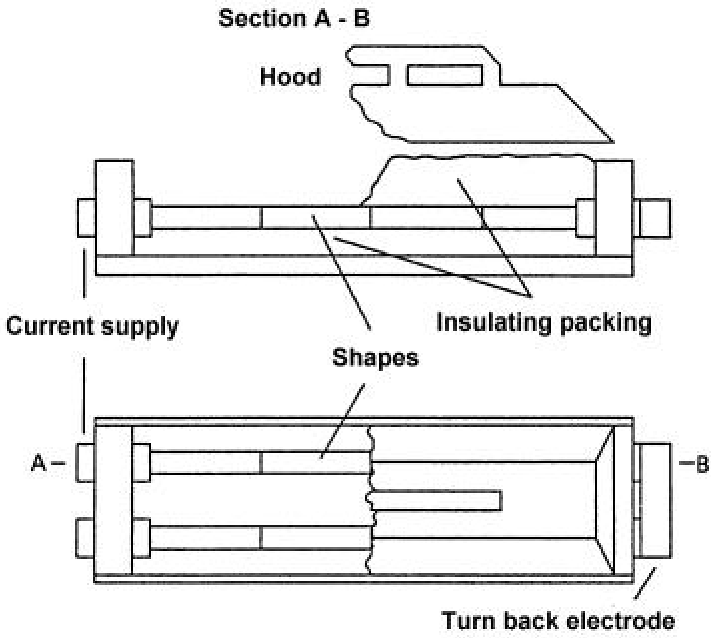


Figure 8.4: Castner graphitising furnace

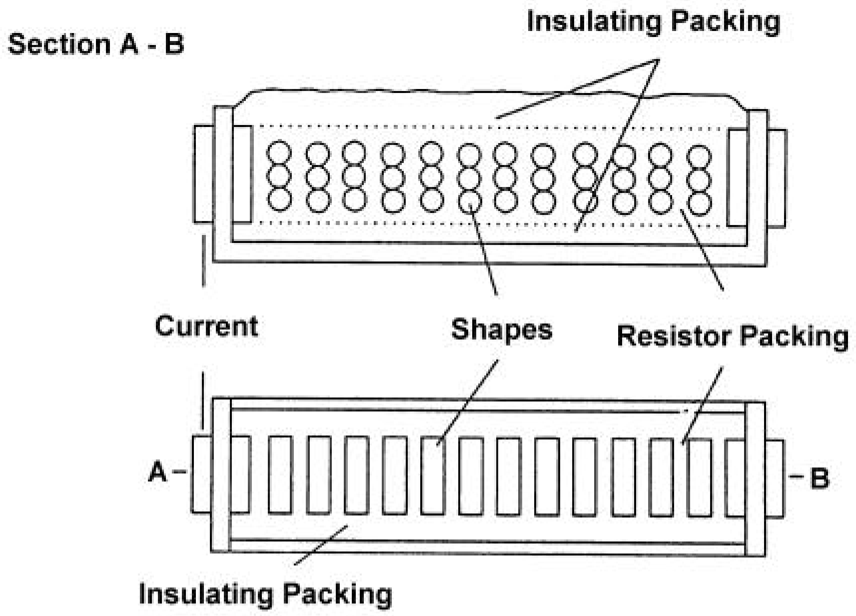


Figure 8.5: Acheson graphitising furnace

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 fumaces 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.

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.

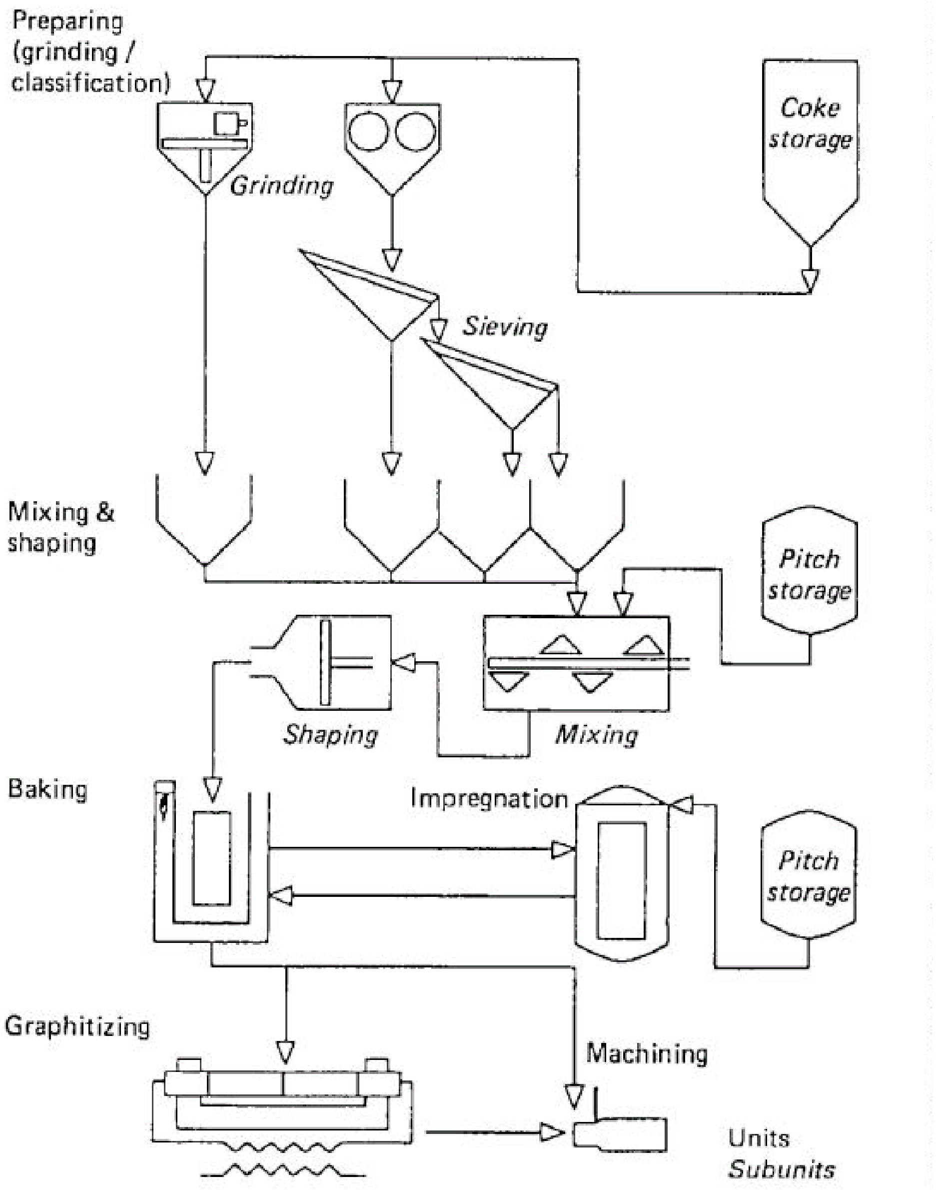


Figure 8.6: Graphite shape production

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.

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.

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.

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].

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.

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.

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.

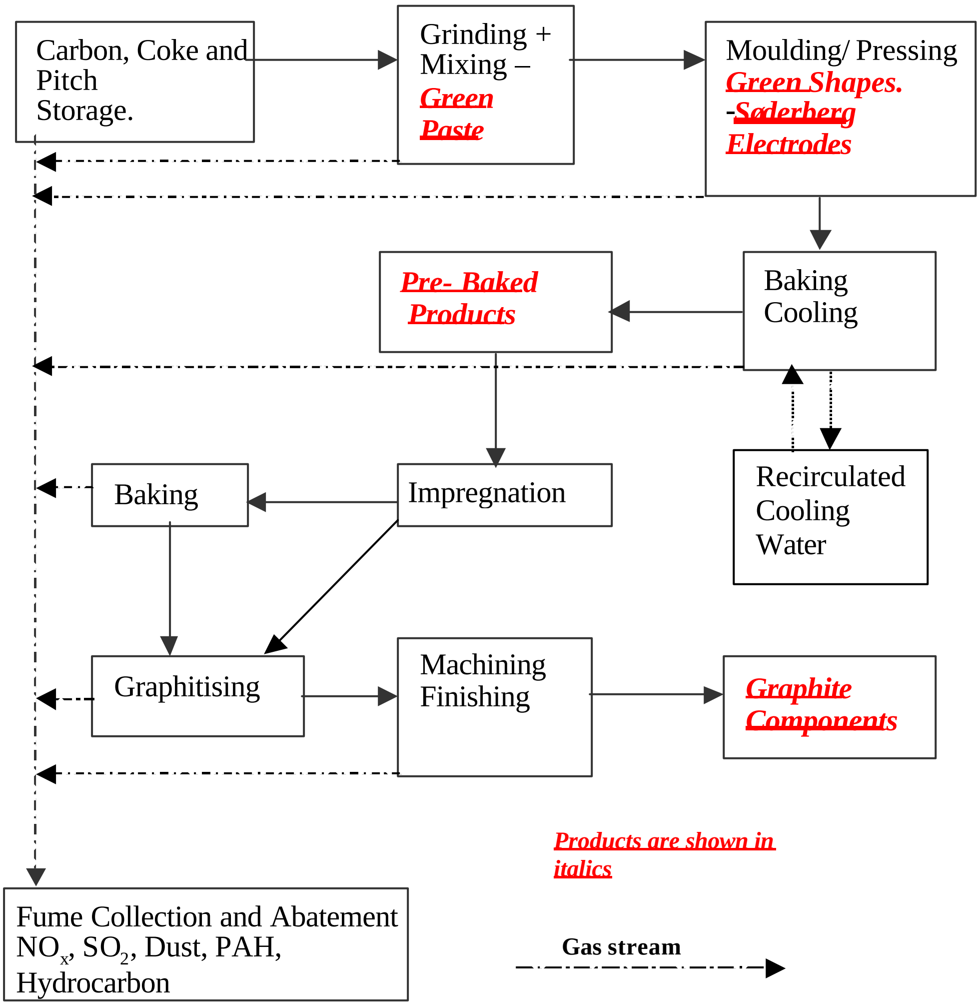


Figure 8.7: Generic emission diagram of the processes used

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.

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.

Gaseous fraction ~ 30%	- Burnt off in process -
Condensable fraction ~ 25%	- Collected in abatement
Carbonised fraction ~ 45%	- Formed into product

Figure 8.8: 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.

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.

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.

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.

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.

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].

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.

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.

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.

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 8.1: 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 8.2: 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 8.3: 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 8.4: 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 8.5: Examples of some ranges of PAH reported using different groups of compounds
***) VDI –I+II without benzo(b)naphol(2,1-d)thiophene.**

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).

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.

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.

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	Tanks or drums in	Secure pipeline or	Grinding or	Oil collection if

other oils. Solvents or resins.	bunded areas.	manual system.	milling. Blending, Impregnation	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 8.6: Techniques to consider for storage, handling and pre-treatment methods

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 8.7: Treatment methods for gaseous components

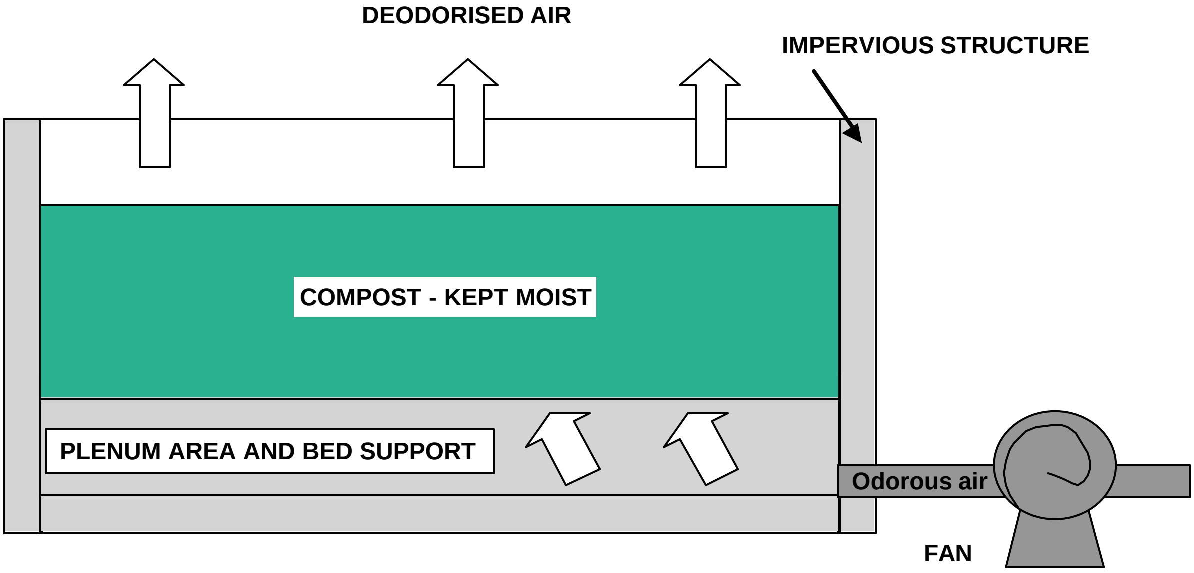


Figure 8.9: Example of a Bio-filter

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]

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.

Process residues

The principles of the minimisation and re-used of process residues are techniques that form part of BAT.

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.

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 8.8: Storage, handling and pre-treatment methods considered to be BAT

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.

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 8.9: Sources and treatment of abated and fugitive emissions from carbon and graphite production

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 8.10: 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 8.11: 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 ìg/Nm^3	Afterburner (CTO/RTO)*	
PAH (VDI I+II)	< 100 ìg/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 8.12: 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 8.13: 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 8.14: 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 8.15: 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 8.16: 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

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.

Process residues

Residues from the production processes are capable of re-use within the process or in other processes.

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.

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.

9 CONCLUSIONS AND RECOMMENDATIONS

9.1 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.

9.2 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.

9.3 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.

REFERENCES

[tm 1, Davy Consultants (UK) 1993]
HMIP (UK)
Davy Consultants (UK) 1993
Pollution Control for Magnesium Production Processes

[tm 2, McLellan and Partners Ltd, Surrey 1993]
HMIP - UK
McLellan and Partners Ltd, Surrey 1993
Pollution Control in the Secondary Aluminium Industry

[tm 3, McLelland and Partners Ltd., Surrey 1993]
HMIP - UK
McLelland and Partners Ltd., Surrey 1993
Pollution Control in the Titanium Industry

[tm 4, Hatch Associates Ltd 1993]
HMIP - UK
Hatch Associates Ltd 1993
Pollution Control for Secondary Lead Production

[tm 5, B R Lerwill, St. barbara Consultancy Services 1993]
HMIP - UK
B R Lerwill, St. barbara Consultancy Services 1993
Pollution Control in the Precious Metals Industry

[tm 6, McLellan and Partners Ltd, Surrey 1993]
HMIP - UK
McLellan and Partners Ltd, Surrey 1993
Pollution Control in the Primary Aluminium Industry

[tm 8, St. Barbara Consultancy Services 1993]
HMIP
St. Barbara Consultancy Services 1993
Pollution Control for the Refractory Metals Industries

[tm 9, Hatch Associates Ltd 1993]
HMIP - UK
Hatch Associates Ltd 1993
Pollution Control for the Tin, Bismuth and Silicon Industries

[tm 10, Hatch Associates Ltd. 1993]
HMIP - UK
Hatch Associates Ltd. 1993
Pollution Control for Cadmium and Mercury Production

[tm 11, Saint Barbara Consultancy Services 1993]
HMIP - UK
Saint Barbara Consultancy Services 1993
Pollution Control in the Cobalt and Nickel Industry

[tm 12, Hatch Associates Ltd 1993]
HMIP - UK
Hatch Associates Ltd 1993
Pollution Control for Primary Zinc Production

[tm 13, HMIP - UK 1994]
HMIP - UK
HMIP - UK 1994
Process for the Production of Zinc and Zinc Alloys

[tm 14, HMIP - UK 1994]
HMIP - UK
HMIP - UK 1994
Processes for the Production of Lead and Lead Alloys

[tm 15, HMIP - UK 1994]
HMIP - UK
HMIP - UK 1994
Processes for the Production of Refractory Metals

[tm 16, HMIP - UK 1994]
HMIP - UK
HMIP - UK 1994
Processes for the Production, Melting and Recovery of Camium, Mercury and their Alloys

[tm 17, HMIP - UK 1994]
HMIP - UK
HMIP - UK 1994
Processes for the Production of Aluminium

[tm 18, HMIP - UK 1994]
HMIP - UK
HMIP - UK 1994
Processes for the Production of Copper and Copper Alloys

[tm 19, HMIP - UK 1994]
HMIP - UK
HMIP - UK 1994
Processes for the Production of Precious Metals and Platinum Group Metals

[tm 20, HMIP - UK 1994]
HMIP - UK
HMIP - UK 1994
The Extraction of Nickel by the Carbonyl Process and the Production of Cobalt and Nickel Alloys

[tm 21, HMIP - UK 1994]
HMIP - UK
HMIP - UK 1994
Tin and Bismuth Processes

[tm 22, DGXI 1991]
European Commission, DG XI
Technical BAT Note Heavy Metal Emissions from Non-Ferrous Industrial Plants

[tm 23, OSPARCOM 1996]
OSPAR
OSPAR 1996
Draft PARCOM Recommendation concerning BAT and Best Environmental Practice for the Primary Non-Ferrous metal Industry (Zinc, Copper, Lead and Nickel)

[tm 24, DFIU 1996]
DFIU-University Karlsruhe (D)
DFIU-University Karlsruhe (D) 1996
Emission control at stationary sources in Germany; part I - sulphur and nitrogen oxides

[tm 25, DFIU 1996]
DFIU-University Karlsruhe (D)
DFIU-University Karlsruhe (D) 1996
Emission control at stationary sources in Germany; part II - heavy metals

[tm 26, OSPARCOM 1996]
Oslo and Paris Commissions

Oslo and Paris Commissions 1996
Description of BAT for the Primary Production of Non-Ferrous Metals (Zinc, Copper, Lead and Nickel)

[tm 27, McLellan and Partners Ltd., Surrey 1993]
HMIP - UK
McLellan and Partners Ltd., Surrey 1993
Pollution Control in the Copper Industry

[tm 28, WRC 1993]
European Commission DG XI
M Barry, T F Zabel and C Young 1993
Study on the Technical and Economic Aspects of Measures to reduce (on the Basis of Best Available Technology) the Pollution of Water and Other Environmental Areas from the Non-Ferrous Metal Industry (Contract B6612-90-006931)

[tm 29, OSPARCOM 1997]
Oslo and Paris Commissions
Oslo and Paris Commissions 1997
Description of Existing Techniques and Best Available Techniques in the Aluminium Electrolysis Industry

[tm 30, EPA (IRL) 1996]
Environmental Protection Agency (IRL)
Environmental Protection Agency (IRL) 1996
Integrated Pollution Control Licensing - Batneec Guidance Note for the Extraction of Alumina

[tm 31, Hydro Aluminium a.s., Elkem Aluminium ANS (N) 1994]
Hydro Aluminium a.s., Elkem Aluminium ANS (N)
Hydro Aluminium a.s., Elkem Aluminium ANS (N) 1994
The Norwegian Aluminium Industry and the Local Environment

[tm 32, NL Al 1998]
Dutch Ministry of Environment, Dept. Air /Energy
Witteveen+Bos, Deventer (NL) 1998
Dutch Notes on BAT for the Production of Primary Aluminium

[tm 33, Mantle 1988]
E C Mantle, Metallurgical & Environm. Consultant 1988
Potential for Air Pollution Emissions form the Aluminium Industry and the Best Available Technology for Abatement (final report)

[tm 34, US EPA 1995]
US EPA
US EPA 1995
EPA Office of Compliance Sector Notebook Project Profile of the Nonferrous Metals Industry

[tm 35, UNECE 1995]
Economic Commission for Europe
Heavy Metals Emissions - Long-range Transboundary Air Pollution

[tm 36, Panorama 1997]
European Commission - DG III
Panorama of EU Industry 1997 - An extensive review of the situation and outlook of the manufacturing and service industries in the EU

[tm 37, Mounsey 1995]
COPPER 95 International Conference
Mounsey, E.N. 1995
Copper Bearing Materials

[tm 38, Ausmelt 1995]
Ausmelt Ltd., Australia
EAF Dust Processing with Ausmelt Technology

[tm 39, Lightfoot 1994]
Ausmelt Ltd., Australia
Lightfoot, Brian 1994
Waste Treatment by Ausmelt Technology

[tm 40, Ausmelt 1996]
Ausmelt Ltd, Australia
Treatment of Incinerator Ash in an Ausmelt Furnace System

[tm 41, Ausmelt 1996]
Ausmelt Ltd., Australia
Treatment of Lead and Zinc Residues using the Ausmelt Process

[tm 42, Ausmelt 1996]
Ausmelt Ltd., Australia
Application of Ausmelt Technology to the Recycling of Spent Pot Liner for the Aluminum Industry

[tm 43, Ausmelt 1996]
Ausmelt Ltd., Australia
Short, W.E.; Sutton, D.J.; Swayn, G.P. 1996
Commercial application of Ausmelt's top submerged lance technology in the lead industry

[tm 44, Ausmelt 1997]
Ausmelt Ltd., Australia
Sofra, J.; Mounsey, E.N.; Piret, N.L. 1997
Technology in Secondary Copper Smelting and Converting

[tm 45, Floyd 1996]
Ausmelt Ltd., Australia
Floyd, J.M. 1996
The Third Decade of Top Submerged Lance Technology

[tm 46, Svens 1985]
Metal News, Vol 7
Svens, K. 1985
Outokumpu Mercury Recovery

[tm 47, Mahmound 1996]
International Precious Metals Institute
Dr. Mahmound I. El Guindy 1996
Precious Metals 1996 - Proceedings of the Twentieth International Precious Metals Conference, Newport Beach, California

[tm 48, Järvinen, O.]
Wenmec Systems Oy
Järvinen, O.
Wenmec/Outokumpu Technology Update of Current Developments for Anode Slime

[tm 49, Järvinen, O.]
Wenmec Systems Oy
Järvinen, O.
Current Developments for Anode Slime Precious Metals Treatment

[tm 50, Hyvärinen 1989]
Journal of Metals
Hyvärinen, O.; Lindroos, L.; Yllö, E. 1989
Recovering Selenium from Copper Refinery Slimes

[tm 51, Kuusisto 1986]

Outokumpu Oy
Kuusisto, R. 1986
Process Equipment for Electrolyte Purification and Anode Slime Treatment

[tm 52, Hyvärinen 1984]
113th AIME Annual Meeting
Hyvärinen, O. 1984
Selenium and Precious Metals Recovery from Copper Anode Slimes

[tm 53, newman, C.J.; Probert, T.I.; Weddick, A.J. 1998]
Kennecott Utah Copper Corporation, Magna, Utah
newman, C.J.; Probert, T.I.; Weddick, A.J. 1998
Kennecott Utah Copper Smelter Modernization

[tm 54, Asteljoki 1985]
Annual meeting of AIME, New York, Feb. 85
Asteljoki, J.; Kytö, M. 1985
Alternatives for Direct Blister Copper Production

[tm 55, Biswas]
Biswas, A.K.; Davenport, W.G.
Extractive Metallurgy of Copper

[tm 56, Kojo]
Kojo, I.V.; Riekkola-Vanhanen, M.
Copper Production by Leaching - Solvent Extraction - Electrowinning

[tm 57, Knuutila 1997]
Outokumpu Harjavalta Metals Oy, Finland
Knuutila, K. 1997
Nickel electrolysis process

[tm 58, Knuutila]
Outokumpu Harjavalta Metals Oy, Finland
Knuutila, K.; Hultholm, S.-E., Saxén, B
New Nickel Process Increasing Production

[tm 59, Kojo]
Outokumpu Engineering Contractors Oy, Finland
Kojo, I.V.; Mäkinen, T.; Hanniala, P.
Direct Outokumpu Nickel Flash Smelting Process (DON)

[tm 60, Hanniala 1994]
Outokumpu Engineering Contractors Oy, Finland
Hanniala, P. 1994
Outokumpu Flash Technology for the Existing Copper Smelters

[tm 61, Kytö 1996]
Outokumpu Engineering Contractors Oy, Finland
Kytö, M.; Kojo, I.V.; Hanniala, P. 1996
Outokumpu Flash Technology Meeting the Environmental and Business Challenges of the Next Century

[tm 62, Hanniala 1996]
Outokumpu Engineering Contractors Oy, Finland
Hanniala, P. 1996
Advances in Copper Smelting Technology: Aconomic and Quality Considerations

[tm 63, Helle]
Outokumpu Engineering Contractors Oy, Finland

Helle, L.; Kojo, I.
Copper production by flash-converting technology: process and equipment

[tm 64, Kennecott 1995]
Mining Environmental Management
Kennecott's smelter and refinery modernisation

[tm 65, Hanniala 1996]
Outokumpu Engineering Contractors Oy, Finland
Hanniala, P. 1996
The Environmental and Economic Benefits of the Outokumpu Flash Smelting Technology for Different Kinds of Concentrates

[tm 66, Outokompu 1997]
Outokompu Harjavalta Metals Oy
Sulphur Dioxide Emissions

[tm 67, George 1995]
Copper 95 - International Conference
George, D.B.; Gottling, R.J.; Newman, C.J. 1995
Modernization of Kennecott Utah copper smelter

[tm 68, Hanniala 1989]
Outokumpu Engineering Contractors Oy, Finland
Hanniala, T.P.T.; Sulanto, J.S. 1989
The Development Trends of the Outokumpu Flash Smelting Process for the Year 2000

[tm 69, Hanniala 1995]
Outokumpu Engineering Contractors Oy, Finland
Hanniala, P.; Kojo, I.V. 1995
Utilization of Outokumpu Flash Technology to meet Environmental Requirements

[tm 70, Mercury Expert Group 1998]
Minas de Almadén y Arrayanes, S.A.
Metalurgia del Mercurio - Métodos de Producción de Mercurio

[tm 71, various 1974]
Conference Barcelona 6 - 10.5.74
various 1974
Congreso Internacional del Mercurio (Tomo I, II),

[tm 72, Ajima 1994]
Metallurgical Review of MMIJ, Vol.11,No.1
Ajima, S.; Hayashi, M.; Shimizu, T. 1994
Copper Smelting and Refining at Naoshima

[tm 73, Shibasaki 1993]
Mitsubishi Materials Corp., Japan
Shibasaki, T.; Hayashi, M.; Nishiyama, Y. 1993
Recent Operation at Naoshima with a larger Mitsubishi Furnace Line

[tm 74, Mitsubishi 1993]
Mitsubishi Materials Corporation, Japan
The Mitsubishi Process - Technical and Environmental Advantages

[tm 75, Theodore 1992]
ETS International, Inc (USA)
Theodore, L.; Buonicore, A. 1992
Air Pollution Control Equipment

[tm 76, Startin 1998]

Cerafil (Ceramic Filter Elements), UK
Startin, A. 1998
Solve your gas filtration problems

[tm 77, Al Expert Group 1998]
European Aluminium Association EAA
Nordheim, E. 1998
Minutes from IPPC BREF Notes - Aluminium Expert Group Meeting - Brussels 27 April 1998

[tm 78, Soud 1993]
IEA Coal Research
Soud 1993
Particulate control handbook for coal-fired plants

[tm 79, Soud,]
IEA Coal Research (UK)
Soud, H.N.
Developments in particulate control for coal combustion

[tm 80, Warner, 1998]
CIM/CMMI/MIGA Montréal 98
Warner, N.A. 1998
Copper and Nickel Smelting With Virtually Zero Gas Emission - A Vision for the Future

[tm 81, Warner 1998]
TMS, Annual Meeting
Warner, N.A. 1998
Gas Recirculation and Endothermic Dissociation of Sulphur Trioxide for Smelting high Energy Sulphides with Technically Pure Oxygen

[tm 82, Warner, 1998]
AusIMM 98 - The Mining Cycle
Warner, N.A. 1998
Refined Zinc Metal Production at the Minesite

[tm 83, Ministerium in NRW (D) 1997]
Ministerium Umwelt, Raumordnung u. Landwirtschaft
Ministerium in NRW (D) 1997
NE-Metallindustrie - Betreiberleitfaden für Anlagen zum Gießen in verlorenen Formen - Sandgußverfahren

[tm 84, Ministerium NRW (D) 1997]
Ministerium Umwelt, Raumordnung u. Landwirtschaft
Ministerium NRW (D) 1997
NE-Metallindustrie - Betreiberleitfaden für Anlagen zum Gießen in Dauerformen - Druckgußverfahren

[tm 85, NRW (D) 1997]
Ministerium Umwelt, Raumordnung u. Landwirtschaft
NRW (D) 1997
NE-Metallindustrie - Betreiberleitfaden für Anlagen zum Schmelzen von Schwermetallen

[tm 86, Ministerium NRW (D) 1997]
Ministerium Umwelt, Raumordnung u. Landwirtschaft
Ministerium NRW (D) 1997
NE-Metallindustrie - Betreiberleitfaden für Anlagen zum Schmelzen von Leitmetallen

[tm 87, Brueggemann 1998]
ASARCO Inc. (USA)
Brueggemann, M.; Caba, E. 1998

Operation of the Contop Process at the Asarco El Paso Smelter

[tm 88, Torres 1998]
Sulfide Smelting
Torres, W.E. 1998
Current Teniente Converter Practice at the SPL ILO Smelter

[tm 89, Arthur 1998]
ISASMELT
Arthur, P. 1998
MIM Process Technologies
[tm 90, Al Expert Group 1998]
EEA
Nordheim, E. 1998
Aluminium Expert Group Site Visits

[tm 91, OSPARCOM 1998]
Ospar Point Workshop
UBA (D) 1998
Revision of the Draft Decision on Limits for Emissions to the Atmosphere and Discharges into Water of Contaminants from the Primary Non-Ferrous Metal Industry

[tm 92, Copper Expert Group 1998]
Eurometaux (B)
Traulsen, H. 1998
Plant Information - Copper Industry (Draft)

[tm 93, OSPARCOM 1992]
Paris Commission
Paris Commission 1992
BAT for the Preparation of Anodes in the Primary Aluminium Industry

[tm 94, Ni Expert Group 1998]
Eurometaux
Laine, L. 1998
The Support of the Nickel and Cobalt Section of the BREF Note

[tm 95, García-Agocheaga 1998]
ASER (E)
García-Agocheaga, B. 1998
Zinc Recovery Processes

[tm 96, Laine, L. 1998]
Outokumpu (SF)
Laine, L. 1998
NI Production

[tm 97, Ma, T.; Sarvinis, J. et al. 1998]
Hatch Associates ltd. (CAN)
Ma, T.; Sarvinis, J. et al. 1998
Recent Developments in D.C. Furnace Design

[tm 98, Jones, R.T.; Curr, T.R. 1998]
Mintek (South Africa)
Jones, R.T.; Curr, T.R. 1998
Plasma Developments in Africa

[tm 99, Bontoux, L.; Leone, F. 1997]
IPTS, European Commission
Bontoux, L.; Leone, F. 1997
The Legal Definition of Waste and it's Impact on Waste Management in Europe

[tm 100, NL Al 1998]

V.R.O.M. (NL)
Lijftogt, J.A.; van Kuijk, A.H.J. et al 1998
Dutch Notes on BAT for the Production of Primary Aluminium

[tm 101, NL Zn 1998]
V.R.O.M. (NL)
Lijftogt, J.A.; van Kuijk, A.H.J. et al 1998
Dutch Notes on BAT for the Production of Primary Zinc

[tm 102, DFIU Lead 1998]
University Karlsruhe DFIU (D)
Hähre, S. 1998
Report on BAT in German Zinc and Lead Production (Draft)

[tm 103, Rodermund 1997]
Metaleurop Weser Zink (D)
Rodermund, R. 1997
New Gas Cleaning Technology in the Solution Purification of a Zinc Smelter

[tm 104, Various 1990]
Technology of Metalforming

[tm 105, PM Expert Group 1998]
Degussa (D)
Hasenpusch, W. 1998
Precious Metals

[tm 106, Farrell, 1998]
European IPPC Bureau
Farrell, F. 1998
Personal Discussions

[tm 107, Ullmann's 1996]
Ullmann's Encyclopedia
Ullmann's Encyclopedia of industrial chemistry

[tm 108, Winter 1992]
Umweltbundesamt (A)
Bericht über die Umweltsituation an ausgewählten langjährigen Industriestandorten

[tm 109, UNEP 1993]
UNEP
Raffinot, P.; Bozec, C. 1993
Environmental Management of Nickel Production

[tm 110, UNEP 1987]
United Nations Environment Programme (UNEP)
United Nations Environment Programme (UNEP) 1987
Environmental Aspects of Nickel Production

[tm 111, Salmon 1998]
Kennecott Utah Copper Corporation
Salmon, L. 1998
Emission Information

[tm 112, Various 1998]
European IPPC Bureau
Technical information from TWG -meeting presentations

[tm 113, Anthony 1997]

Minerals Industry International
Anthony, T.; Flett, D.S. 1997
Nichel Processing Technology: A Review

[tm 114, Shunan Denko, Japan 1998]
Shunan Denko, Japan
Shunan Denko, Japan 1998
High-Carbon Ferrochrome Smelting Process Cuts Electric Power Consumption

[tm 115, Outokumpu Oy (SF) 1998]
Outokumpu Oy (SF)
Outokumpu Oy (SF) 1998
Outokumpu oy Ferrochrome Process Results in Energy Savings

[tm 116, ALFED 1998]
ALFED (Aluminium Federation ltd) UK
ALFED (Aluminium Federation ltd) UK 1998
Secondary Aluminium Refining and Remelting

[tm 117, Copper Expert Group 1998]
Eurometaux
Eurometaux 1998
Fabrication of Semi-Finished Products from Copper and Copper Alloys

[tm 118, ETSU (UK) 1996]
ETSU (UK)
ETSU (UK) 1996
Waste heat recovery from high temperature gas streams

[tm 119, VDI 3467 1998]
VDI (D)
VDI (3467) 1998
Production of Carbon and Electrographite Materials

[tm 120, Lead and Zinc Expert Group 1999]
Eurometaux
Krüger, J. 1999
Proposal for a BREF-note for Pb, Zn, Cd, Sb (Part 1)

[tm 121, Hoogovens 1998]
Hoogovens (NL)
Laheye, R.; Burggraaf, D. 1998
Greenmelt: An Environmentally Sound Remelting Concept

[tm 122, McLellan 1998]
ETSU
McLellan 1998
Electromagnetic Pumping Improves the Efficiency of Melting Aluminium

[tm 123, McLellan 1998]
ETSU
McLellan 1998
Electromagnetic Pumping of Aluminium; Audit of Fluxless Melting Technology at Calder Aluminium Ltd., Willington

[tm 124, DFIU Cu 1999]
University Karlsruhe (DFIU)
Rentz, O,; Krippner, M.; Hähre, S. 1999
Report on BAT in German Copper Production (Final Draft)

[tm 125, ETSU 1994]
Dept. of the Environment

ETSU 1994
Oxy-Fuel Melting of Secondary Aluminium

[tm 126, Robson 1998]
UK Environment Agency
Robson, T.G.; Coleman, J. 1998
A Review of the Industrial Uses of Continuous Monitoring Systems: Metals Industry Processes

[tm 127, ETSU 1994]
ETSU
ETSU 1994
Energy Efficiency in the Provision and Use of Industrial Gases

[tm 128, Euro Alliages (B) 1998]
Euro Alliages (B)
Euro Alliages (B) 1998
Ferromolybdenum Notes

[tm 129, Madelin 1991]
EMC '91: Non-Ferrous Metallurgy
Madelin, B; Ferquel, S.; Martin, J.L. 1991
Lead blast-furnace evolution: a new approach

[tm 130, Chadwick 1994]
Mining Magazine
Chadwick, J. 1994
Zaldivar Copper Mine

[tm 131, Davies 1998]
UK Environment Agency
Davies, N. 1998
Emissions from Carbon Fibre Production

[tm 132, Kola 1997]
XX International Mineral Processing Congress
Kola, R. et alles 1997
Depuration and upgrading of waelz oxides in a new hydrometallurgical plant

[tm 133, Eurometaux Copper Industry 1998]
Eurometaux Copper Industry
Eurometaux Copper Industry 1998
Draft Report from IPPC BAT Copper Experts Group Meeting, Hamburg July 1998

[tm 134, Nordheim 1998]
European Aluminium Association
European Aluminium Association 1998
Aluminium BREF Note - Primary Aluminium Section on Spent Potlinings

[tm 135, Ahmadzai, H. 1994]
Swedish EPA
Ahmadzai, H. 1994
Survey and Trends Pertaining to Control Methodologies in the Primary Smelting Industry

[tm 136, Torfs 1996]
Iron Control in Hydrometallurgy
Torfs, K.J. 1996
The Union Minière Goethite Process: Plant Practice and Future Prospects

[tm 137, Copper Expert Group 1998]
Metallurgiacal Consulting Traulsen GmbH
Eurometaux, Copper Industry 1998
Technologies Applied Outside the EU and New Technologies (draft 2nd version)

[tm 138, Gershel 1998]
EMCI
Gershel, T. 1998
Copper and its Alloys

[tm 139, Finland Zn 1999]
Finnish EPA
Fugleberg, S. 1999
Finnish Expert Report on BAT in Zinc Production

[tm 140, Finland Cu 1999]
Finnish EPA
Riekkola-Vanhanen, M. 1999
Finnish Expert Report on BAT in Copper Production and By-Production of Precious Metals

[tm 141, Niemelä, P. 1999]
Finnish EPA
Niemelä, P. 1999
Finnish Epert Report on BAT in Ferrochromium Production

[tm 142, Finland Ni 1999]
Finnish EPA
Riekkola-Vanhanen, M. 1999
Finnish Expert Report on BAT in Nickel Production

[tm 143, Ferro-Alloy-Expert-Group 1998]
Euroalliages (B)
Ferro-Alloy-Expert-Group 1998
BAT for Ferro-Alloy-Production

[tm 144, Elkem Asa 1998]
Elkem Asa
Elkem Asa 1998
Company Profile Including Development in Stack Emission Filtration Technology

[tm 145, Boin, U.; Linsmeyer, T.; Neubacher, F.; Winter, B. 1998]
UBA (A)
Boin, U.; Linsmeyer, T.; Neubacher, F.; Winter, B. 1998
Stand der Technik in der Sekundäraluminiumerzeugung im Hinblick auf die IPPC-Richtlinie

[tm 146, Byrdziak 1998]
Environment & Innovation in Mining & Mineral Tech.
Byrdziak, H.; Dobrzanski, J.; Garbaczewski, J. 1998
Environmental Measures by the Polish Copper Industry

[tm 147, Binder, F.; Ettmayer, P.; Schaschel, E. 1986]
Carl Hanser Verlag München Wien
Binder, F.; Ettmayer, P.; Schaschel, E. 1986
Chemische Technologie

[tm 148, Dairymple, I. 1999]
EA Technology ltd. Chester (UK)
Dairymple, I. 1999
Setting New Standards of Performance and Economy for Effluent Treatment and Heavy an Precious Metal Recovery

[tm 149, Kemmer, F. N. 1988]
Nalco Chemical Company
Kemmer, F. N. 1988
The Nalco Water Handbook (second edition)

[tm 150, FL Smidth (DK) 1992]

FL Smidth (DK)
FL Smidth (DK) 1992
GSC Processing of Carbonate Rocks

[tm 151, Kolbeinsen, L. et al. 1995]
INFACON (N)
Kolbeinsen, L. et al. 1995
Energy Recovery in the Norwegian Ferro Alloy Industry

[tm 152, Schei, A.; Tuset, J.; Tveit, H. 1998]
Tapir Forlag, Trondheim (N)
Schei, A.; Tuset, J.; Tveit, H. 1998
Production of High Silicon Alloys

[tm 153, Wintersto, D.]
Elkem ASA (N)
Wintersto, D.
Company Profile Including Development in Stack Emission Filtration Technology

[tm 154, Nestaas, I.; Lindstad, T.; Kolbeinsen, L.]
DNV Industri Norge AS (N)
Nestaas, I.; Lindstad, T.; Kolbeinsen, L.
Results of a Comprehensive Survey of Emissions of Air Pollutants from Ferrosilicon and High Purity Silicon Metal Furnaces

[tm 155, Tveit, H.]
INFACON 8
Tveit, H.
Environmental Aspects of the Ferro Alloy Industry

[tm 156, Lindstad, T.]
INFACON 8
Lindstad, T.
CO_2-Emissions and the Ferroalloys Industry

[tm 157, Lindstad, T.; Kolbeinsen, L. 1994]
SINTEF, Trondheim (N)
Lindstad, T.; Kolbeinsen, L. 1994
10th International Ferro-Alloys Conference

[tm 158, Monsen, B.; Lindstad, T.; Tuset, J.K.]
SINEF, Trondheim (N)
Monsen, B.; Lindstad, T.; Tuset, J.K.
CO_2 Emissions from the Production of Ferrosilicon and Silicon metal in Norway

[tm 159, VDI 3478 1996]
VDI (D)
VDI 3478 (D) 1996
Biologische Abgasreinigung - Biowäscher und Rieselbettreaktoren Biological Waste Gas Purification - Bioscrubbers and Trickle Bed Reactors

[tm 160, Winter, B., Stubenvoll, J.; Wiesenberger, H. 1999]
UBA (A)
Winter, B., Stubenvoll, J.; Wiesenberger, H. 1999
Stand der Technik in der Sekundärkupfererzeugung im Hinblick auf die IPPC-Richtlinie

[tm 161, Petersen 1999]
Umweltbehörde, Hamburg (D)
Petersen, K. 1999
Determination of specific emission values (BAT)

[tm 162, Coulton, G. 1999]
London & Scandinavian Metallurgical Co. ltd.

Coulton, G. 1999
IPPC BREF Notes- Refractory Metals (Chromium) and Ferro Alloys (Ferro Titanium)

[tm 163, Steudtner 1998]
TÜV Ecoplan, Umwelt GmbH, Mönchengladbach (D)
Steudtner 1998
Bericht über die Durchführung von Emissionsmessungen im Rahmen des Projektes RWO an den Dachreitern der Konverterhalle sowie des Nebenhaubenfilters (Esse 48) in der Rohhütte Werk Ost bei der Firma Norddeutsche Affinerie Hamburg

[tm 164, Bobeth 1999]
Sächsisches Landesamt für Umwelt und Geologie
Bobeth, A. 1999
Precious Metals

[tm 165, Waquier, G.; Bendixen, O.R. 1999]
Haldor Topsoe A/S (DK)
Waquier, G.; Bendixen, O.R. 1999
Topsoe WSA Technology for Desulphurization of Off-gas from Pb and Zn Smelters

[tm 166, Waquier, G.; Bendixen, O.R. 1996]
Haldor Topsoe A/S (DK)
Waquier, G.; Bendixen, O.R. 1996
Topsoe WSA Technology for Desulphurization of SO2 Gas from PB Sintering Machine at Metaleurop, Noyelles-Godault, France

[tm 167, Bendixen, O. R. 1997]
TOPSOE Technologies (DK)
Bendixen, O. R. 1997
H_2SO_4 from Low Strength Gases

[tm 168, Neuhaus, W. 1999]
Global Symposium on Recycling, Waste Treatment etc
Neuhaus, W. 1999
Enforcement Programme Concerning Avoidance and Recycling of Waste at non-ferrous Metal Smelting Plants and Foundries in North-Rhine Westphalia

[tm 169, Clark, J.H. 1995]
Blackie Academic & Professional
Clark, J.H. 1995
Chemistry of Waste Minimization

[tm 170, U.S. Department of Commerce, Springfield (USA) 1995]
National Technical Information Service (NTIS)
U.S. Department of Commerce, Springfield (USA) 1995
Revitalize the US Silicon/Ferrosilicon Industry Through Energy-Efficient Technology, Final Report, Addendum Furnace Modeling

[tm 171, Steil 1999]
DFIU, University Karlsruhe (D)
Steil, H.U.; Hähre, S. 1999
Personal Communication

[tm 172, Cunningham, L.D. 1997]
U.S.G.S.
Cunningham, L.D. 1997
Columbium (Niobium) and Tantalum

[tm 173, Papp, J.F. 1997]
U.S.G.S.

Papp, J.F. 1997
Chromium

[tm 174, Jones, T.S. 1997]
U.S.G.S.
Jones, T.S. 1997
Manganese

[tm 175, Shedd, K.B. 1997]
U.S.G.S.
Shedd, K.B. 1997
Tungsten

[tm 176, Blossom, J.W. 1997]
U.S.G.S.
Blossom, J.W. 1997
Molybdenum

[tm 177, Gambogi, J. 1997]
U.S.G.S.
Gambogi, J. 1997
Titanium

[tm 178, Blossom, J.W. 1997]
U.S.G.S.
Blossom, J.W. 1997
Rhenium

[tm 179, Hedrick, J.B. 1997]
U.S.G.S.
Hedrick, J.B. 1997
Zirconium

[tm 180, Fenton, M. 1997]
U.S.G.S.
Fenton, M. 1997
Ferroalloys

[tm 181, Winter 1998]
UBA (A)
UBA (A) 1998
Emissionserklärung Treibacher Chemische Werke

[tm 182, International Tungsten Industry Association (UK) 1999]
International Tungsten Industry Association (UK)
International Tungsten Industry Association (UK) 1999
BREF Note for Tungsten

[tm 183, Encyclopaedia Britannica 1996]
Encyclopaedia Britannica
Encyclopaedia Britannica 1996
Extraction and Processing Industries

[tm 184, London & Scandinavian Metallurgical Co ltd. 1999]
London & Scandinavian Metallurgical Co ltd.
London & Scandinavian Metallurgical Co ltd. 1999
Titanium Sware Degreasing Plant

[tm 185, London & Scandinavian Metallurgical Co ltd. 1999]
London & Scandinavian Metallurgical Co ltd.
London & Scandinavian Metallurgical Co ltd. 1999
Production of Chromium Metal

[tm 186, ABB (S) 1999]
ABB (S)
ABB (S) 1999
Information on Systems for Pollution Control

[tm 187, Elkem (N) 1999]
Elkem (N)
Elkem (N) 1999
Energy recovery from hot gas in ferroalloy and silicon industry

[tm 188, SFPO (F) 1999]
SFPO (F)
SFPO (F) 1999
Energy balance

[tm 189, Kramer, D. 1997]
U.S.G.S.
Kramer, D. 1997
Magnesium

[tm 190, Ober, J.A. 1997]
U.S.G.S.
Ober, J.A. 1997
Lithium

[tm 191, Lurgi 1998]
Lurgi GmbH
Radial Flow Scrubber for Dedusting, Cooling, Gas Absorption

[tm 192, Lurgi 1998]
Lurgi GmbH
Electrostatic Precipitators

[tm 193, Lurgi 1998]
Lurgi GmbH
Corrosion-Proof Wet Precipitators

[tm 194, Lurgi 1997]
Lurgi GmbH
Low Pressure Pulse Technology

[tm 195, SFPO 1999]
SFPO
Dedusting Equipment of the Casting Area on BF Nr. 7 of SFPO

[tm 196, Elkem 1998]
Elkem-Spigerverket a/s, Oslo, Norway
Semi-Closed Furnace with waste Heat Boiler and Filter

[tm 197, Mezger 1999]
Ministerium für Umwelt und Verkehr Baden-Württemb.
Mezger, G. 1999
German Aluminium Expert Group

[tm 198, Lurgi AG, Frankfurt/M. (D) 1991]
Lurgi AG, Frankfurt/M. (D)
Lurgi AG, Frankfurt/M. (D) 1991
Cleaning of Process and Waste Gases

[tm 199, Finkeldei, L. 1999]
Finkeldei, L.

Finkeldei, L. 1999
Personal Discussions

[tm 200, Kantola, E. 1999]
Lapin Ympäristökeskus
Kantola, E. 1999
Dust emissions from closed electric arc furnaces for ferro-chrome production

[tm 201, Velten 1999]
Norddeutsche Affinerie
Velten 1999
Primary Smelter, Converter Secondary Hood System

[tm 202, EnviroSense 1995]
EnviroSense
Closed Ferro-Alloy Furnace with Dry Removal

[tm 203, Amundsen 1999]
Norsk Hydro ASA
Amundsen 1999
Primary magnesium production techniques

[tm 204, Amundsen 1999]
Norsk Hydro ASA
Amundsen 1999
Primary magnesium production techniques

[tm 205, Sadaci S.A. (B) 1999]
Sadaci S.A. (B)
Sadaci S.A. (B) 1999
Production of Sulphuric Acid with a WSA plant

[tm 206, TGI 1999]
Fundación Entorno, Empresa y Medio Ambiente
Tecnología y Gestión de la Innovación S.A. 1999
Metalurgia no Férrea, Epígrafes 2.5.a, 2.5b

[tm 207, TGI 1999]
Fundación Entorno, Empresa y Medio Ambiente (E)
Tecnologia y Gestión de la Innovación S.A. (E) 1999
Fabricación de Carbono y Electrografito

[tm 208, Alwast, H. et al. 1998]
Ministerium NRW (D)
Alwast, H. et al. 1998
Abschlußbericht zur Untersuchung der NE-Metall-Schmelzanlagen und NE-Metall-Gießereien

[tm 209, Stephens, R.L. 1999]
Journal of Metals
Stephens, R.L. 1999
Innovations in Smelter Gas Control

[tm 210, Copper Expert Group 1999]
Eurometaux Copper Industry Expert Group
Traulsen, H.
Information on the Copper Industry Section 6 and 7

[tm 211, Noyes 1994]
Robert Noyes
Unit Operations in Environmental Engineering

[tm 212, Noyes 1993]
Robert Noyes
Pollution Prevention Technology Handbook

[tm 213, PRAM 1999]
OSPARCOM
Progress Report 3-7 May 1999

[tm 214, Vaartjes 1999]
Chemisch 2 Weekblad 8
Jarosite Processing

[tm215, Mining Engineering 1999]
Newman, Probert, Weddick
Kennecott Utah Modernisation

[tm 216, Gryllia 1999]
Greek Directorate for the Environment
Olympias Project

[tm 217, VDI 2442 1987]
VDI (D)
VDI (2442) 1987
Waste gas treatment by Thermal Combustion

[tm 218, VDI 2443 1995]
VDI (D)
VDI (2443) 1995
Waste gas purification by oxidative gas scrubbing

[tm 219, VDI 3674 1998]
VDI (D)
VDI (3674) 1998
Waste gas treatment by adsorption

[tm 220, VDI 3476 1990]
VDI (D)
VDI (3476) 1990
Catalytic exhaust gas purification

[tm 221, VDI 3677 1997]
VDI (D)
VDI (3677) 1997
Filtering separators

[tm 222, VDI 3678 1998]
VDI (D)
VDI (3678) 1998
Electrostatic precipitators

[tm 223, VDI 3679 1998]
VDI (D)
VDI (3679) 1998
Wet separators for particle separation

[tm 224, VDI 3927 1998]
VDI (D)

VDI (3927) 1998
Abatement of halide, sulphur oxides and nitrogen oxides in off-gases from combustion processes

[tm 225, VDI 3460 1997]
VDI (D)
VDI (3460) 1997
Emission Control, Thermal treatment of waste

[tm 226, VDI 2102 1999]
VDI (D)
VDI (2102) 1999
Emission Control, secondary copper smelting and refining plants

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, <u>shaft furnace</u>, converter, anode plant.
1990	1100 – 1300	Anode copper 80000 – 100000 t/a	Material handling/storage, <u>electric furnace</u>, converter, anode plant.
1991	1250 – 1400	Anode copper, 60000 t/a	Material handling/storage, <u>TBR furnace</u>, 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

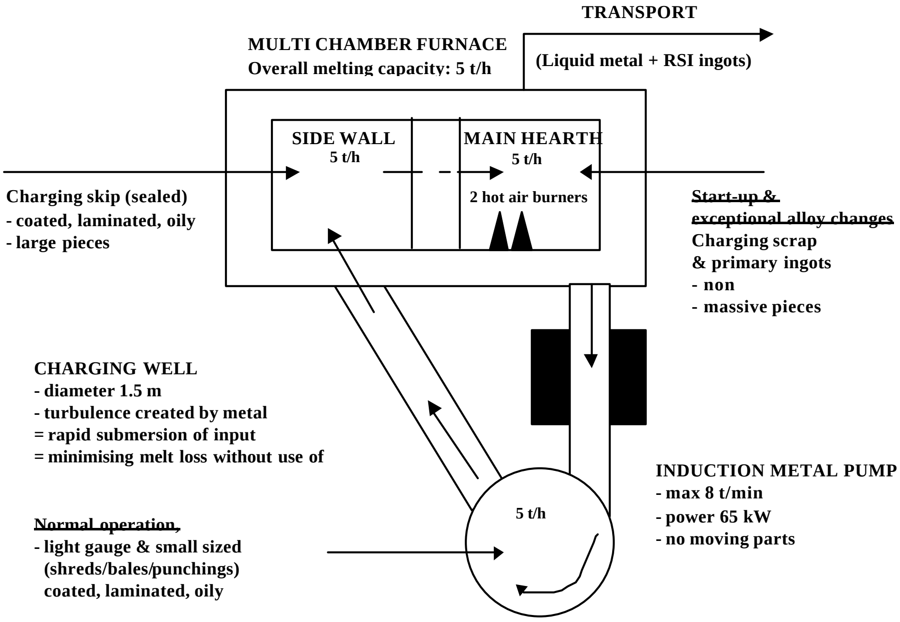
Abatement equipment costs:

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 Nm³/h	61000 Nm³/h
Dust inlet	10 - 20 g/Nm³	10 – 15 g/Nm³
Dust outlet	150 - 200 mg/Nm³	200 - 300 mg/Nm³
Efficiency	99.9%	99.8%
EP characteristics:	4 fields, 3000 m² collection area, single unit	3 fields, 4800 m² 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 Nm³/h	730000 Nm³/h	70000 Nm³/h
Dust outlet	< 10 mg/Nm³	< 10 mg/Nm³	< 10 mg/Nm³
Total installed cost: Million €	**20 *)**	**14 **)**	**2 – 2.5 ***)**
Main consumption: Electricity	2.5 - 3 kWh/1000 Nm³	2 – 3 kWh/1000 Nm³	1.5 – 4 kWh/1000 Nm³
Others	1 g/Nm³ 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: Equipment supplied:	Wet gas cooling and cleaning section for combined SO_2 gas of furnace and converter gases 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	Wet gas cooling and cleaning section for combined SO_2 gas of furnace and converter gases 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: Equipment supplied:	Double catalysis sulphuric acid plant Single strand, 4 pass converter with inter-pass absorption after the 2nd pass	Double catalysis sulphuric acid plant Single strand, 5 pass converter with inter-pass absorption after the 3rd pass
Design basis gas cleaning: Operating temperature Gas flow Precipitation efficiency for dust	370 °C inlet, 27 °C outlet 91000 – 123000 Nm^3/h 96.7%	370 °C inlet, 27 °C outlet 45000 – 115000 Nm^3/h 96.7%
Design basis contact plant: Gas flow SO_2 Conversion SO_2/SO_3 H_2SO_4 production	91000 – 123000 Nm^3/h 10 – 15.1% (av. 13%) > 99.5% 1700 t/d	45000 – 115000 Nm^3/h 6 – 11.3% > 99.5% 1350 t/d
Installed costs: **Million €**	**44 – 45**	**51 – 52**
Main consumption: Electricity Fuel oil Natural gas Catalyst Labour	*) 75 – 80 kWh/t acid 3 - 4 Nm^3/t acid 0.02 –0.04 l/t acid 0.1 h/t acid	*) 55 – 60 kWh/t acid 2 – 3 kg/t acid 0.02 –0.04 l/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 value5)
Dust	Belgium	Pb Other non-ferrous	mg/Nm^3 mg/Nm^3	10 20
	France	Zn/Pb pyro Zn/Pb pyro	mg/Nm^3 kg/h	10 2.5
	Germany	Non-Ferrous Pb	mg/Nm^3 mg/Nm^3	20 10
	Netherlands	Zn Sn General Ind.	mg/Nm^3 mg/Nm^3 mg/Nm^3	30.0 5 25
	Norway	Zn Cu, Ni	kg/h kg/h	50.0 2.0
	Spain	Zn Pb (general) Pb (refining) General Ind. Cu smelting Cu refining Cu hydrometallurgy	mg/Nm^3 mg/Nm^3 mg/Nm^3 mg/Nm^3 mg/Nm^3 mg/Nm^3 mg/Nm^3	50 50 10 150 150 300 300
	Sweden	Cu, Pb,Zn Cu, Pb,Zn Cr-Ni-Pb-Zn Cr-Ni, Pb-Zn	mg/Nm^3 t/y kg/t feedmat t/y	20 250 0.1 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 Cu refining Cu hydromet.	mg/Nm^3 mg/Nm^3 mg/Nm^3	150 300 300
		Zn, Cu, Pb	t/y	10

Table continued on following page.

Contaminant	Country	Industry	Unit	Limit value5)
Mercury	France	Zn/Pb pyro	kg/h	0.01

	Germany	All	mg/Nm^3	0.2[2]
	Sweden	Zn, Cu, Pb Cr, Ni, Pb, Zn	t/y g/t feed mat	0.35 0.4
Manganese	Germany	All	mg/Nm^3	5[3]
Nickel	Germany	All	mg/Nm^3	1[1]
Lead	France	Zn/Pb pyro Zn/Pb pyro	kg/h t/y	0.5[3] 50
	Germany	All	mg/Nm^3	5
	Spain	Pb (flow < 300 m/min) Pb(flow > 300 m^3/min)	mg/Nm^3 mg/Nm^3	80 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/Nm³.

[2] The sum of Cadmium, Mercury and Thallium (if the mass flow is 1 g/h or more) shall not exceed 0.2 mg/Nm³.

[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/Nm³.

[4] Smelting of cathode copper in a shaft furnace: emission of copper shall not exceed 10 mg/Nm³.

[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 Ni (carbonyl process) Ni (other processes)	10 30 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$_{org}$	50

of which Benzo(á) pyrene		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 Sulphur dioxide +	Netherlands	Zn	mg/Nm^3	100
	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	kg/t	0.009
			Al smelters	kg/t	0.02
Arsenic	Belgium	Total	All	mg/l	1
	Germany	Qualified random sample or 2 hour mixed sample	All	mg/l	$0.1^{2)}$
				g/t(*)	$2^{1)\ 2)}$
	Norway	Monthly average	Cu, Ni	kg/d	4
	Sweden		Zn, Cu, Pb	t/y	20
			Cr-Ni-Pb-Zn	t/y	0.001
	Spain		All Dissolved metal	mg/l	0.5
Cadmium	Belgium	Total existing plants	Zn, Pb	mg/l	0.9
		Monthly average, existing Plants	Zn, Pb	mg/l	0.3
		Total, new plants	Zn, Pb	mg/l	0.5
		Monthly average, new plants	Zn, Pb	mg/l	0.2
		Total	Cu, Ni, Sn	mg/l	1
	France		Zn	mg/l	0.5
	Germany	Qualified random sample or 2 hour mixed sample	All	mg/l	$0.2^{2)}$
				g/t	$3^{1)\ 2)}$
	Norway	Monthly average	Cu, Ni	kg/d	0.01
			Zn roasting &	mg/l	0.2
			H_2SO_4 production	kg/d	0.03
			Zn leaching plant	mg/l	0.2
				kg/d	0.3
	Sweden		Zn, Cu, Pb	t/y	0.4
			Cr-Ni-Pb-Zn	t/y	0.001
	Spain	Monthly average	All	mg/l	0.2
		Daily average	Dissolved metal	mg/l	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	All	mg/l	2
		total	All	mg/l	5
	Germany	total	Pb, Cu, Zn	mg/l	$0.5^{2)}$
				g/t	$10^{1)\ 2)}$

	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	Zn Pb Ni	mg/l	2
		dissolved	Cu	mg/l	3
		total	Zn Pb Ni	mg/l	4
		total	Cu	mg/l	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	All	mg/l	2
		total	All	mg/l	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 Zn roasting & H_2SO_4 production Zn leaching plant Zn electrolysis and discarding	kg/d mg/l kg/d mg/l kg/d kg/d	4 5 0.75 5 7.5 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 (mg/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.