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ENVIRONMENTAL ASSESSMENT AND MANAGEMENT IN THE PRODUCTION OF SIX NON-FERROUS METALS

(ALUMINUM, NICKEL, COPPER, LEAD, ZINC, AND TIN)

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Preface

This study presents an overview of the main environmental implications of the production of six of the most important non-ferrous metals, aluminum, nickel, copper, lead, zinc and tin. The purpose of this work is to provide a concise document which surveys the main technical aspects of the various production processes, from mining to metal refining, with special emphasis on the impact of the existing and emerging production technologies on the environment.

In the chapters covering the individual metals additional aspects of the manufacturing processes were also considered in order to put into perspective the environmental and economic consequences of possible technological options. These include the possibilities of metals production from by-product utilization, potential for metal recycling, cost implication for pollution control or reduction, environmental standards recommended for emissions of pollutants, and worker health, safety and protection. In each chapter a case study was presented for the metal under consideration in order to bring examples of the actual applications of the concepts expressed in the rest of the document.

This document was prepared with the co-operation of Dr. Piero M. Armenante, Assistant Professor at the Department of Chemical Engineering and Chemistry at the New Jersey Institute of Technology.

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Glossary of terms

ACGIH	American Conference of Governmental Industrial Hygenists. An organization including professional personnel in governmental agencies and educational institutes whose aim is the development of administrative and technical aspects of workers' health protection and the promotion of standards and techniques in industrial hygiene. Its Committee on Threshold Limit Values keeps under constant revision the permissible concentration of a list of 400-500 substances.
CWPB	Central-worked pre-bake. It refers to electrolytic cells for aluminum production in which the graphite anodes are manufactured (baked) in a separate part of the plant. In addition, alumina feeding to the cell takes place by breaking the cryolite solid crust in a "central" space placed between two lines of anodes.
KWhr DC	1 Kilowatt x 1 hour of direct current.
Nm^3	Normal cubic meter. The gas content of one cubic meter space measured at standard temperature and pressure, i.e. 0°C and 1 atmosphere.
SWPB	Side-worked pre-bake. It refers to electrolytic cells for aluminum production. Similar, in principle, to the CWPB (see above), the SWPB cells have an alumina feeding system which consists of breaking the cryolite solid crust around the whole circumference of the anode complex.
TSS	Total suspended solids.
TWA	Time-weighed average. It refers to the concentration of pollutants in the air averaged over a period of time.

I. INTRODUCTION

The non-ferrous metal industries considered in this study: aluminum, nickel, copper, lead, zinc and tin, play a major role in the economy of several industrialized and developing countries. Unfortunately, they are also among those industrial sectors which entail emission or release of enormous amounts of pollutants into the environment. Each one of the steps required for the production of a metal can be associated, to a certain extent, with a detrimental impact on the environment. This impact is made even more significant by the sheer size of the industry and by the type of pollutants generated. To take a specific case as an example, one single nickel/copper production facility releases through its stacks some 2,500 tons of sulphur dioxide into the atmosphere every day.

Mining is the first step in the metal production and cannot be undertaken without some environmental impact. Both underground and open-cast mining require the moving and transportation of large volumes of material, with consequent potential release into the environment of dust, oxidation products, and/or soluble salts leached out during storage or at the ore processing stage. Underground mining has the least negative impact on the environment although large amounts of waste material are produced and must be disposed of in landfills or disposal areas. Rain water run-off may then leach out some of the soluble salts contained in the waste mineral with consequent pollution. Open-cast and strip mining have a greater potential to create a negative environmental impact. The overburden material can be used in principle, for backfilling followed by revegetation and complete land reclamation. Rehabilitation is not possible where the extent and layer depth of the mined area is too large.

Ore processing is, in general, a dust generating operation and appropriate measures must be taken to prevent or control this problem. When feasible, flotation is often practiced. On one hand this eliminates the need for further processing of large amounts of gangue material; on the other it may have a significant environmental impact because of the large volumes of water involved and of the contaminants contained in the water itself. Tailings disposal is also a major environmental problem.

Smelting of sulphide ores as in the case of nickel, copper, lead and zinc is typically associated with two potential environmental problems, namely dust and fume emissions, and sulphur dioxide emissions. The former problem may become even more significant if the dust contains appreciable amounts of harmful heavy metals such as lead, cadmium, and mercury or elements such as arsenic, antimony and bismuth. The latter hazard, SO_2, has been found to be directly responsible for the acid rain problem which has already caused significant environmental damage. Modern smelters can be equipped with devices which collect dust and fumes and convert sulphur dioxide to usable chemicals, thus greatly reducing their negative environmental impact. In addition, new smelting technologies already exist or are undergoing trial tests, which reduce the amounts of pollutants produced or produce pollutants which are amenable to removal or conversion to harmful chemicals. Yet older smelters remain a potentially large source of contamination especially since they can hardly be retrofitted to significantly reduce pollution.

Smelting of oxidized ores as in the case of aluminum, nickel, and tin is associated with dust emissions or different (such as fluoride emission) kinds of environmental problems.

Because of these aspects it is necessary that the non-ferrous metal industries keep increasing their control efforts to minimize the environmental impact caused by their activities. Already in the past decades new technological innovations coupled with some major changes in the market structure of the business and new more stringent environmental regulations have produced significant shifts in strategies adopted by the industry with positive environmental implications. Hopefully this trend will continue in the future.

2. ALUMINUM

2.1 Introduction

Aluminum is the most abundant metal in the earth's crust. Because of its remarkable properties, such as light weight, resistance to corrosion, and good mechanical strength, aluminum has become the most important of the non-ferrous metals. Since World War II its consumption has increased faster than any other metal. Only plastics have outpaced the growth of aluminum. In 1985 world primary aluminum production was 15.4 million tons.[1]

Aluminum production can be considered a three step process:

- Mining of the bauxite ore
- Extraction of alumina (Al_2O_3) from the ore
- Electrolytic reduction of alumina to aluminum (smelting).

This overall process is referred to as primary aluminum production, meaning that the metal is produced from raw ore. By contrast, secondary aluminum is produced from manufacturing scrap, recycled items, and other residues which contain economically recoverable amounts.

Primary aluminum production is very energy consuming. Some 18,000 KW-hr and 10 million Kilocalories are required to produce one ton of metal from bauxite.[2] As a result, aluminum smelters are usually built close to a sizeable power plant. A typical 150,000 ton/year production capacity plant requires some 300,000 KW of installed electric power capacity. An aluminum production plant can generate a noticeable environmental impact. Wastes resulting from industrial operations can be significant. In addition, the environmental aspects of transporting and handling alumina must be considered.

2.2 Primary aluminum production processes and pollutants produced

Although many processes have been developed over the years the standard aluminum production process consists of the Bayer process (for Al_2O_3 production) followed by the Hall-Heroult process (for aluminum smelting). They are examined in this study together with the environmental problems associated with their use.

2.2.1 Alumina production: the Bayer process

The starting material used in aluminum manufacturing is bauxite ore. Major sources of this mineral exist in Brazil, Guyana, French Guyana, Surinam, Costa Rica, Jamaica, Haiti, Ghana, Guinea, Sierra Leone, Cameroon, Java,

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1/ World Metal Statistics Yearbook 1986, World Bureau of Metal Statistics, May 1986.

2/ "The Aluminium Industry and the Environment", Industry and Environment, No. 3, 1979.

Borneo, Sumatra and Australia.[3] On the average, the bauxite ore contains 40-60 per cent Al_2O_3, chemically bound water (12-30 per cent), Fe_2O_3 (7-30 per cent), SiO_2 (1-15 per cent), TiO_2 (3-4 per cent), plus impurities (less than 0.5 per cent).

The Bayer process is a method for bauxite refining consisting of the alkaline hydrometallurgical extraction of alumina from the ore. Caustic soda is used at elevated temperature and pressures and at different concentrations. For trihydrate bauxite the conditions of extraction are in the following range: soda concentrations of 100-150 g/l of Na_2O at temperatures between 120 and 170°C and pressures between 3.40 and 4.75 atmospheres. The corresponding figures for monohydrate bauxite are 200-300 g/l of Na_2O, 200-250°C and 35 atmospheres.[4]

Alumina is extracted in the liquid phase forming a saturated aluminate solution. An insoluble residue (red mud or bauxite residue), is left as a result of the process. The amount of the waste product varies from one half to one ton (dry weight) per ton of alumina produced, depending on the bauxite used and the process variables adopted.

Red mud contains only 20-30 per cent of solids. A typical composition is the following (on a dry basis):[5]

Fe_2O_3	30-60 per cent
Al_2O_3	10-20 per cent
SiO_2	3-20 per cent
Na_2O	2-10 per cent
CaO	2- 8 per cent
TiO_2	Trace-10 per cent
pH	12-12.5 (measured on soluble fraction)

Additional minor components can be found in red mud depending on the type of ore. For example, the red mud obtained at the three major Hungarian plants (Magyaróvár, Ajka, Almásfüzitó) contains the following:[6]

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[3] Environmental Guidelines, Office of Invironmental Affairs, The World Bank, July 1984, p. 1.

[4] Battelle Laboratories: Development Document for Proposed Effluent Limitations Guidelines and New Source Standards of Performance for the Bauxite Refining, Primary Aluminium Smelting and Secondary Aluminium Smelting Industry, Environmental Protection Agency Contract Completion Report No. 68-01-1518, Document 440/1-73-019, 1973.

[5] Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984, p. 2.

[6] Anon, "Information on the Environmental Aspects of Alumina Production in Hungary", Document ALU 80/495C, Budapest, 1980.

V_2O_5	0.03 g/l
P_2O_5	0.07 g/l
NaF	0.09 g/l
SO_3	0.3 g/l

The amount of red mud produced in those plants is 1.2 tons per ton of aluminum produced.

The supernatant (containing the aluminate) is separated from the residue (mud) and some 50 per cent of its alumina content is precipitated by cooling and adding seed crystals of previously obtained small grain size Al_2O_3. Alumina is then separated, washed and calcined at 1000-1200°C in natural gas or fuel oil fired rotary as well as stationary kilns. A block diagram for the process is given in figure 2.1. Caustic soda losses are minimized by recycling. The raw materials and their fates (also as potential pollutants) are summarized in table 2.1.

Meanwhile, the bauxite residue which was separated by sedimentation is washed with water in order to recover soluble matter before being discharged into the environment. The red mud is the waste produced in the largest quantity by alumina plants and has the greatest potential for negatively impacting the environment.

About 90 per cent of the red mud is stored on land while 10 per cent is stored or disposed of at sea.[7] The liquid phase and the whole slurry cause environmental problems, whether disposal occurs on land or into the seas.[8][9]

In 1979 the world production of bauxite residue amounted to 32 million tons (dry basis).[10] Assuming that at least 2 tons of water are associated with each ton of residue, about 96 million tons of residue were produced. These quantities of red mud have the potential for a noticeable environmental impact. Furthermore handling such amounts of waste requires considerable effort.

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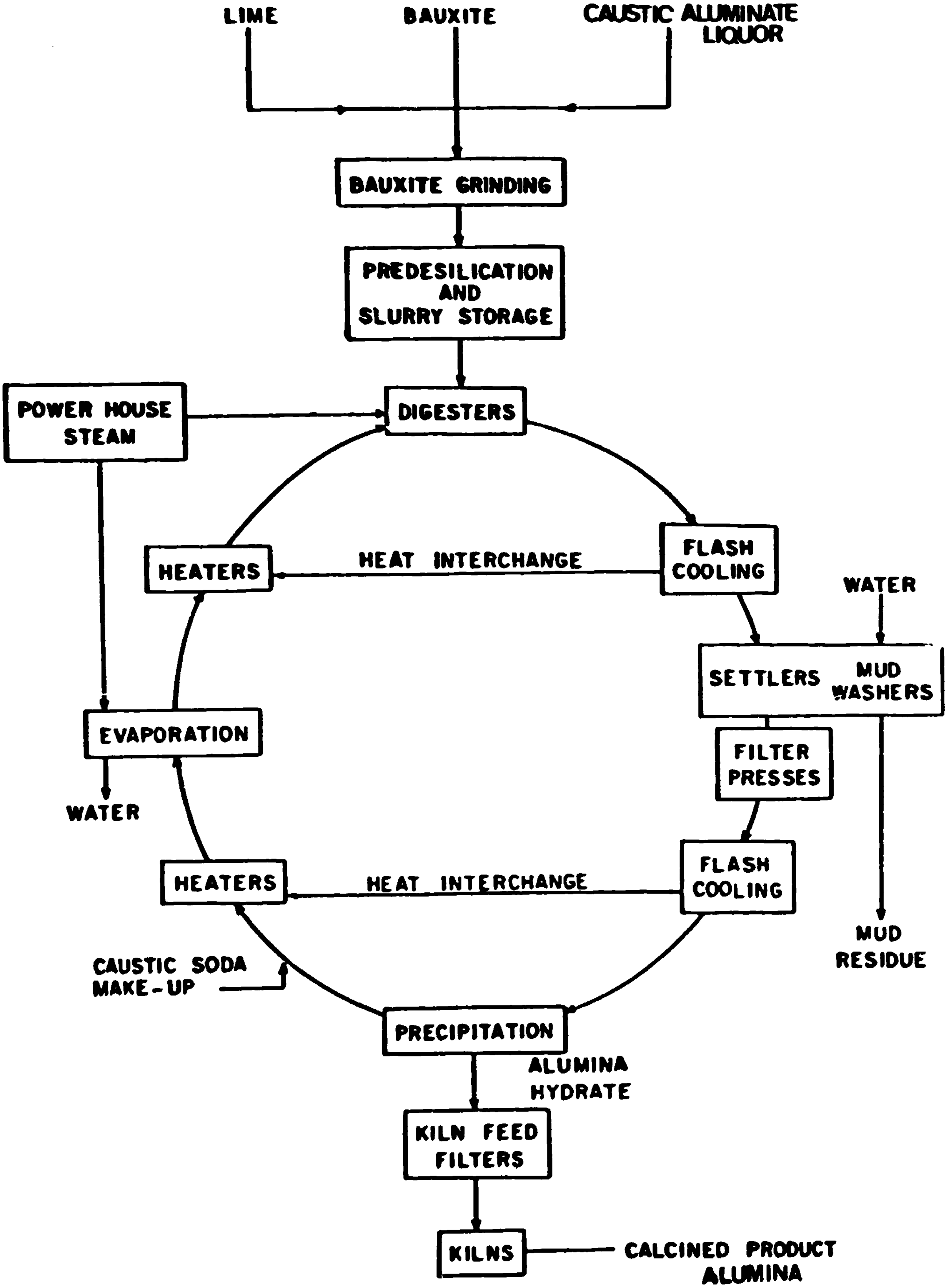
[7] Bielfeldt, K. and G. Winkhaus, "Challenge to Alumina Production Technology in the 80's", Alumina Production until 2000, ICSOBA, Tihany, Hungary, October 1981.

[8] Secretariat Report on the Environment Aspects of Alumina Production, United Nations Environment Programme, Industry and Environment Office, Paris, November 1981 (UNEP/WS/A1.2 Final).

[9] UNEP/UNIDO, "Record of the Workshop on the Environmental Aspects of Alumina Production", Paris, (UNEP/WS/A1.7 Final), 1981.

[10] Bensch, H., "Land Disposal of Bauxite Residue in the Aluminum Industry", UNEP Industry and Environment, July/August/September, Vol. 4, No. 3, 1981.

Figure 2.1. Generalized block and line flowsheet of the Bayer process



Source: "Environmental Aspects of Alumina Production", UNEP Industry and Environment Technical Review Series, 1985, p. 26.

Table 2.1. Raw materials used in the Bayer process and their end products/fate

Raw material		Use	End product/fate
1.	Bauxite	Source of alumina and various impurities.	Calcined alumina, red mud and water.
2.	Caustic soda	Solvent for alumina extraction and caustic descaling.	Recycled in plant, with some lost in red mud and alumina and with spillages.
3.	Burnt limestone	Phosphorus control preparation of catalysts, salt causticization, liquor stabilization, diaspore dissolution, precoat/filter aid.	Lost with red mud in the form of various calcium compounds. Small portion lost with alumina.
4.	Fuel oil	For steam and electricity generation, calcination of alumina and lime burning.	SO_2, CO_2, NO_x energy/ waste heat.
5.	Coal	For steam and electricity generation.	SO_2, CO_2, NO_x, fly ash, energy/waste heat.
6.	Synthetic flocculant	Settling aid for residue.	Lost with red mud.
7.	Water	For mud washing, dilution, boiler feed (steam generation).	Lost with red mud evaporation.
8.	Starch	Settling aid for residue.	Lost with red mud, accumulates as organic material in the circuit.
9.	Sodium sulphide and bisulphide	For zinc control.	Lost with red mud, accumulates as sulphate in the process.
10.	Acids (hydrochloric and sulphuric)	For chemical descaling.	Spent acid discarded to acid pit or red mud lake.
11.	Soda ash	For generation of 'make up' caustic via causticization with burnt limestone.	Converted to caustic soda.
12.	Natural gas	Calcination, steam and electricity generation.	CO_2, SO_2, NO_x and energy/waste heat.

Source: "Environmental Aspects of Alumina Production", UNEP, Industry and Environment Technical Review Series, 1985, pp. 30-31.

Several methods are currently employed to dispose of the bauxite residue on land.[11/12/13/] They can be classified as disposal in unsealed natural basins, in artificially sealed impoundment areas, and dry stacking.

Disposal in natural basins is done in sites which are made of impervious materials such as clays, in order to minimize the possibility of seepage of the slurry or liquid through the ground. The site should be carefully selected and must not be located near drinking water reservoirs or wells. The disadvantage derives from the possibility that leakage occurs anyway with consequent contamination of groundwater. For this reason, natural or artificial sealants are sometimes applied. This disposal method is usually the cheapest. In addition the site has the potential for being eventually rehabilitated, although this will require considerable effort and may not be possible until many years have passed.

The same technique is also used, with some variation, in flat areas. In this case artificial ponds are created by erecting earth dams and bunds (which can be as high as 10-30 meters) around the impoundment area. Artificial impoundment areas may extend for as much as 80-300 hectares.[14/15/]

Dry mud stacking is extensively used in the Federal Republic of Germany, Brazil, Spain and the Virgin Islands. It consists of thickening the mud by reducing its liquid volume in rotary vacuum drum filters. The clarified liquor has a pH value around 10.5 and can be recycled back to the plant. The liquor in excess can be discharged only after neutralization with acid. The mud is then disposed of in the impoundment area, but still retains a high concentration of liquids. The name dry stacking is somewhat misleading since the mud is neither dry nor stacked. The advantages of this method are: the reduced amount of residue to transport, the possibility of reaching impoundments as high as 30 meters, and the reduced risk of groundwater contamination.[16/17/]

11/ UNIDO, "Study on the Disposal and Utilization of Bauxite Residues", prepared by ALUTERV-FKI, Budapest, Hungary, October 1980.

12/ International Primary Aluminium Institute, "Methods for Disposal of Residue from the Production of Alumina from Bauxite Ores", May 1982.

13/ International Primary Aluminium Institute, "Methods for Disposal of Residue from the Production of Alumina from Bauxite Ores", May 1982.

14/ Bensch, H., "Land Disposal of Bauxite Residue in the Aluminum Industry", UNEP Industry and Environment, July/August/September, Vol. 4, No. 3, 1981.

15/ "Environmental Aspects of Alumina Production", UNEP Industry and Environment Technical Review Series, 1985, p. 51.

16/ Tielens, A.J., "Dry Disposal Can Eliminate Decant Tailings Pond for Thixotropic Mill Wastes", Engineering and Mining Journal, January 1977.

17/ Secretariat Report on the Environment Aspects of Alumina Production, United Nations Environment Programme, Industry and Environment Office, Paris, November 1981 (UNEP/WS/A1.2 Final).

The method of total impoundment is used in all plants operating in the USA. These plants include storm water, process water and bauxite residue lakes, as an integral part of the plant. This method can only be used in arid regions where evaporation exceeds rainfall because all effluents are impounded. As a result, no liquid streams are discharged to the environment. Table 2.2 shows the type and characteristics of those streams which can be generated from such plants.

Table 2.2. Characterization of principal waste streams from United States bauxite refineries

Waste	Quantity	Characterization
Red mud (bauxite residue)	500-3,600 tons/day (dry basis)	15-20 per cent solids
	1,000-7,200 tons/day (wet, settled)	5-12 g/l soda
	3,000-20,000 tons/day (slurry at 18 per cent solids)	2-5 g/l aluminum pH = 12.5
Spent cleaning acid	Variable. 5-10 tons/ week intermittently discharged	Na_2SO_4 plus some free H_2SO_4, HCl or HAc may also be used pH = 1
Salts from salting-out evaporator	Variable. Up to several thousand kg/day	Na_2SO_4 - alkaline solutions pH = 12.5
Barometric condenser cooling water	Millions of litres/hr	Temperature rise of up to 15°C (25°F). May contain traces entrained alkali
Boiler and cooling tower blowdown	Variable. Thousands of litres/hr	Dilute alkaline solutions pH = 12.5
Water softener sludge	One to few tons/day	Lime and suspended solids from intake water
Sanitary waste	375 l/day/capita	BOD 70 g (0.15 lb) day/capita

Source: Battelle Laboratories, Development Document for Proposed Effluent Limitations Guidelines and New Source Standards of Performance for the Bauxite Refining, Primary Aluminum Smelting and Secondary Aluminum Smelting Industry, Environmental Protection Agency Contract Completion Report No. 68-01-1518, Document 440/1-73-019, 1973.

2.2.2 From alumina to aluminum: the Hall-Heroult process

Process outline

The Hall-Heroult process is the most commonly used primary aluminum smelting process. The process consists of the electrolysis of a molten-salt bath containing alumina and cryolite ($Na_3 Al F_6$) with minor additions of other fluorides. The process is carried out in cells (pots) consisting of carbon-lined steel boxes which contain the electrolyte in which a cathode and a carbon anode are immersed.

Alumina is dissolved in the molten cryolite bath at about 950°C and electrolized by direct current at a voltage of about 4.5 volts. Cells are connected in series. Carbon anodes are suspended from above. The current flows from the carbon anode, through the bath to the cathode, and then, through an aluminum busbar to the neighboring cell. Alumina is periodically added to the molten bath and is consumed as electrolysis proceeds. Fluorides are also added to the pot to compensate for losses during normal operation.

The topmost layer of the molten bath solidifies due to the cooling effect of the atmosphere, forming a crust which must be regularly broken to allow fresh alumina to be loaded to the bath. Liquid aluminum is deposited at the cathode, on the bottom of the pot, and periodically withdrawn from it by vacuum suction. The liquid metal is alloyed and/or cast into ingots. Ingots are shaped for final use by casting, rolling, forging and/or extruding.[18/] The fumes emitted from the pots are collected by hoods or gas skirts, and processed before emission into the environment.

Two main cell systems are currently used. They differ according to the type of carbon anodes employed, as described here:

Söderberg anode pots

These anodes are made *in situ* in the pots with fresh paste (i.e. a mixture of pitch and coke), through the baking action caused by the heat from the molten bath. The paste is fed continuously to the pot. The current is brought into the anode by horizontal iron studs (horizontal stud Söderberg or SS) or vertical studs (VSS). In both cases the studs are pulled out and reinserted at higher levels as the anode is gradually consumed.

Prebaked anode pots

The anodes are manufactured (prebaked) separately and are periodically replaced in the cell as they are consumed. There are two cell designs which utilize such anodes: in the first one (Side-worked Prebake or SWPB), fresh alumina is added to the cell after the molten-salt crust has been broken around the circumference of the entire anode complex. In the second (Central-worked Prebake or CWPB), the crust is broken at selected points

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[18/] Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984, p. 1.

between the anodes placed in each cell. An essential part of a smelting plant utilizing prebaked anode cells consists of a facility for manufacturing the anodes.

A typical pot-line is housed in two buildings, each of them 800 meters long and 22 meters wide. Each building contains 120 cells arranged side by side in groups of 30. Such a line has an annual capacity of 220,000 tons Al/year. The plant also includes a facility for producing green anodes (i.e. the paste which will be used for actual anode manufacturing), an anode bake oven, and a cast-house to produce the final product.[19]

Pollutants produced during the Hall-Heroult process

A block diagram for aluminum smelting is shown in figure 2.2, which also gives the pollutants generated at each stage.

Gas-borne pollutants

The gas-borne pollutants produced before gas treatment consist mainly of gaseous hydrogen fluoride, solid fluorides (such as dust particles), dust, SO_2 and tar. Fluoride pollutants come from the use of cryolite and other fluorides in the bath. The specific pollutants and concentrations are reported in table 2.3.

Table 2.3. Fume evolution before cleaning (expressed in kg/ton of aluminum)

Pollutant	Pots		Green anode shop	Bake oven	Cast-house
	Prebaked	Söderberg			
Gaseous fluorides (as F)	6-20	16-26	-	0.7	-
Particulate fluorides (as F)	6-10	4	-	-	-
Total fluorides (as F)	12-30	20-30	-	-	-
Dust	30-60	12-40	-	1.2	-
SO_2	25	13	0.8	6.0	2.8
Tar	-	70	0.7	0.6	-

Source: "Environmental Aspects of Aluminum Smelting", UNEP Industry and Environment Technical Review Series, Vol. 3, 1981, p. 14.

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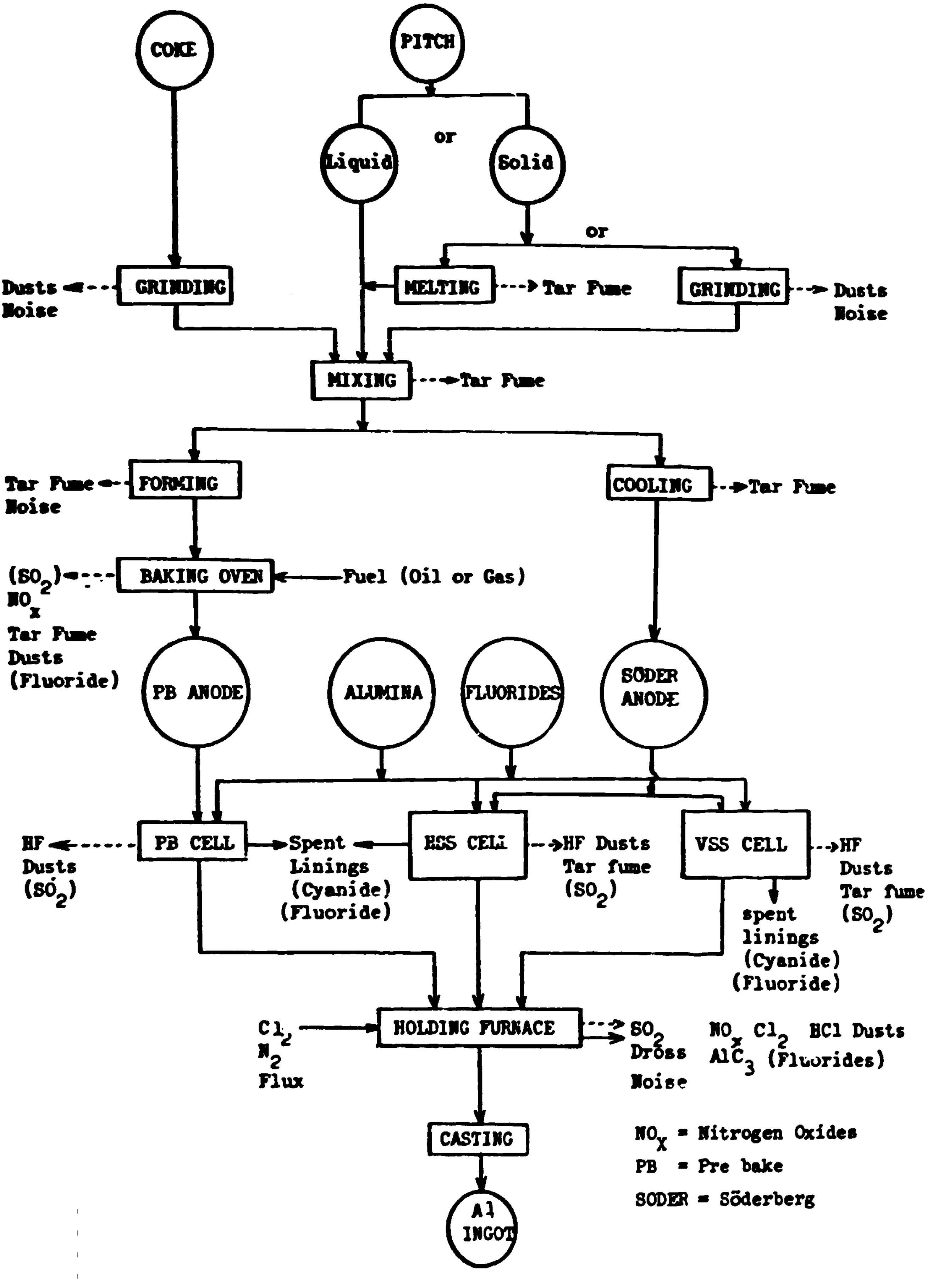
[19] "Guidelines for Environmental Management of Aluminium Smelters", UNEP, Industry and Environment Guidelines Series, 1986, p. 4.

Figure 2.2. Potential sources of pollutants and aluminum smelting process flow chart for monitoring and control



Source: "Guidelines for Environmental Management of Aluminium Smelters", UNEP Industry and Environment Guidelines Series, 1986, p. 9.

Gaseous fluorides are mainly generated from the pots, but they are also contained in the exhaust gases of the anode baking furnace. The latter emission arises from the recycling of anode butts. The amount of fluorides so generated depends on the cleanliness of the butts. This source can make a substantial contribution to the overall fluoride emissions from the plant, if no scrubbing is provided.

The molten cryolite bath has a considerable vapor pressure at the operating temperature, thus producing sub-micron aerosols which are partially hydrolized to give HF Removal of this pollutant is discussed in section 4.2.1.

Fluoride emission can also occur in the cast-house if the metal is processed with fluxes containing fluorides. In general, this source is negligible. Also carbon, alumina and fluoride dusts are produced from the electrolytic pots. In addition carbon dust is obtained from the grinding of coke and pitch and from the anode baking process (in the anode house). Alumina dust comes from all alumina handling operations.

The particle size of the dust collected by the pot hoods is extremely small. Some 81 per cent of the dust (by weight) has particles smaller than 3.3 microns in diameter. This fraction contains 88 per cent fluorides.[20/]

Aluminum chloride dust (as white smoke) is also generated when hot metal is treated with gaseous chlorine or fluxed with chloride-containing materials in the cast-house.

Sulphur dioxide is generated in different parts of the plant. The first source is the pots if sulphur-containing coke is used in anode manufacturing. This amount is usually small and becomes important only in areas where SO_2 pollution is already a problem.[21/] A second source of SO_2 is the anode baking furnace and cast-house furnace, if sulphur-containing fuels are burned.

Söderberg anode cells produce tar fumes too. These fumes are also produced by pitch melting, mixing, cooling of the anode paste and the manufacturing of the prebake anodes. Some amounts of the potentially carcinogenic polycyclic aromatic hydrocarbons are contained in the tar fumes. These compounds can constitute a health hazard to the plant workers.

Liquid effluents

A typical plant with a production capacity of 200,000 tons Al/year consumes about 70 m^3/hr of fresh water which is mainly used as cooling water in the anode shop, in the rodding shop, in the compressor house, for the

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20/ "Environmental Aspects of Aluminium Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981.

21/ "Review of the Petroleum Coke Situation and Its Potential Impact on Sulphur Dioxide Emissions from Primary Aluminium Plants", IPAI (International Primary Aluminium Institute), December 1978.

rectifiers and in the cast-house. The main contamination comes from the oil and grease used in the cast-house. Water pollutants are suspended solids, oil and grease, sulphur compounds and combustion products. If recycle is used to minimize water consumption the discharge should not exceed 7 kg/day of oil and grease (equivalent to 13 g/ton Al produced).[22] Some other organics may be present due to coal tar products released during anode baking. In addition, wet scrubbing of fumes will produce a water stream contaminated by gas-borne pollutants. This is the case for cryolite recovery by wet systems. A wastewater stream results which contains significant amounts of fluorine, total organic carbon, and suspended solids. Degassing with chlorine (in the cast-house) also requires wet air pollution control methods, resulting in a wastewater stream. Table 2.4 shows a conventional chemical analysis of pollutants.[23]

Table 2.4. Conventional and nonconventional pollutants in primary aluminum raw wastewater

	Number of		Concentration, mg/L		
Pollutant	Analyses	Times detected	Range	Median	Mean
COD (Chemical Oxygen Demand)	2	2	3.4-5,700		2,900
TOC (Total Organic Carbon)	2	2	150-440		295
TSS (Total Suspended Solids)	2	2	2,300-11,400		6,850
Total phenol	3	3	0.11-0.27	0.13	0.17
Oil and grease	2	2	4.2-5.5		4.85
Ammonia	1	1		120	120
Fluoride	3	3	2.4-13,000	190	4,400

<u>Source</u>: EPA Treatability Manual Vol. II Industrial Descriptions, United States Environmental Protection Agency, July, 1980, p. II. 10-7

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[22] "Environmental Aspects of Aluminium Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981.

[23] EPA Treatability Manual, Vol. II, Industrial Descriptions. United States Environmental Protection Agency, July 1980, pp. II. 10-7.

Solid wastes

Spent carbon cathodes and refractory bricks are the most important solid wastes. The bricks must be replaced every four to six years because they become impregnated with fluorine and sodium. The total solid waste amounts to 30-50 kg per ton of Al produced, of which 54 per cent is bricks and 46 per cent is carbon. For a plant producing 200,000 tons Al/year the amounts that must be disposed of are given in table 2.5.[24]

Table 2.5. Solid waste produced by aluminum smelters

	Quantity (t/year)	Percentage of fluorine (F)	F (t/year)	kg F/t Al
Bricks	5,400	8	450	2.25
Carbon	4,600	14	650	3.25
Total	10,000	22	1,100	5.50

Source: "Environmental Aspects of Aluminum Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981, p. 17.

2.3 Pollution control technologies for aluminum production plants

2.3.1 Pollution control during alumina production

Since red mud (alkaline bauxite residue) is the largest quantity of effluent from an alumina plant the methods used for its disposal, impoundment, or storage are especially important.

The envisaged potential impacts caused by land disposal methods are:[25]

(1) Seepage of alkaline liquor into the ground. Possible contamination of ground water may result.

(2) Spills due to cracked pipelines or containment dam failure.

24/ "Environmental Aspects of Aluminium Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981.

25/ "Guidelines for the Environmental Management of Alumina Production", UNEP, Industry and Environment Guidelines Series.

(3) Dust pollution in arid regions.

(4) Reduction of availability of usable land.

(5) Aesthetic impact.

As a result, the most effective pollution control (or containment) methods consist of the proper siting of the plant and disposal area, careful construction and monitoring of the impoundment area, and minimization of seepage through use of sealant for lining of the impoundment area. At sea, the discharged liquid residue rapidly reacts with the magnesium contained in sea water. This chemical reaction produces a finely divided precipitate which may be harmful to marine life. Hence, this disposal method should be used only as a last resort. Disposal in shallow water should be avoided altogether. Should disposal at sea be dictated by a dramatic shortage of land, a careful environmental impact study should be carried out, followed by intensive monitoring. This disposal method will be more expensive than disposal on land.

2.3.2 Pollution control during aluminum production

In the Hall-Heroult process, gaseous waste streams are produced from pot rooms, pot lines, green anode and anode baking plants, and cast-house. Most plants effectively collect and remove the different pollutants. Therefore very little is released to the atmosphere. The different emission sources will now be examined.

Pollution control of fumes produced in the electrolytic cells

The fumes produced in the cells must be first efficiently collected. In prebaked anode cells this is done through hoods made up of several shields. Each time an anode is replaced only two or three of these shields must be removed. As a result, collection efficiency does not drop significantly during this operation. It is estimated that only 20 per cent of the total fluoride generated in the cells is not collected by the hoods during the anode change.[26] As for Söderberg pots, attempts (not completely effective) have been made to use panels above the skirt in order to collect the fumes which might escape.[27] In all cases good fume collection is essential to protect the worker's health from exposure to toxic pollutants. After collection, the coarser particles in the fumes are removed through cyclones. Typical removal rates are shown in table 2.6.

The fumes are then passed through wet or dry cleaning devices. Both have a high fluoride removal efficiency. Some wet scrubbers are less efficient for sub-micron particles removal. Wet systems consist of contacting devices where

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26/ "Environmental Aspects of Aluminium Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981.

27/ Aluminum Péchiney, Ph. Le Cardinal, Hooding of Söderberg Pots in Saint-Jean-de-Maurienne Plant, AIMA, 1976.

Table 2.6. Dust removed by cyclones

Location of plant	Dust collected kg dust/t Al	Pressure loss (mm water gauge)	Content of dust Al_2O_3 (per cent)	F (per cent)
USA	38.5	76	60	10
Fed.Rep.Germany	32.0	100	64-74	15-20
New Zealand	47.0	160	70	9.2
France	12.37	40	60-80	10-19

Source: "Environmental Aspects of Aluminum Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981, p. 51.

the fumes are scrubbed with caustic soda, lime or soft water. In the process, the fluorides are removed as cryolite or CaF_2. In addition, SO_2 may be also partially removed, thus limiting air pollution. On the other hand, the scrubbing solution requires some processing before being discharged into the environment. In the dry process the fume collected from prebake pots is contacted in a reactor at 100°C with the alumina which is going to be fed to the pots. The reactor is a fluidized bed or pipe where alumina is injected concurrently with the gas. Although contact time is only about one second, HF (in concentration of 100-200 mg F/Nm^3) is effectively removed (99 per cent efficiency). The alumina particles entrained by the cleaned gas are then removed by a fabric filter. All alumina is fed back to the pots.

Pollution control for green anode pots

All equipment (pitch melter, paste mixer, grinder, screener, anode forming machine) should be enclosed and the tar fume processed before being exhausted. Wet or dry methods can be used.

Pollution control for the anode bake oven

Pollutants generated are SO_2, nitrogen oxides (as combustion products), tar fumes, carbon dust, and fluorides (from anode butts). The solid particles can be collected by an electrostatic precipitator, wet scrubbing or dry alumina contacting. Nitrogen oxides and the remaining SO_2 usually escape to the atmosphere.

Pollution control for the cast house

Fluxing fumes containing fluorides and dust are usually produced in limited amounts. These fumes can be harmful to the workers and attention should be paid that their concentration in air is always low. If chlorine gas is used for degassing of the liquid metal the fume should be scrubbed with alkaline solutions.

Pollution control of liquid effluents

The water used in wet scrubbing is the most polluted. It contains fluorides, sulphates and, in the case of Söderberg pots, hydrocarbons. The water should be treated, as schematically described in figure 2.3. Fluorides are usually recovered as cryolite.

Pollution control of solid wastes

Storage and disposal of anode butts and spent cell linings must be provided. During outdoor storage, some fluorides and cyanide may be leached out by runoff water, and cause soil contamination. Consequently, the spent material should be transformed into non-hazardous waste before final disposal. A block diagram of a recommended solid waste treatment process (CaF_2 recovery) is shown in figure 2.4.

2.4 Potential for by-product re-use

Since it is by far the largest quantity of waste generated and because of its potentially large negative impact, possible uses of red mud (bauxite residue) have been extensively studied. Some 250 publications deal with utilization of red mud.[28] Several applications were found which utilized the whole residue. These include road construction, building construction, soil conditioning, heavy ceramic production, flocculant production, use as pigment or gas scrubbing agent, and as a plastic filler. As one example the pre-dried residue can be mixed with clay in a 3:1 ratio, milled, extruded at a pressure of 10 atmospheres, dried at low temperature (45°C), and calcined at high temperature (950°C). The resulting material has been used as a building material and has very good mechanical properties (compression strength = 400 kg/cm^2).[29] Many other examples are reported in the literature.[30][31][32][33][34][35] Unfortunately residue re-use is highly process specific.

28/ Secretariat Report on the Environment Aspects of Alumina Production, United Nations Environment Programme, Industry and Environment Office, Paris, November 1981 (UNEP/WS/A1.2 Final).

29/ Tauber, E., R.K. Hill, D.N. Cooke, and K.J. Murray, Journal of the Australian Ceramic Society, 7, 1, 1971.

30/ "Environmental Aspects of Alumina Production", UNEP Industry and Environment Technical Review Series, 1985, p. 51.

31/ Puskas, F., Hungarian Patent N171 820.

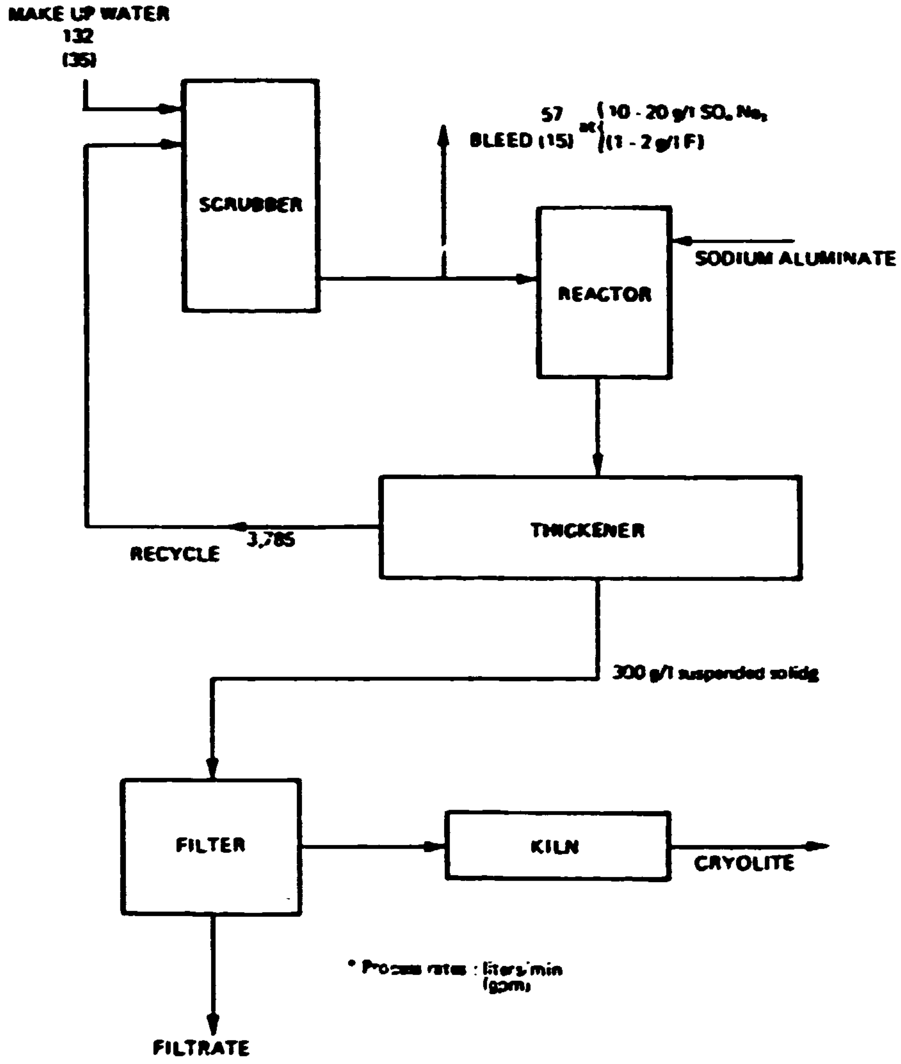
32/ Logomerac, V.G., International Colloquium of ICSOBA, 1972.

33/ Pettelkau, J.H. "Utilization and Storage of Red Mud from Aluminium Oxide Production in the Federal Republic of Germany", Umweltbundesamt, September 1977.

34/ Hahnel, K.O., "Red Mud as Raw Material for Coloured Gears", Glass-tech. Ber. 76, 1953.

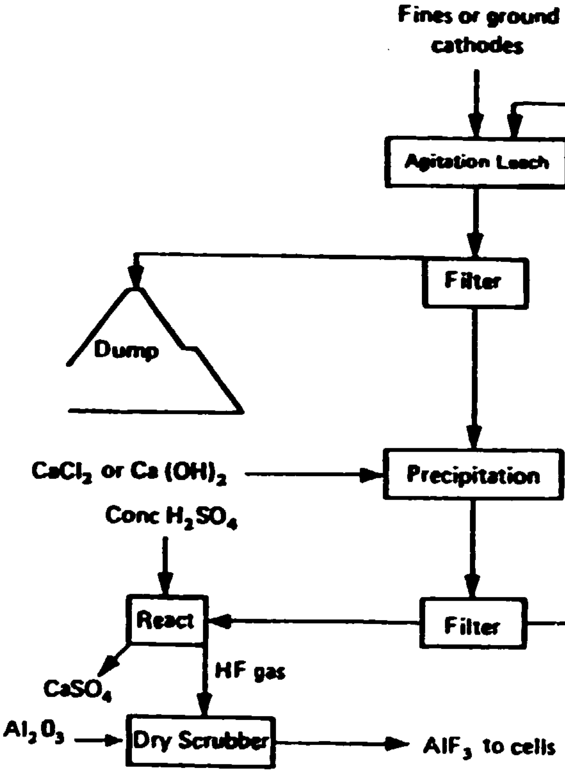
35/ Land, G.W., "Controlling Sulphur Dioxide Emissions from Coal Burning", Nat. Eng., 73, 1, 1969.

Figure 2.3. Process schematic recycle system for fluoride removal



Source: "Environmental Aspects of Aluminium Smelting", UNEP Industry and Environment Technical Review Series, Vol. 3, 1981, p. 117.

Figure 2.4. Treatment of spent pot-linings grinding and water leaching of percolation



Source: "Environmental Aspects of Aluminium Smelting", UNEP Industry and Environment Technical Review Series, Vol. 3, 1981, p. 124.

Gallium can also be considered an aluminum by-product. Since gallium is often present in bauxite ore it can be recovered during the aluminum manufacturing process in appreciable quantities. For example the Hungalu Ajka Alumina and Aluminum Works (Hungary) supplies about 5 per cent of the world gallium consumption.[36] Purified, gallium is then used in the electronic industry.

2.5 Aluminum recycling (secondary aluminum production)

Secondary aluminum production consists of smelting aluminum scrap as raw material. The process usually consists of six steps: charging the scrap material to the furnace, adding the fluxing agent, the alloying material, removing magnesium (demagging), degassing, and skimming. Scrap containing iron in high concentrations undergoes pre-smelting for iron removal. Some facilities also process the residue to recover both a high aluminum fraction (for smelting) and a low aluminum fraction for steel making. A typical secondary aluminum smelting process is shown in figure 2.5.

A special source of aluminum scrap is the recycling of beverage cans. In 1983 more than nine out of ten beverage cans sold in the USA were made of aluminum, and about 55 per cent of them were recycled.[37] In 1982 alone, the United States aluminum industry recycled more than 2.1 million tons of scrap aluminum. Some 53 per cent of this was can scrap.

A solid waste separator is utilized for such a raw material. A heavy duty shredder cuts the waste material into pieces small enough to be conveniently processed. The lightest materials are then removed by an air stream, whereas the ferrous metals are captured by using magnetic systems. Other equipment is used to separate the aluminum from glass and other non-ferrous materials.

2.6 Retrofitting of existing plants to reduce pollution

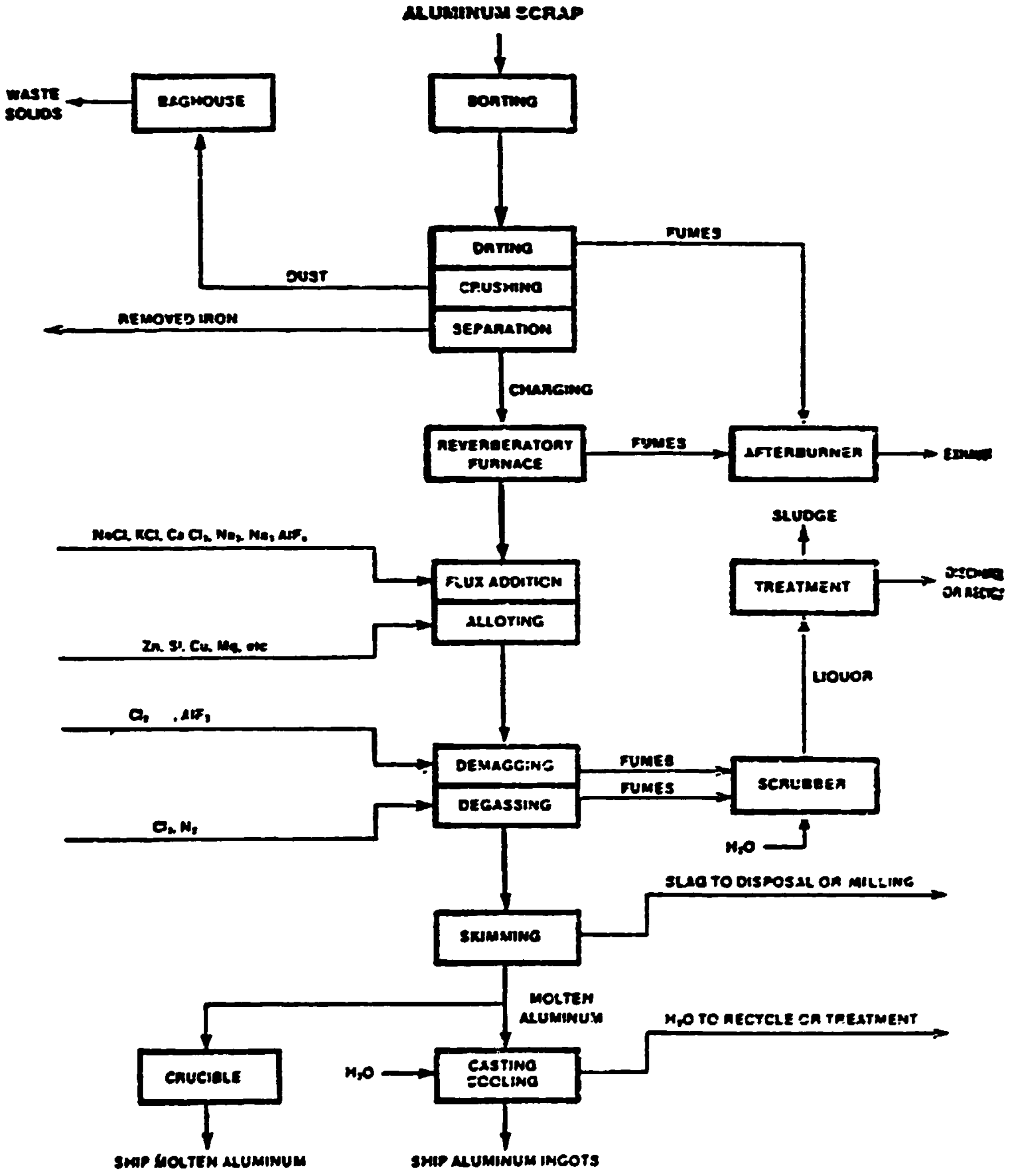
Because of the technological advances in aluminum production and environmental control, significant progress was made over the past 30 years in reducing the amount of fluorides produced by smelting plants. As an example, some 12-25 kg of total fluorides were emitted per ton of Al produced by a typical smelting plant in 1950. This figure was lowered to 0.5-1 kg in 1985. The first step in retrofitting should be to fit hoods to the existing pots for effective fume collection. Table 2.7 shows the results obtained by using different collection techniques.[38]

36/ Hungalu Ajka Alumina and Aluminum Works, Illustrative Brochure, Budapest, 1983.

37/ Pritsky, W.W., "Aluminium Recycling in North America", UNEP, Industry and Environment, July, August, September 1983, Vol. 6, No. 3.

38/ "Environmental Aspects of Aluminium Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981.

Figure 2.5. Secondary aluminum smelting process



Source: United States Environmental Protection Agency Document EPA 440/1-79/019a.

Table 2.7. Different fume collection techniques

			Evacuation flow rates		
Potline	Amperage KA	Collection technique	Nm^3/s/pot	Nm^3/t Al 10^5	Collection efficiency (per cent)
CWPB	150	Multiple shielded hood	1.1	0.9	95-99
CWPB	180	Multiple shielded hood	2.0	1.3	97-99
SWPB	130-140	Hood with one panel on each side	0.9-1.2	0.8-1.0	80-90
SWPB	90	Local hood	0.1	0.13	65-75
VSS	100-120	Skirt with one or two burners	0.13	0.15	65-85

Source: "Environmental Aspects of Aluminum Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981, p. 25.

A further step would be to use cyclones for coarse dust removal and recycle the dust back to the pots. An additional step would then be to install scrubbers after the cyclones. This would reduce the fluoride particle content and HF by about 50 per cent (cyclone alone) and 95 per cent (cyclone plus scrubber) respectively. New, larger plants (200,000 tons Al/year) should be equipped with a dry process system and stack. Table 2.8 summarizes this information.[39] It should be noted though that, in general, industry does not find it convenient to retrofit old smelters with adequate pollution control equipment. Consequently, some industries and governments have decided to launch a modernization and plant replacement program.[40]

39/ Ibid.

40/ "The Aluminium Industry and the Environment", UNEP, Industry and Environment, July, August, September 1979, Vol. 2, No. 3.

Table 2.8. Pollution control technologies for aluminum production plants of different capacities (central worked prebake pots only; 97 per cent collection efficiency)

Step Nº	Annual capacity	Evolution kg/t al					Cleaning technology	Emission kg/t al					Emission
		Total	Vent. air	Collected fume				Total	Vent. air	Stack fume			F_t
		Ft	Ft	Fg	Fp	Ft		Ft	Ft	Fg	Fp	Ft	per year
1	50,000	18	0.54	8.73	8.73	17.46	Cyclone + stack	14.51	0.54	8.73	5.24	13.97	725
2	50,000	18	0.54	8.73	8.73	17.46	Cyclone + wet scrubber + stack	3.60	0.54	0.44	2.62	3.06	180
3	200,000	>20	0.6	10.67	8.73	>19.4	Dry process + stack	0.95	0.6	-	-	0.35	190

<u>Source</u>: "Environmental Aspects of Aluminum Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981, p. 50.

2.7 Innovative and emerging production technologies

Several dozen alternative processes exist as a result of hundreds of available patents.[41] The main reasons for such an abundance of alternatives are:

- The difficulty to dispose of the alkaline residue (red mud) if the Bayer process is used;

- The high energy consumption and high concentration of fluorides produced in the Hall-Heroult process.

Some of the new possible processes will be outlined here.

2.7.1 Direct ore reduction processes

These processes are mainly based on the production of a master alloy made of Al, Si, Fe and Ti followed by subsequent purification. The master alloy contains some 50-60 per cent of Al and is manufactured in submerged arc furnaces starting fom bauxite with kaolin and clay added. One of the following purification methods is then used.

The first method consists of contacting the master alloy with $AlCl_3$ at high temperature (about 1250°C), thus producing AlCl. AlCl then decomposes at 700°C into Al, as pure liquid, and $AlCl_3$ which is recycled back.

Another purification process consists of diluting the master alloy with pure electrolytic aluminum. The final product consists of an aluminum alloy containing 13 per cent Si and 0.4 per cent Fe.

A third alternative method is based on the extraction of Al from the master alloy using liquid zinc. From the filtered Al-Zn molten solution, Zn is then vaporized, condensed and re-used, leaving pure Al.

The process of clay chlorination in the presence of carbon is a fourth alternative. Through this process $AlCl_3$, as well as chlorides of other metals, is produced. $AlCl_3$ vapors are separated by partial condensation and distillation and later oxidized to recover the chlorine, and produce alumina. The waste products of this process are solid wastes (mainly silica), carbon monoxide and dioxide, HCl and $SiCl_4$.[42] The above methods produce minimal pollution. Unfortunately they are not economical at present and are not in production.

41/ Ménégoz, D.C., "New and Alternative Processes for the Manufacture of Aluminium", UNEP, Industry and Environment, July, August, September 1979, Vol. 2, No. 3, p. 5.

42/ "Aspects Ecologiques de L'Industrie de L'Aluminium", Programme des Nations Unies pour l'Environnement, Paris, Mai 1977.

2.7.2 Production processes using different ores

Soluble aluminum salts can be obtained by contacting ores such as kaolin, clay, shale and slate, high-silica bauxite, and anorthosite with hydrochloric or nitric acid. The solid residue can be disposed of or used as filling material. This process is promising, but it is not yet profitable.

For ores such as labradorite, nepheline, anorthosite, and syenite the lime-caustic soda process is used. This involves sintering the ore with soda ash and limestone at 1300°C. This calcinated material is then ground and leached with aluminate liquor to recover the alumina product. The leachate can be fed to a conventional Bayer process or precipitated by different means. The residue is used in cement manufacturing. This process is used in the USA and in China where plants operate in conjunction with Portland cement production facilities.[43/][44/] The quantity of solids poses no significant solid waste management problems. On the other hand corrosive dust particles and gases are generated. The gases can be recycled to the process but the dust must be removed with cyclones or electrostatic precipitators.[45/]

2.7.3 Alternative processes for aluminum reduction

Processes such as condensation of aluminum vapors or carbothermic aluminum reduction are available, but also not profitable.[46/] At the moment the only possible competitor of the Hall-Heroult process is the ALCOA process. Very pure $AlCl_3$ is produced from alumina. $AlCl_3$ is then electrolyzed at 700°C in a bath of NaCl and LiCl in superimposed cells with bi-polar electrodes.[47/][48/] Chlorine is recycled back to produce $AlCl_3$. Carbon electrodes are used, but they are inert. Consequently the production of CO_2, CO and SO_2 is minimal, in comparison to the traditional process. Only small amounts of H_2S, SO_2, CO and HCl are produced.

43/ Sizyakov, V.M., "Review of Environmental Protection in Production of Alumina from Non-Bauxitic Ores", UNEP/WS A1.3, Paris, 1980.

44/ China Division of Foreign Affairs, Utilization of Red Mud in Cement Production, May 1980.

45/ Sizyakov, V.M., "Review of Environmental Protection in Production of Alumina from Non-Bauxitic Ores", UNEP/WS A1.3, Paris, 1980.

46/ "The Aluminium Industry and the Environment", UNEP, Industry and Environment, July, August, September 1979, Vol. 2, No. 3.

47/ Ibid.

48/ "Aspects Ecologiques de L'Industrie de L'Aluminium", Programme des Nations Unies pour l'Environnement, Paris, Mai 1977.

2.8 A case study

As an example of a relatively new production plant the Valesul facility (Brazil) was chosen.[49] Valesul Aluminio S.A. is the newest primary aluminum producer in Brazil, with a production capacity of 86,000 tons a year using a pre-baked anode technology. The plant cost 370 million dollars and started to be fully operational in April 1983. The choice of the pre-baked technology was dictated by the low energy requirement (0.83 A/cm^2). The objective was to obtain a low energy consumption in the order of 14.0 kWh DC/kg Al.

In the carbon baking area, Valesul selected the Riedhammer type baking furnace consisting of 48 covered sections with vertical head flow and capacity for 200 t/day of baked anodes.

In the cast house, a heat exchanger was introduced in the furnace exhausting stack, to improve the energy balance and 300,000 kcal/h was saved (20 per cent of the total energy requirement) by using combustion air preheated to 260°C.

Located on the outskirts of the city of Rio de Janeiro, Valesul put great weight on the implementation of air pollution control with the purpose of meeting local and international standards of fume emission and particulate levels.

In the fume collecting system the pots are totally enclosed, with the use of twenty side fume hoods and two fume hoods at the ends. The crust breaking and the alumina addition equipment are in the centre line of the pot, providing a closed pot operation. A high efficiency of fumes and dust collection results. The fume hoods are removable for anode changing, metal tapping, bath sampling, and metal and temperature measurements. The efficient fume collection system enables the potroom to be operated in an environment with minimum particulates and fumes. The total fluorides and particulates measured at the roof sampling points is in the range of 0.10-0.60 kg/t Al for fluorides, with an average of 0.28 kg/t Al, and 0.20-0.90 kg/t Al for particulates, with an average of 0.60 kg/t Al.

The potroom fume treatment system is a dry scrubbing system, utilizing the physical property of alumina to adsorb fluoride gases. The treated alumina is then collected in baghouses.

The pot effluents, before treatment, are:

	Range
Total particulates	200-800 mg/Nm^3
Gaseous fluorides	60-120 mg/Nm^3
Particulate fluorides	60-100 mg/Nm^3

49/ Andrade, C.M., "Energy and Environmental Conservation at Valesul Aluminium Smelter"' UNEP, Industry and Environment, July, August, September 1983, Vol. 6, No. 3.

At the point where the fumes of all pots are gathered, the alumina is introduced into the fume flow. The adsorption of fluorides begins soon after the point of alumina injection and continues until filtration in the baghouse.

Each system has twelve baghouse filters placed in parallel, and each baghouse has 616 filtering bags with a total area of 672 m^2. After filtering, fumes are released to the atmosphere through a 40 meter stack.

Analysis of the fumes emitted indicates that the system meets entirely the objectives proposed. The results are as follows:

	Stack emissions (kg/t Al)	
	Range	Average
Total particulates	0.50-2.81	1.10
Total fluorides	0.06-0.33	0.20

The effluents of the anode baking process include: carbon dust, combustion products of bunker C oil, hydrocarbons resulting from pitch coking, sulphur oxides and fluorides. Emissions are in the following range (mg/Nm^3).

	Range	Average
Carbon dust	20-560	161
Tar	70-820	419

A fume treatment system was installed, consisting of a conditioning tower, an electrostatic precipitator, two exhausters, one stack and interconnection ducts, as well as a bypass duct isolating the tower and the precipitator in the case of emergency.

The fumes coming from the furnace at a temperature of 90-120°C, enter the conditioning tower where a water spray reduces the temperature to 70-80°C, in order to condense the tar mist in suspension, and allow more efficient filtering.

Most of the water used in gas cooling evaporates, but the remaining water accumulates in the bottom of the tower and is discharged by two side drains. The water, with a pH of 1.5-2.0 is neutralized in a tank before being discharged. A small amount of tar also settles down in the lower part of the tower and is discharged into containers. The gas coming from the conditioning tower enters the electrostatic precipitator and is evenly distributed inside the precipitator.

At all points where dust is generated, Valesul has installed baghouse dust collection filters with an efficiency of 98 per cent. There are thirteen bag filters with a total exhaustion capacity of 360,000 m^3/h. In all areas where bath or alumina handling takes place, the dust collection product returns into the alumina circuit, to be re-used in the electrolytic process.

2.9 Pollution control costs

According to reference 50 the cost of establishing an impoundment area (in Hungary) is about 0.3-0.4 $US/m^3 of storing capacity provided that the sludge of fly ash coming from the power plant is used for building the dikes. If earthen dikes are built the cost rises to 0.7-0.8 $US/m^3. Operating costs run between 0.1 and 0.15 $US/ton of alumina depending on the distance between the plant and the impoundment area.[50/]

A report prepared by the International Primary Aluminum Institute (IPAI)[51/] and other studies show that pollution control costs for new plants are considerably lower than costs of retrofitting existing plants.

The data in table 2.9 provide separate operating and capital costs and recovery credits (where applicable) for different types of pollution control systems.[52/] They were calculated on the basis of a plant with a production capacity of 50,000 ton/year of aluminum. To give some idea of retrofitting costs, the addition of a secondary wet scrubber to an existing plant would cost at least double if a primary scrubber had been installed first. The average capital investment for fluorine control is an additional seven per cent of the initial production plant capital cost (on the basis of a cost of $US 2,000 per ton of installed production capacity). The additional operating costs would range between 0.8 and 6.6 per cent.

Another survey was conducted by OECD in 1977 and covered aluminum production plants in the USA, Canada, Japan and Norway.[53/] The report concluded that capital construction cost for new plants was $US 2,300 while operating costs varied between $US 780 and $US 1,040 per ton of Al. Based on these figures the report concluded that the maximum additional cost of pollution control was 6.3 per cent of total production costs while the corresponding operating costs were in the range of 2.2-7.2 per cent of the initial capital investment. For existing potrooms the report estimated the additional cost for pollution control to be $US 17.5 per ton of installed Al capacity. The corresponding operating costs were estimated to be $US 22.4 per ton of Al with a considerable standard deviation of $US 18.7.

Pollution removal efficiencies obtained by Rush, Russel and Ireson are given in figure 2.6.[54/] The figure clearly shows that comparatively new methods, such as the injected alumina dry method, produce very good removal efficiencies at a relatively low cost. Other systems of pollution control are not only less efficient, but also more expensive.

[50/] Anon, "Information on the Environmental Aspects of Alumina Production in Hungary", Document ALU 80/495C, Budapest, 1980.

[51/] International Primary Aluminum Institute Report.

[52/] Atkins, M.H. and J.F. Lowe. The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979, p. 36.

[53/] "Pollution Control Costs in the Primary Aluminium Industry", O.E.C.D., Paris, 1977, p. 36.

[54/] Rush, Russell and Ireson, "Air Pollution on Primary Aluminium Potlines: Effectiveness and Cost", Journal of the Air Pollution Control Association, February 1973, Vol. 23, No. 2.

Table 2.9. Costs of five types of control equipment for primary aluminum smelters

Control Type	Capital cost *	Annual capital charge +	Operating cost +	Recovery credit +	Total annual cost +
Tall stack	50	8.85	3.04	1.72	10.17
Wet secondary only	110	19.40	7.97	-	27.37
Wet primary	108	19.20	14.30	8.50	25.00
Dry primary	75	13.30	11.20	10.50	14.00
Primary + wet secondary	174	30.80	17.20	11.80	36.20

* Dollars per metric ton of annual production capacity.
\+ Dollars per metric ton of aluminum produced.

Source: IPAI Report, op.cit.

2.10 Emission standards

The main pollutants from an aluminum production plant are fluorine and SO_2. Emission standards have been set in most industrialized countries. In 1976 the United States Environmental Protection Agency (EPA) published standards of performance to be applied to any new electrolysis plant, which limits the total fluorine emission to 0.95 kg per ton of Al produced. For the bake oven the limit is 0.05 kg so that the total is 1 kg of F per ton of Al. These limits are observed in several countries.

In addition, emission concentrations are set. For example the State of Washington (USA) imposes that F emissions be less than:[55]

3.68 microg/m^3 over 12 hours

2.86 microg/m^3 over 24 hours

1.64 microg/m^3 over 1 week

0.82 microg/m^3 over 1 month

0.50 microg/m^3 over from 1 March until 31 October

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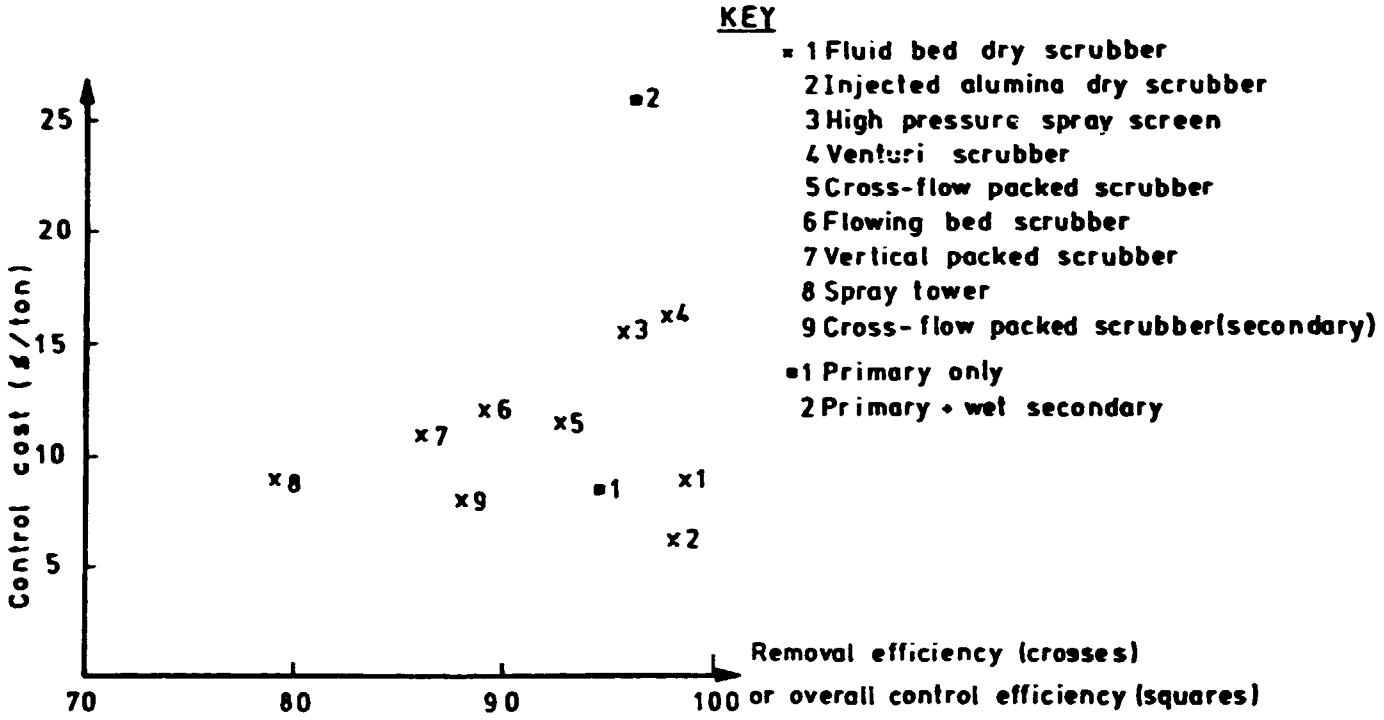
[55] "Environmental Aspects of Aluminium Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981.

Figure 2.6. Pollution control in the non-ferrous metals industry



Source: Rush Russell & Ireson

Source: Atkins, M.H. and J.F. Lowe, The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979, p. 45.

Similar standards are also enforced in countries such as the Federal Republic of Germany and Japan. Fluorine emissions from the plant do not usually cause any harm to the population since no fluorosis (a skeletal disorder caused by fluorine intake) has been observed in the vicinity of modern aluminum plants.[56]

As for SO_2, the United States standards are that an industrial plant must not cause an increase in the ambient air concentration in the vicinity of the plant which is in excess of 40 microg/m^3 (annual average) or 182 microg/m^3 (24 hour average).

Standards are also set for liquid effluents. In the United States the discharge limitations for primary aluminum smelters are:[57]

Primary aluminum-smelting

	Maximum 24-hour	
Fluorides (total)	0.05 kg/ton aluminum	
TSS	0.10 "	"
pH	6-9 units	"

Secondary aluminum-smelting

	Maximum 24-hour	
Fluorides (total)	0.4 kg/ton aluminum	
TSS	1.5 "	"
NH_3 (as N)	0.01 "	"
Al	1.0 "	"
Cu	0.003 "	"
pH	6-9 units	"

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[56] Ibid.

[57] Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984, p. 239.

2.11 Health protection for workers

In bauxite ore extraction and subsequent alumina production, potential problems in the working environment result from:

- Operating heavy equipment and machinery,
- Handling corrosive chemicals such as caustic soda and acid, and
- Being exposed to heat, noise, fumes, dusts, welding fumes, and certain toxic chemicals.[58]

Consequently adequate protection systems and safety regulations must be applied. Most of these potential problems and required practices are not unique to alumina production plants. For aluminum smelters, the exposure of workers to harmful pollutants varies considerably with the different operations that the worker undertakes during his shift. In most industrialized countries health protection standards require that a given time-averaged concentration value of the pollutant not be exceeded during an eight hour working period. Table 2.10 shows typical values pertaining to the most common pollutants found in smelting plants.

However the worker may be exposed to higher pollutant concentrations during certain operations which last only a few minutes. Examples are replacement of anodes in prebake pots or stud removal from Söderberg pots. Peak concentrations can be as high as:[59]

HF	= 20 mg/m^3
Fluoride (F)	= 25 mg/m^3
CO	= 200 mg/m^3
SO_2	= 100 mg/m^3

Consequently the work area is always ventilated, even in older plants. New plants generally have a system for distributing the ventilation air from the plant floor so that the worker is situated in a rising flow of clean air. Additional improvements to limit the concentration of pollutants in the work area are:

(a) Reduction of the sulphur content of the anode coke with consequent reduction of the amount of SO_2 generated;

(b) Increased hood collection efficiency;

58/ "Guidelines for the Environmental Management of Alumina Production", UNEP, Industry and Environment Guidelines Series.

59/ "Environmental Aspects of Aluminium Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981, p. 29.

(c) Reduction of the SO_2 adsorption efficiency of the dry alumina process.[60] This is the most effective measure since most of the SO_2 escapes through the stack.

(d) Collection of skirt fumes by placing panels above the skirt to form a sort of hood in Söderberg pots.[61]

Another possible harmful effect is caused by noise. In a smelter there are many situations where the NIOSH organization (USA) limit of 90 dB is exceeded (e.g. coke or pitch grinding, forming of prebaked anodes, crust breaking, metal tapping by vacuum siphon). This nuisance factor can be reduced in several ways, such as encasing the equipment in noise-absorbing porous materials.[62][63]

60/ Alcan, W.D. Lamb, The Role and Fate of SO_2 in the Aluminium Reduction Cell Dry Scrubbing Systems, AIME 1979.

61/ UNEP/UNIDO, "Record of the Workshop on the Environmental Aspects of Alumina Production", Paris, (UNEP/WS/A1.7 Final), 1981.

62/ Intalco Aluminum Corporation, K.G. Sandell, Noise Control in an Aluminum Reduction Plant, AIME 1974.

63/ Swiss Aluminium, W. Schmidt-Hatting, Investigations of Noise in Aluminium Electrolysis Cells, AIME 1975.

Table 2.10. Threshold Limit Values (TLV) concerning health protection of workers

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A. Fluoride (USA, NIOSH)

HF as F	2 mg/m^3
Particulate fluorides as F	2.5 mg/m^3
Total HF as F and particulate fluorides as F	2.5 mg/m^3
F$^-$ in urine*	4 mg/l preshift after 48 h. of non-exposure 7 mg/l postshift taken on 4th or later day of the workweek

*Not an official TLV, but applied at all smelters. Both of these values of 4 mg/l and 7 mg/l are applicable to work groups (e.g. anode changer) and the number represents geometric mean values for each of these individual job groups.

B. Other contaminants (USA)

SO$_2$	5 mg/m^3
Total suspended particulates	10 mg/m^3 (respirable 5 mg/m^3)

C. Coaltar pitch volatiles (USA)

Benzene soluble organics	0.2 mg/m^3

This TLV is still applied, but research has shown that the dangerous Particulate Aromatic Hydrocarbons (PAH) are found in varying concentrations. Research is under way to develop a simple chromatographic method which would allow several specific PAH's to be measured.

There is a tendency to replace benzene by the less toxic cyclohexane as solvent.

D. Polycyclic aromatic hydrocarbons (thin layer chromatography)

Norway - Total PAH	40 microg/m^3
Sweden - Benzo-3, 4-Pyren alone	5 microg/m^3

Source: "Guidelines for Environmental Management of Aluminum Smelters", UNEP, Industry and Environment Guidelines Series, 1986 p. 37.

3. NICKEL

3.1 Introduction

Nickel is currently produced in more than twenty different forms. They can be grouped into two major classification types on the basis of the purity of the metal produced, namely Class I and Class II nickel.[64/] Class I is associated with higher purity (Ni content exceeding 98 per cent). It includes nickel cathodes and carbonyl pellets (99 per cent purity), briquettes, and Nickel 98. Class II includes alloys such as INCOMET* (95 per cent purity), Sinter 75* (containing 75 per cent nickel) and other ferronickel alloys containing 20-55 per cent nickel. For many applications, this class is more than adequate (e.g. stainless and alloy steel production).

Two main types of ores are used for nickel production: sulphide ores and laterite (or oxide) ores. Both sources can be used to produce either class nickel, although limonitic and silicate types (subgroups of lateritic ores) are more suited for Class I and Class II productions, respectively. The type of ore is crucial to determine what type of production process can be used. Nickel oxide ores cannot be concentrated by physical means. Therefore the metal is extracted in a chemical form by either leaching or smelting (as ferronickel). Conversely, physical methods (such as wet grindings) are extensively used with sulphide ores.

In 1985 the world nickel production was about 760,000 tons/year. Some 60 per cent of it was obtained by sulphide ores in widespread locations. The most important mining sites are those of Sudbury and Thompson (Canada), Kalgoorlie (Australia), and Narilsk (USSR). The remaining 40 per cent was extracted from lateritic ore mines usually located in tropical or subtropical areas. About 80 per cent of the identified land-based resources of nickel are in the oxide form. Virtually all of the new nickel capacity which came on stream during the last decade was based on this type of ore. Consequently the production methods associated with it will become more important in the future.

3.2 Nickel from sulphide ores: production processes and pollutants produced

A schematic of this process is shown in figure 3.1.

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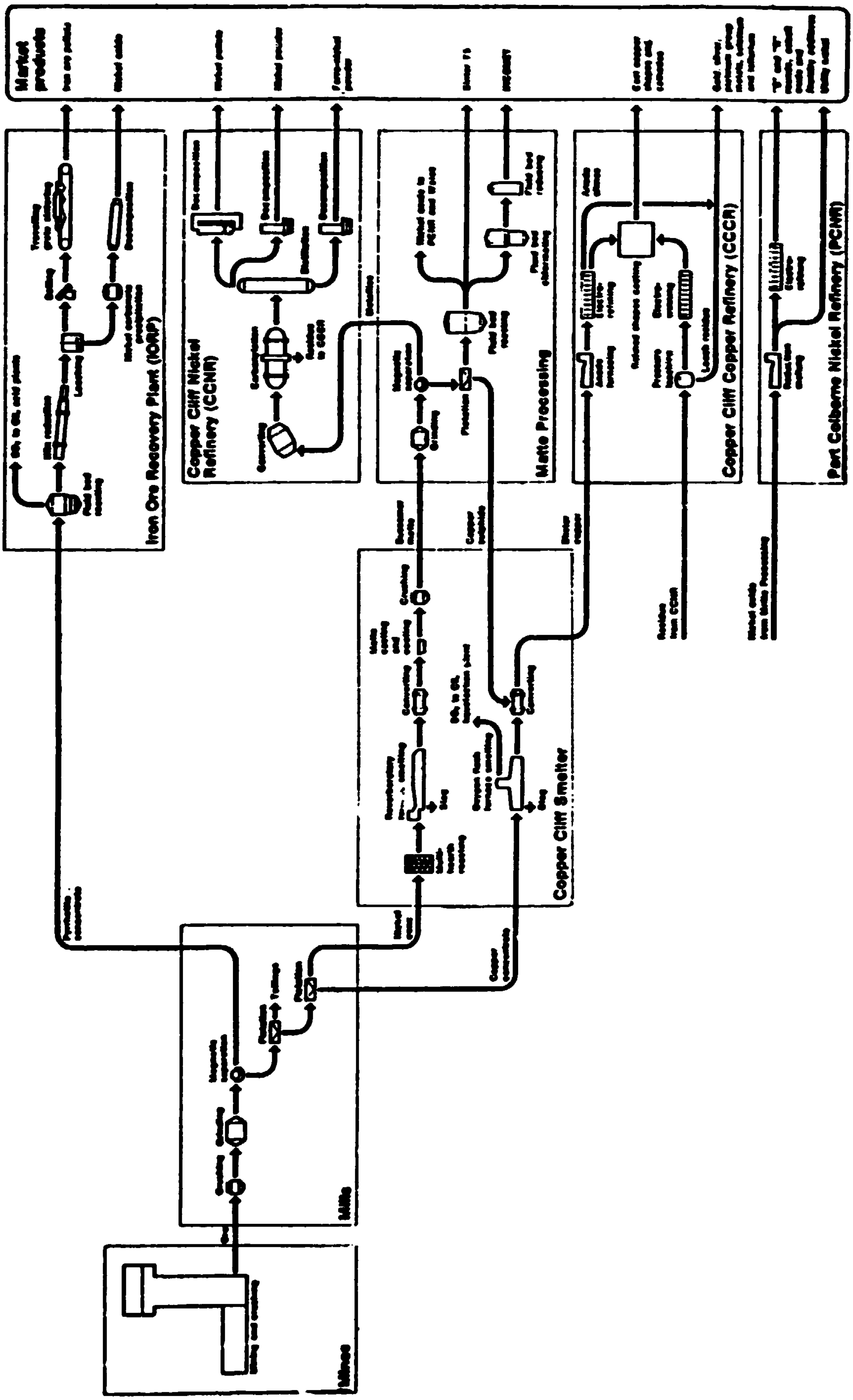
* trade names

64/ Renzoni, L.S., "Extractive Metallurgy at International Nickel - A Half-Century of Progress", Canadian Journal of Chemical Engineering, 47, February 1969, pp. 3-11.

Figure 3.1. Treatment of Sudbury ores in 1980 by INCO Metals Co.



Source: Lemmon, W.A., "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April 1981.

3.2.1 Mining

Mining of sulphide ores is usually conducted using underground mining methods (because of the location of the ores), although open pit mining is used in the USSR. Drilling, blasting, hauling, and crushing the ore to below 200 mm diameter are potentially dust generating operations, but are usually contained within the mining site. Land reclamation and run-off water control are the main potential problems.

3.2.2 Ore processing

The nickel sulphide content of the ore is concentrated by repeated crushing, grinding, and flotation operations. In general it is sufficient to grind 90 per cent of the material to a size less than 200 microns in diameter to liberate the individual mineral grains. The purpose of such operations is to:[65]

(a) Separate most of the iron ore from the total ore. This is achieved by separating pyrrhotite (85 per cent Fe_7S_8 and 1 per cent Ni) by magnetic separation, regrinding and flotation;

(b) Separate the barren rock tailing from the processed ore by another flotation;

(c) Separate some 80 per cent of the copper into a copper concentrate stream (28 per cent copper, 1 per cent nickel) from a nickel rich stream (10 per cent nickel, 2 per cent copper). This is also achieved via flotation.

The main environmental problems at this stage consist of handling and disposing of the fine solids generated, and improving the quality of the water effluents produced. As an example of the dimension of the problem, the INCO Ltd. production facility at Sudbury (capacity: 270,000 tons Ni/year in 1977) produces 50,000 tons of fine tailings per day, and consumes some 4,500 m^3 of water per thousand tons of ore. In addition, some of the water is discharged together with the tailings and contains small amounts of highly toxic flotation agents (such as cyanides). These pollutants are, in general, at a concentration which is sufficiently low to be tolerated by the receiving water streams where they are rapidly degraded[66]

Polythionates and thiosulphates can also be present in the water effluent due to the reaction of the iron sulphides present in the ore with the alkaline solution used to process the nickel ores. These compounds are stable during processing, but may be oxidized to sulphuric acid after being discharged into the environment, with consequent negative impact. The waste tailings may also generate sulfuric acid, after disposal, as a result of the oxidizing action on

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65/ Lemmon, W.A. "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April 1981.

66/ Ibid.

the iron sulphides caused by bacteria. In turn, under acid conditions, other sulphides (such as copper, chromium, cobalt) may dissolve and seep from the tailings.

3.2.3 Smelting (pyrometallurgy)

The two most important streams of the previous process, the copper-rich and the nickel-rich concentrates are processed separately as shown in figure 3.2.[67]

The copper concentrate is usually mixed with sand flux, dried, and then oxidized in a flash furnace.[68] Several streams are produced at this point. The off-gas stream contains some 80 per cent of sulphur dioxide. The slag contains waste material to be discarded. The molten copper sulphide from the furnace is then further processed in the copper refinery.

The nickel sulphide concentrate stream is processed in a variety of ways which may differ in terms of equipment, but whose purpose is always the same: to remove the remaining rock, iron and a large fraction of the sulphur from the concentrate. The first stage of smelting is called roasting and consists of heating the nickel rich stream at some 800°C with flux, without forming a liquid phase. The result is the partial removal of sulphur from the nickel,which forms nickel subsulfide (Ni_3S_2). The roasted concentrate is then melted in reverberatory furnaces at 1200°C where the liquid oxide slag formed from the rock left in the concentrate is removed. The nickel subsulfide forms a homogeneous melt called "matte" which is fed to the converters where the final oxidation step takes place. Air at about 1200°C is injected to remove other sulphur (as SO_2) and the remaining iron (as slag).

Other processes have been developed such as flash smelting and electric furnace smelting. In any case the main environmental problems at this stage are brought about by the large amounts of dust, fumes and gases produced. Sulphur dioxide is by far the most important and abundant pollutant. It is produced in concentrations ranging between 0.1 and 80 per cent. Moreover, a number of impurities, including elements such as lead and arsenic are volatized at the high temperatures used in smelters and may condense in cooler parts of the flues generating toxic dusts.

3.2.4 Refining

The matte obtained from smelting undergoes a separation process[69] consisting of slow cooling of the liquid matte to produce large crystals of Cu_2S and Ni_3S_2 (plus a nickel-copper alloy). The solidified matte is

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67/ Schabas, W., "The Sudbury Operations of Inco Metals Company", Canadian Mining Journal, 98, 5, May 1977, pp. 10-102.

68/ Inco Staff, The Oxygen Flash Smelting Process of the International Nickel Company of Canada Ltd., Trans. CIMM, LVIII, 1955, 1958-166.

69/ Sproule, K., G.A. Harcourt and L.S. Renzoni, Treatment of Nickel-Copper Matte, Exractive Metallurgy of Copper, Nickel and Cobalt, Paul Queneau, Editor, AIME, 1961, pp. 33-54.

then crushed below 70 microns. The individual grains can then be separated by flotation producing concentrated streams of copper sulphide (to be processed in copper smelters) and nickel sulphide. The latter product is finally oxidized to nickel oxide in reactors at high temperature (1200°C) with air. Nickel oxide can be a final product, but usually it undergoes a refining step. Several processes exist such as the electrolytic process (to pure nickel), the conversion to gaseous nickel carbonyl,[70/] and later to nickel powder or pellets, and the hydrometallurgical process. At this stage the major environmental problems originate from dust, fumes and gases, especially SO_2. Aqueous effluents may contain dissolved metals and suspended solids.

3.2.5 Hydrometallurgical refining

A diagram of this process is shown in figure 3.3.[71/] In most hydrometallurgical operations the matte is ground and dissolved in leaching and oxidizing aqueous solutions (with oxygen or chlorine as oxidizing agents) containing ammonia, chloride or sulphate. Concentrations of airborne nickel in the process areas are given in table 3.1.[72/] Nickel powder or nickel cathodes are produced at the end of the process. The powder is recovered by reduction with H_2S under pressure. The cathodes are produced in electrolytic cells. In the latter case hydrogen may be generated at the cathode and oxygen (or chlorine) at the anode with potential formation of mists containing nickel electrolyte. Tailings and an acidic waste stream are also generated and must be processed before being disposed of in the environment.

3.3 Pollution control technologies for sulphide ore processing plants

Water is used in mines to dampen the ore. This method plus adequate forced ventilation limits the concentration of airborne dust to some 1 mg/m³.[73/] Water must be treated before being discharged from mines and tailings areas at central wastewater facilities. Usually the stream is neutralized to pH 9 to precipitate the heavy metals. Flocculation and clarification is then applied, providing good quality water, acceptable for discharge.

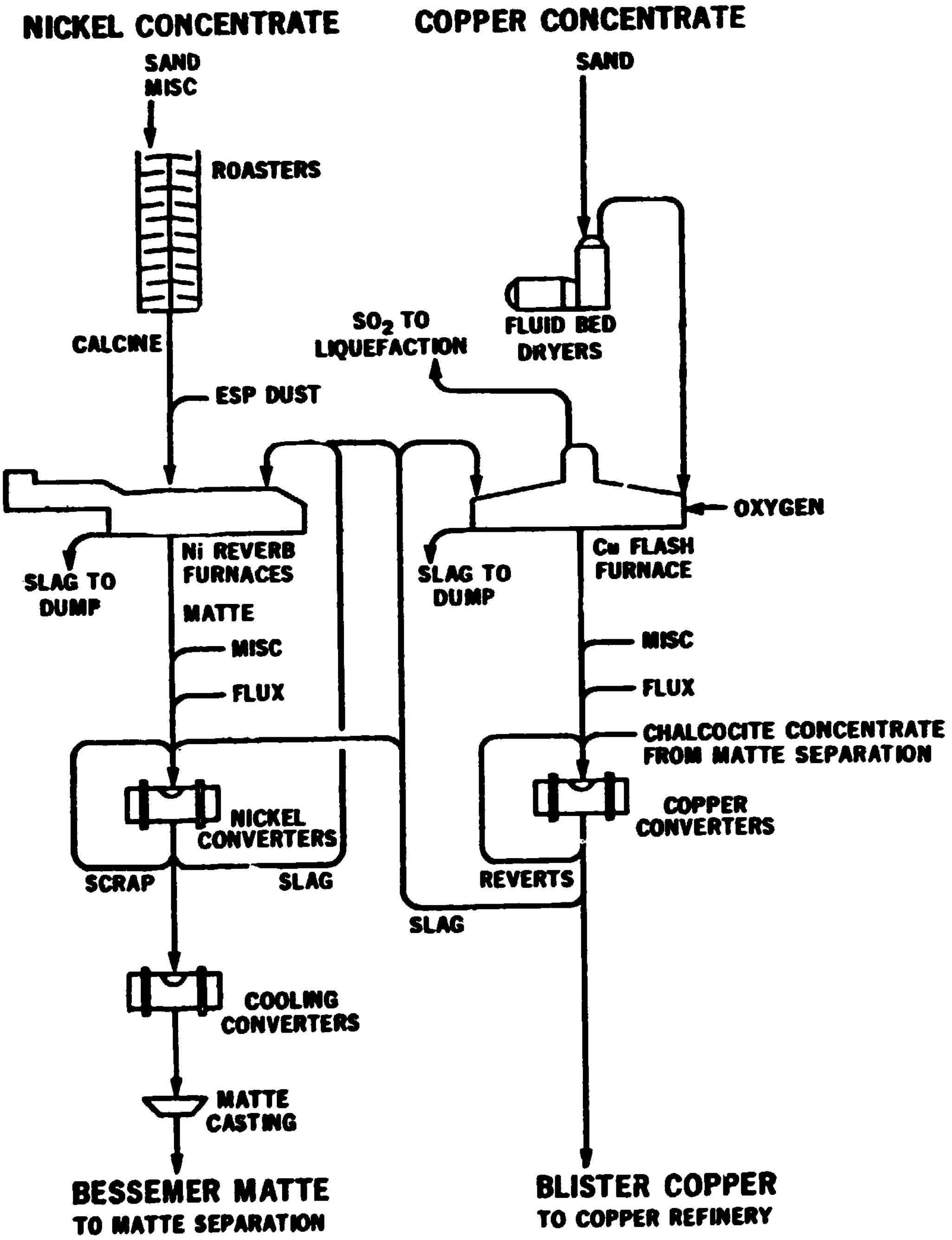
70/ Queneau, Paul, C.E. O'Neill, A. Illis, and J.S. Warner, "Some Novel Aspects of the Pyrometallurgy and Vapometallurgy of Nickel", Journal of Metals, July 1969.

71/ Mackiw, V.N. and H. Veltman, Recovery of Metals by Pressure Hydrometallurgy - The Sheritt Technology. Paper presented in the People's Republic of China during the 1968 Non-Ferrous Metals mission.

72/ Warner, J.S., "Occupational Exposure to Airborne Nickel in Producing and Using Nickel Products", in "Nickel in the Human Environment", International Agency for Research on Cancer, Oxford University Press, 1984.

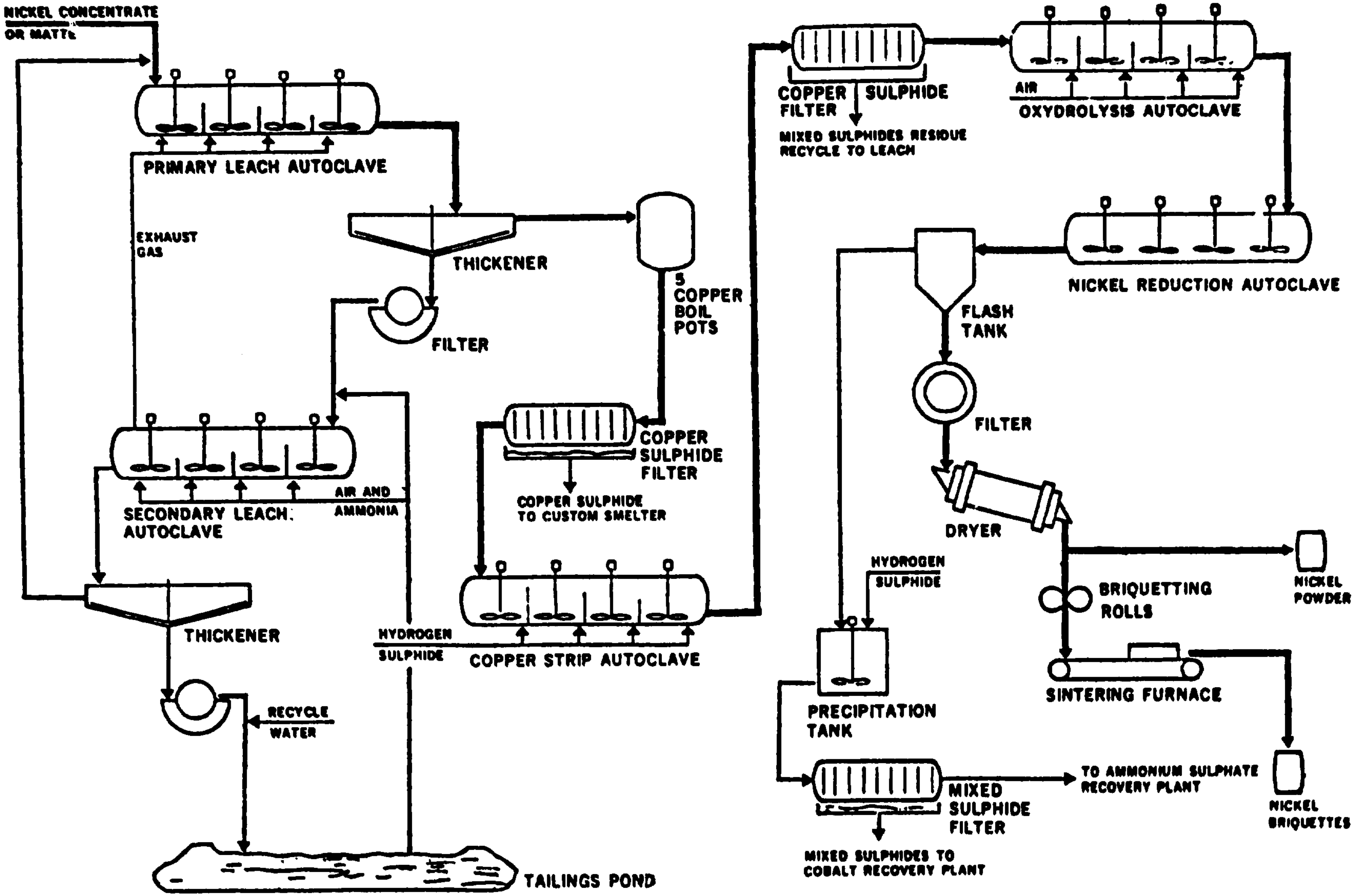
73/ Ibid.

Figure 3.2. Copper Cliff smelter flowsheet



Source: Lemmon, W.A., "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April 1981.

Figure 3.3. Sherritt ammonia leach process



Source: Lemmon, W.A., "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April 1981.

Table 3.1. Concentrations of airborne nickel in some hydrometallurgical operations

Operation	Number of samples	Range of concentrations ($mg Ni/m^3$)	Average concentration ($mg Ni/m^3$)
Acid leach of matte	-	0.005-1.630	0.099
Purification of nickel electrolyte:			
Tube filterman	12	0.013-0.316 0.011-0.316[a]	0.144 0.129
Filter pressman	16	0.061-0.535 0.031-0.246[a]	0.209 0.152
Filter-press area	11	0.064-0.508 0.052-0.466[a]	0.242 0.221
Purification of nickel electrolyte (area samples)			
Cementation of copper on nickel in Pachuca tanks	39	0.048-0.644 0.001-0.133[a]	0.168 0.038
Removing iron slimes with a tube filter	56	0.027-0.653 0.003-0.433[a]	0.200 0.085
Oxidizing cobalt with chlorine	47	0.030-0.672 0.001-0.267[a]	0.183 0.066

[a] Soluble nickel

Source: Warner, J.S., "Occupational Exposure to Airborne Nickel in Producing and Using Nickel Products", in "Nickel in the Human Environment", International Agency for Research on Cancer, Oxford University Press, 1984.

In addition, water is recycled (as much as 85 per cent at some facilities). Improved concentration yields during the ore concentration step have been proven to be very beneficial to both the nickel industry and the environment. For example, at the Inco facility in Sudbury the nickel concentrate stream used to contain 4 per cent nickel and 60 per cent nickel ferrous pyrrotite. This meant that for each ton of nickel produced 26 tons of concentrate were processed, 17 tons of iron sulfide were burnt producing 13 tons of SO_2 and 26 tons of slag. Currently for each ton of nickel produced the corresponding figures are respectively 10, 6, 4.3 and 10 tons.

The problem of tailings disposal has been partially circumvented by mine backfilling with the coarser fraction of the tailings. Some 20 per cent of the tailings is so disposed of at some locations. Still the problem remains for the finer fraction of the tailings which tends to create dust. A method which has been used to control the situation is that of wetting the disposal area followed by its revegatation. At the Sudbury facility this method has been employed since the mid 1950's for tailings basins.[74/][75/] Grass species (e.g. timothy), legumes (alfalfa), and trees (birch, willow) were successfully utilized at the INCO area at Copper Cliff.[76/] The environmental advantages are self-evident. In addition, the vegetation can reduce rainfall seepage through the ground and decrease ground moisture content, by transpiration. This, in turn, reduces the chance of tailings leaching into the ground.

Removal of other pollutants such as thiosulphates and polythionates which are formed in the water used in ore processing has been successfully accomplished by proper impoundment, and subsequent oxidation to sulphuric acid by bacteria and sunlight. The acid can then be neutralized with lime.

Fine dusts are produced during many steps in the pyrometallurgical and refining operations (e.g. in roasters, reverberatory furnaces, electric furnaces, converters). These dusts may contain as much as 5-10 per cent nickel and 10-20 per cent sulphate. This problem is usually tackled by improving the hood collection efficiency followed by dust removal with several devices (such as electrostatic precipitator or scrubbing systems) which are described in other chapters.

The problem of SO_2 generation is most likely the most serious. Two approaches are possible based on collection of SO_2 from flue gases followed by its conversion to other chemical species. The first consists of the conversion of SO_2 to marketable chemicals such as elemental sulphur, liquid sulphur dioxide, ammonium sulphate or sulphuric acid. This method should be used whenever economically feasible. In alternative SO_2 can be converted to chemicals such as gypsum, and then be disposed of. The gypsum is not saleable due to contamination by heavy metals. This method is not currently used.[77/][78/]

74/ Young, C.A. and T.H. Peters, The Use of Vegetation to Stabilize Mine Tailings at Copper Cliff, 68-77. Proceedings of the 15th Ontario Industrial Waste Conference, June 1968.

75/ Michelutti, R., "How to Establish Vegetation on High Iron-Sulphur Mine Tailings", Canadian Mining Journal, October 1974. pp. 54-58.

76/ Peters, T.H., Inco Metals reclamation program, The Canadian Mining and Metallurgical Bulletin, December 1978.

77/ "Background Information for New Source Performance Standards: Primary Copper, Zinc and Lead Smelters", EPA-450/2-74-002 a.

78/ Environment Canada, A Study of Sulphur Containment Technology in the Non-Ferrous Metallurgical Industry, Report EPS 3-AP-79-8, April 1980.

3.4 Nickel from lateritic ores: production processes and pollutants produced

3.4.1 Mining and ore processing

All land-based laterite ores are mined by open pit methods since the ore usually lies under a soft earth layer.[79] This mining is easier than sulphide ores mining, since it is mainly an earth moving operation. On the other hand, nickel cannot be collected into nickel-rich particles and more complex separation techniques must be used. Ore processing is minimal. It consists of coarse crushing followed by screening to remove waste material. This waste material (mainly clay) can then be used to backfill the mined-out areas. The ore is then dried. Both pyrometallurgical and hydrometallurgical processes are used in the subsequent purification steps.

3.4.2 Pyrometallurgy

Reduction smelting

A diagram of this process (which is used in Guatemala, Indonesia and New Caledonia) is shown in figure 3.4. The ore is dried in rotary kilns to a moisture content of about 20 per cent by hot air. After crushing the ore is reduced in another kiln, in three steps. During the first the moisture is removed. In the second step the ore loses the 10-12 per cent water of crystallization it contains. During the third step (toward the end of the kiln), the nickel oxide ore is sulphided by injecting sulphur. This method may seem illogical since much energy is used to remove the sulphur from sulphide ores, as previously described. However the injection of elemental sulphur permits nearly complete separation of iron from nickel. By carefully controlling the amount of sulphur added it is possible to obtain a sulphur deficient matte containing nickel subsulphides, which can then be refined by the same methods described for the sulphide ores.

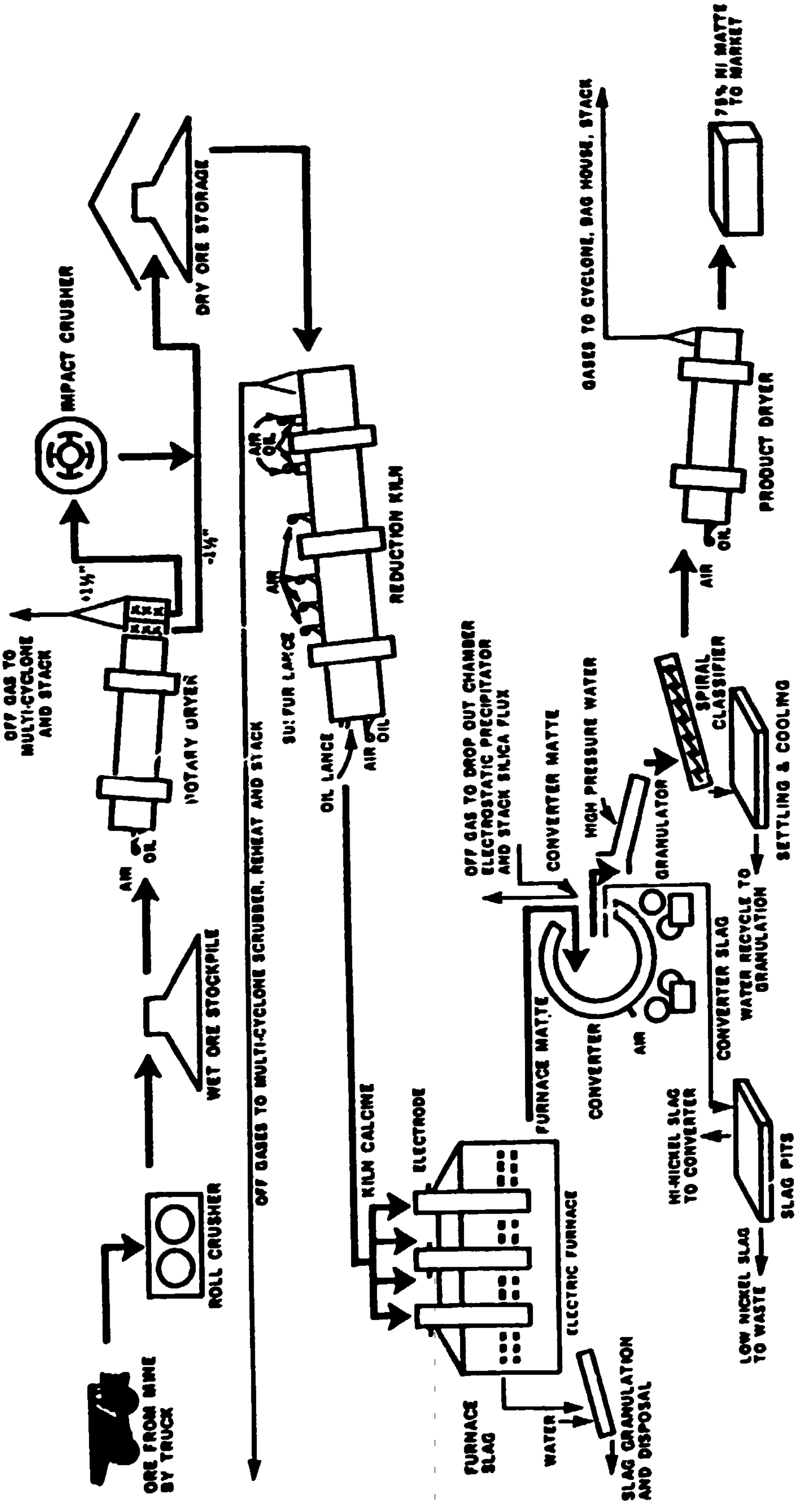
Ferronickel process

This process is used in New Caledonia, USA, Domenican Republic and Greece. It gives a ferronickel alloy containing 35 per cent nickel.

The dried ore is contacted with cracked naptha (produced in gasification units with air) as reducing agent at 1150°C in furnaces. The reduced calcined ore is smelted to crude ferronickel in electric furnaces. The impurities are removed as slag. The metal is tapped and then refined in induction furnaces to remove phosphorus and sulphur.

79/ Boldt, J.R. and P. Queneau, "The Winning of Nickel", Logmans Canada Ltd., Toronto, 1967.

Figure 3.4. Exmibal process flow diagram (Guatemala)



Source: Lemmon, W.A., "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April 1981.

3.4.3 Hydrometallurgy

Sulphuric acid leaching process

This process is used at Moa Bay (Cuba) and gives high recovery efficiency (90 per cent) at relative low energy consumption. After screening, water is added to the ore (45 per cent solids). The mixture is heated with steam to 230°C, and pressurized to 40 bars in autoclaves. Concentrated sulphuric acid is then added. After two hours, 95 per cent of the nickel and cobalt initial content are selectively dissolved. The leach liquid is separated from the tailings and neutralized with lime. Precipitation of nickel and cobalt occurs by injecting H_2S. Control of pH at this stage is crucial for good recovery without iron contamination. The final concentrate assays 55 per cent Ni, 6 per cent Co and 37 per cent S. Refining is carried out afterwards. No environmental data for this process are available.

Ammonia leaching process

This process has a low recovery efficiency (about 76 per cent) compared to other processes. The ore is firstly dried to 5 per cent water in rotary kilns, and ground. Then it is reduced in hearth reduction furnaces with coal gas. By controlling the temperature nickel and not iron is reduced. The cooled reduced ore is fed to a leach solution containing 6.5 per cent ammonia and 3.5 per cent CO_2. While nickel is complexed, the iron is precipitated as hydroxide and separated. Ammonia is partially removed by air and steam injections. Nickel carbonate then precipitates. It is is later calcined to nickel oxide (76.5 per cent Ni), before being refined to 88 per cent. The major environmental problem connected to this process is the presence of ammonia in tailings and water streams.

3.5 Pollution control technologies for plants processing lateritic ores

After the mining step the laterite surface is exposed to the atmosphere. Rain may leach out some of the metal ore. Controls on the run-off water are required.[80] Proper techniques should be used to reclaim the stripped land and preserve its fertility, with additional seeding if necessary.

In the reduction smelting process, the dryer off-gases contain dust which must be removed prior to discharge. This is usually done through multicyclones which also permit recycling the solid back to the kiln. Wet Venturi scrubbers are sometimes used. Electrostatic precipitators are used to clean the gases from the converters, as dust particles are very fine. Dust is also collected from the product dryer and the loading areas.

In the ferronickel process the reducing gases used in the reduction furnaces should be produced by cracking low sulphur naptha to minimize contamination problems. The off-gases from one furnace are de-dusted in

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80/ Musu, R. and J.A.E. Bell, P.T. Inco's Indonesian Nickel Project. Paper presented at the International Laterite Symposium, New Orleans, Louisiana, February 19-21, 1979.

cyclones before being re-used in another set of furnaces. The final exhaust gases are also processed through cyclones or wet scrubbers. In the latter case the wet solids collected are returned to the mine.

The slag produced during smelting has a typical composition of 46 per cent SiO_2, 28 mg O, 22 per cent FeO, 3 per cent Al_2O_3, 0.01 per cent S and 0.15 per cent Ni. The slag is usually discharged into a slag dump.

In the ammonia leaching process the dust removal step is also carried out using cyclones or other dust separators. Recycling of dust is also employed. Ammonia is removed from the tailings in several wash thickeners. Prior to discharge, the tailings slurry is heated to strip out the ammonia using steam. This operation recovers ammonia for economic reasons and minimizes the amount released into the environment with the tailings. Tailings disposal for this process is a major environmental problem.

3.6 Potential for by-product re-use

Because of the presence of several metals in most nickel-containing ore nickel production is often coupled with the recovery of copper, iron, cobalt, gold, silver, platinum group metals, selenium, and tellurium. In the process described above for nickel production from sulphide ores, one of the main purposes for ore concentration was to separate most of the iron ore from the nickel ore. The iron ore is then further processed. For example, at the INCO facility in Sudbury the major portion of pyrrotite (an iron-rich ore) which is diverted from the smelter is processed through the iron ore recovery plant. Nickel, iron, and sulphur are recovered as nickel oxide, iron ore pellets and sulphuric acid, respectively. This plant can process up to one million tons per year of ore concentrate. Ore in excess of this capacity is stockpiled for future use.

The other two major streams emerging from the ore concentration step are the copper concentrate and the nickel concentrate. Copper is recovered from both streams as copper sulphide. It is then refined to give cast copper, shapes and cathodes.

Most precious metals are contained in the nickel sulphide matte. Some 90 per cent of them are recovered in the matte separation process based upon slow cooling. This promotes the growth of discrete and separate crystals of metallics such as nickel-copper alloy. After the grinding and magnetic separation steps the metallics are fed to the refinery plant for final recovery.

3.7 Nickel recycling

Unlike copper and aluminum nickel and nickel alloys are not systematically recycled.[81/] Some nickel scrap is used in the steel industry as the nickel source. Investigations are underway to recover the nickel oxide from fumes collected from steel plants utilizing nickel scrap.

81/ "Environmental Aspects of Selected Non-Ferrous Metals Industries", UNEP, Industry and Environment Overview Series, 1984.

Other studies have been carried out on the recovery of nickel and other metals from nickel scrap using hydrometallurgical methods. These have not yet resulted in economically feasible processes and are not practiced on an industrial scale.

3.8 Retrofitting of existing plants to reduce pollution

Improvement of emission quality can be obtained by either altering the process to reduce primary pollutant production (as carried out by INCO at its Sudbury and Thompson plants) or cleaning the off-streams leaving the plant. Improved end-of-the-pipe treatments means improved dust removal efficiency from gases, and SO_2 emission control. Whenever feasible dry systems are be preferred for dust removal. Wet scrubbers may result in polluted wastewater streams. If not presently fitted, a cyclone should be retrofitted to all dust laden streams in old plants. Electrostatic precipitators offer higher removal efficiencies, especially for finer particles, but are more expensive.

Removal of SO_2 from flue gas is possible through the contact sulphuric acid production process, the chemical absorption process, or the elemental sulphur production process. Existing large nickel production facilities are not readily amenable to the introduction of simple SO_2 removal processes, especially if SO_2 emissions concentrations are low. In contrast, new plants have been built which include facilities for the recovery of as much as 80 per cent of the SO_2 generated.

3.9 Innovative and emerging production technologies

In the field of pyrometallurgy the greatest efforts have been concentrated toward sulphur dioxide emission control. The use of fluid bed roasters and electric furnaces instead of sintering furnaces result in more concentrated, continuous streams of SO_2-rich off-gases. These can be treated in acid plants, permitting the removal of high percentages of SO_2. This method is used at the Falconbridge smelter in Sudbury, Canada (commissioned in 1978). Flash smelting processes, using oxygen-rich gas streams, may also produce off-gases containing SO_2 in high concentration (80 per cent). This technology must also be used together with SO_2 recovery plants. Investigations are underway to simultaneously flash smelt the nickel concentrate and convert the matte, in a confined section of a single vessel. This process is still in the early stage of development.

Hydrometallurgical processes have the greatest potential for development. The main advantages lie in the possibility of operating on a continuous basis, automating the plant, and eliminating the sulphur dioxide emissions. Starting from sulphide ores the sulphides can be oxidized with pressurized oxygen (7 bars) at 50°C. By choosing the appropriate conditions elemental sulphur (up to 80 per cent) and sulphates (about 20 per cent) can be produced, thus eliminating the need for gas purification from SO_2. Considerable investigations have also been carried out in order to define the optimal leach conditions, such as leaching medium (sulphate or chloride), use of catalysts, dispersing agents, and oxidizing agents. According to reference [82] a typical plant of the future will process low grade nickel concentrate, and produce elemental sulphur which could be then either sold, processed to sulphuric acid or impounded.

82/ Lemmon, W.A. "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April, 1981.

3.10 A case study

The Falconbridge Nickel Mines Ltd. facility at Sudbury is used as a case study.[83] Operations at this plant started in 1933 at the rate of 3,000 tons of ore per day which was later expanded to 7,700 tons per day corresponding to an ultimate capacity of 45,000 tons of nickel per year. In the 1950's a pyrrhotite separation plant was added, involving sulphate roasting in fluidized bed reactors. This operation was discontinued in 1972 because of the high SO_2 emissions. In 1979 a new fluidized bed roaster and electric furnace smelter replaced the old blast furnace smelter, in order to meet local standards for SO_2 emission. The new smelter has two roasters. Each feeds a 36-MVA electric smelting furnace with six Söderberg electrodes. Sulphur dioxide is recovered as sulphuric acid in amounts of up to 600 tons per day.

The nickel-copper matte is shipped to the refining facility at Kristiansand in Norway. Two different processes are used. The first consists of roasting the matte to oxide in a roaster. The calcine is leached with sulphuric acid which selectively dissolves the copper. The remaining calcine is melted in electric furnaces in the presence of coke, as reducing agent. Melted nickel is cast into anodes for electrolysis which produces 99.95 per cent purity cathodes.

The second process consists of selectively dissolving nickel from the matte by adding hydrochloric acid.[84] The nickel chloride is hydrolized at high temperature in a fluidized bed reactor to give nickel oxide and HCl. The oxide is then reduced with hydrogen in rotary furnaces producing nickel pellets.

3.11 Pollution control costs

SO_2 emissions are the most difficult and the most expensive to control. Several control systems exist, but each is tailored to a type of emisson. The characteristics of the gas streams which are suitable for treatment are reported in table 3.2[85] for each of the most common removal systems. No economic process is currently available for treating low SO_2-content gases, although studies are underway.

83/ Ibid.

84/ Thornhill, P.E., E. Wigstol and G. Van Weert, The Falconbridge Matte Leach Process. Paper presented at the Annual Meeting of the AIME, New York, February 26-March 4, 1971.

85/ Environment Canada, A Study of Sulphur Containment Technology in the Non-Ferrous Metallurgical Industry, Report EPS 3-AP-79-8, April 1980.

Table 3.2. Characteristics of gas streams required for optimum treatment in sulphur recovery plants

		Percentage SO_2	Percentage O_2	Flowrate and composition
Contact acid	- single	5-8	8-12	Can be variable^1
	- double	5-8	8-12	Can be variable^1
Liquid SO_2	- physical	70-80	Low as possible	Constant
	- chemical	10-11^2	-	Constant
Elemental sulphur		10	1-3	Constant

1. More economical when constant.

2. Plant requires pressure or chemical absorption followed by treatment of strong regenerated stream.

Source: Lemmon, W.A., "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April 1981.

In addition to the cost for SO_2 removal from off-gases, considerable costs are associated with by-product manufacture (such as sulphuric acid, liquid SO_2, elemental sulphur), marketing, transportation, storage or final disposal. For example, 300 Km is considered to be the maximum distance for economically shipping sulphuric acid.[86] By contrast, most nickel plants are located far away from potential markets.

The ratio of sulphur to nickel in concentrates usually varies between 2.2-4.8[87] and can greatly affect SO_2 control cost. Table 3.3[88] presents such cost for different fixation systems assuming that the final product had no value.

86/ Anon., New Smelter, Acid Plant at Falconbridge to Improve Working Conditions, Efficiency, Canadian Mining Journal, 99, 5, May 1978.

87/ Ibid.

88/ Environment Canada, A Study of Sulphur Containment Technology in the Non-Ferrous Metallurgical Industry, Report EPS 3-AP-79-8, April 1980.

Table 3.3. Cost of sulphur fixation per pound of nickel produced*

	Single catalysis acid plant						Double catalysis	
	Continuous gases only		Variable gases only		Continuous and variable gases		Continuous and variable gases	
Sulphur fixation, percentage	50	45	95	97				
Production cost $US/ton S	59	92	54	58				
Neutralization cost $US/ton S	92	92	86	86				
Sulphur/metal ratio in concentrate	Low	High	Low	High	Low	High	Low	High
Sulphur fixation costs cents/lb Ni	2.95	6.43	4.14	9.02	5.12	11.18	5.64	12.31
Neutralization (total cost of making acid and neutralizing it) cents/lb Ni	7.57	16.51	8.29	18.09	13.25	28.91	13.94	30.42

* Gas cleaning costs not included

Source: Lemmon, W.A., "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April 1981.

3.12 Emission standards

Emission standards for SO_2, the major pollutant, can be found in other chapters (Aluminum, Copper). Emission level for particulates in the air should be maintained below 240 micrograms/m^3 over a 24-hour emission peak, and below 75 micrograms/m^3 as annual geometrical mean.[89] The maximum airborne nickel concentration must be below 20 mg/m^3. Concentration of nickel exceeding 50 mg/kg can be toxic to plants. Therefore, the amount of

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[89] Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

nickel salts dispersed on land used for agricultural purposes should be limited, particularly on acid soils. The UK Department of the Environment recommends that not more than 7 g/m^2 (as Ni) should be added to the soil over a period of 30 years.[90] As for liquid effluents from nickel plants, when impoundment is not feasible, the Canadian authorities recommend the following limits:

Total Suspended Solids	15 mg/l (30-day average)
Cu	0.2 "
Ni	0.5 "
Fe	0.5 "
pH	6-9 units

3.13 Health protection for workers

Occupational exposure limits for airborne nickel in working environments have been adopted by several countries and are reported in table 3.4.

Table 3.4. Maximum occupational exposure limits for airborne nickel

					USA		
						ACGIH	
	Fed. Rep. Germany	Japan	Sweden	USSR	Occup. standard	TWA	Short term
Nickel, mg/m^3		1	0.01	0.5	1	1	
Nickel carbonyl, mg/m^3	0.7	0.007	0.007	0.0005	0.007	0.35	0.35

Source: Occupational Exposure Limits for Airborne Toxic Substances, ILO, Occupational Safety and Health Series No. 37, Geneva, 1977.

90/ "Environmental Aspects of Selected Non-Ferrous Metals Industries", UNEP, Industry and Environment Overview Series, 1984.

As an example of actual worker exposure table 3.5[91] shows data made available by Société Métallurgique Le Nickel for its plant in New Caledonia. The data presented indicate that airborne nickel concentrations are quite low although this may be due largely to the low nickel content of the ore.

Table 3.5. Concentrations of airborne nickel in laterite mining and smelting: New Caledonia

Concentration of airborne nickel (mg Ni/m^3)	Area sampling		Personal sampling	
	Frequency of observation (per cent)	Average concentration[a]	Frequency of observation (per cent)	Average concentration[a]
0.05	67.1	0.0047	83.2	0.0022
0.05-0.10	8.3	0.076	1.4	0.081
0.10-1.00	24.6	0.029	15.5	0.274

[a] Sampled for particles less than 30 microns in diameter.

Source: Warner, J.S., "Occupational Exposure to Airborne Nickel in Producing and Using Nickel Products", in "Nickel in the Human Environment", International Agency for Research on Cancer, Oxford University Press, 1984.

In general the hazard to workers depends strongly on the nickel compound involved. Whereas nickel metal and most of its inorganic salts are relatively non-toxic, nickel carbonyl gas (present in some refining processes) is toxic even at low concentrations. Consequently workers must be adequately protected from it. Moreover, experimental studies have concluded that several nickel compounds can produce malignant tumors in animals if inhaled (nickel subsulphate and carbonyl) or injected (nickel subsulphide, oxide, carbonate, hydroxide).[92] Indeed there is now substantial evidence to state that

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91/ Warner, J.S., "Occupational Exposure to Airborne Nickel in Producing and Using Nickel Products", in "Nickel in the Human Environment", International Agency for Research on Cancer, Oxford University Press, 1984.

92/ Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man, Vol. II., International Agency for Research on Cancer, Lyon, 1976. pp. 75-112.

workers in nickel refineries run some risk of nasal and pulmonary cancer. The data came from refineries in Canada, Japan, Norway, GDR, and USSR.[93] Although no conclusive evidence has been found it appears that inhaled dust particles of nickel oxide and nickel carbonyl vapors can be held responsible.[94][95] The analysis of the data also shows that the risk of refinery workers to develop cancer has significantly decreased over time, probably as a consequence of the improved working conditions. Some estimates of the concentrations of airborne nickel in some refining operations where there was in the past an increased incidence of cancer were from one to two orders of magnitude higher than those found in the nickel industry today.[96]

93/ Ibid.

94/ IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Chemicals and Industrial Processes Associated with Cancer in Humans, IARC Monographs Volumes 1-20, IARC Monographs Supplement 1, International Agency for Research on Cancer, Lyon, September 1979.

95/ Warner, J.S., "Occupational Exposure to Airborne Nickel in Producing and Using Nickel Products", in "Nickel in the Human Environment", International Agency for Research on Cancer, Oxford University Press, 1984.

96/ Ibid.

4. COPPER

4.1 Introduction

The use of copper is linked to the general level of industrialization, but especially to electricity generation and transport. Copper is also used in the construction industry for water, gas, and sanitation piping systems. These applications reflect the high electrical conductivity and good corrosion resistance of copper. Copper is also important for its alloys, especially with zinc (brasses) and tin (bronzes). Copper is not usually released into the environment in amounts which can be toxic to humans or ecosystems.

In 1985 the world production of copper was about 9.7 million tons, including both primary and secondary production. Simple remelting of high grade scrap copper or copper alloy without smelting is not included.

Primary copper is produced from the ore by a number of steps. The final result is blister copper, i.e. copper containing several impurities, and whose surface appears dark and blistered because of their presence. Blister copper is refined with the addition of a minimum of scrap.

Secondary copper comes from reprocessing copper scrap obtained from various secondary sources. In most cases this involves re-smelting via blast furnace On the other hand, high copper-content scrap is processed by re-melting only.

Production of blister copper includes mining, smelting, and primary refining. It is commonly carried out on a large scale at locations which are distant from populated areas. Important mines are in Zaire, Zambia, Canada, Congo, Indonesia, Chile, Peru, Philippines, Australia, Poland and the USSR. Further processing is often conducted in more industrialized areas.

4.2 Primary copper production processes and pollutants produced

An overall flow diagram for copper production is shown in figure 4.1.

4.2.1 Mining

The vast majority of copper minerals consist of sulphides such as chalcopyrite ($CuFS_2$), covellite (CuS), and chalcocite (Cu_2S). Some oxide ores are also used. On the average the ores contain about 1.5 per cent of copper[97] but in some cases content can be much higher (e.g. the copper belt mine ore in Zambia contains 3.4 per cent).[98]

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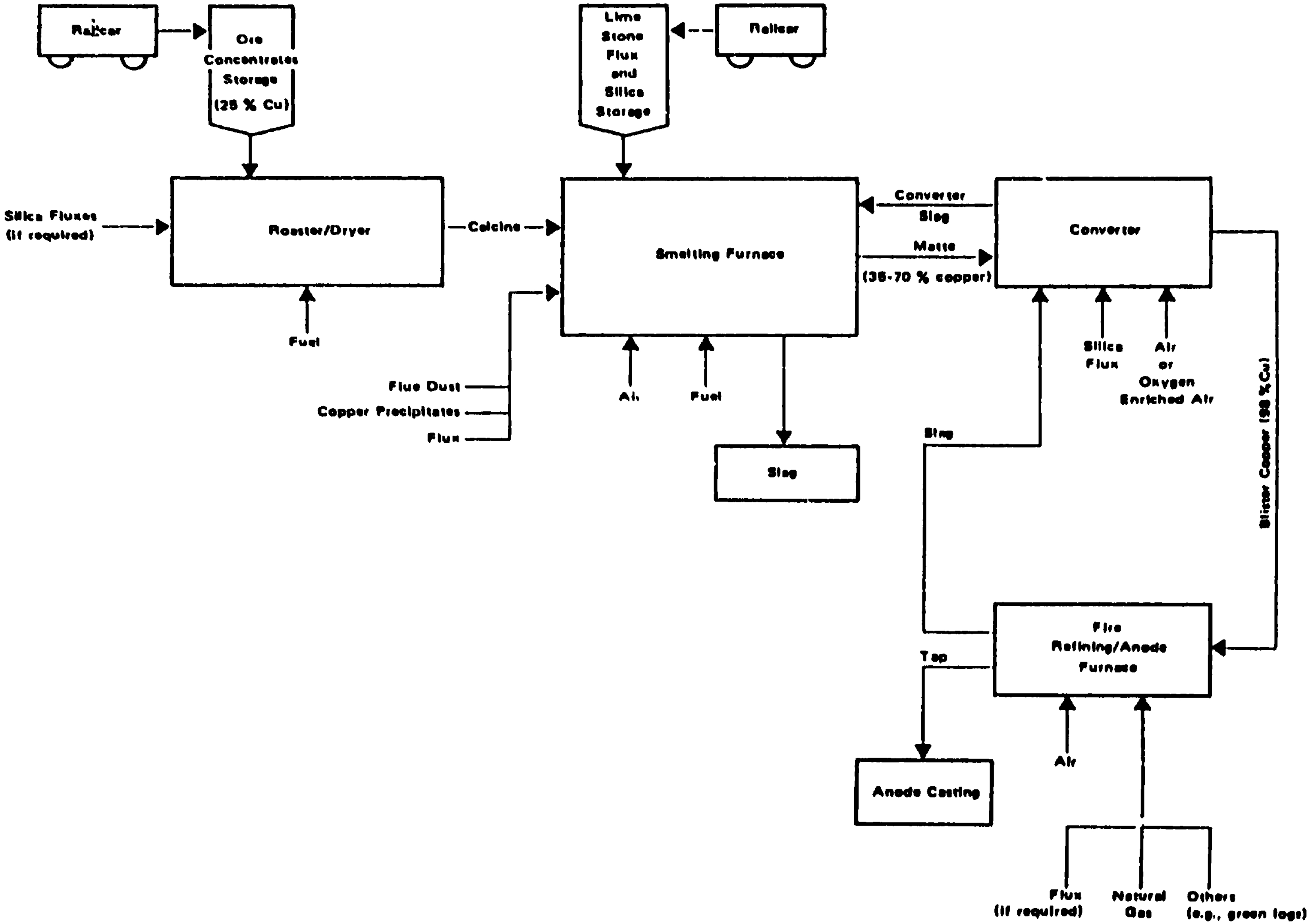
[97] Coray, P.G., A. Lane, "A Guide to the Minerals of Zambia", NCCM and RCM, 1978.

[98] Perera, N.P., "Environmental Problems of Copper Mining and Refining in Zambia", UNEP Industry and Environment, Vol. 5, No. 1, January, February, March 1982.

Figure 4.1. Description of copper process flow



Source: Modified from "Compendium on Low- and Non-Waste Technology", Primary Copper Production Using the Noranda Process, UN Economic and Social Council, 1 May 1984.

Copper ore mines can be either open-pit or underground. In the former case nearly all mining activities are accompanied by dust and gases. About 90 per cent of dust emissions result from truck haulage. Bulk blasting is the largest single point source of dust and gases.

More than 73 per cent of underground mining is carried out by the room-and-pillar method.[99] Dust is generated by drilling of bore holes and blast holes and ore loading and discharging from railway cars or trucks. Gas formation occurs mainly during blasting, but it is confined within the mine. Mine waters are also produced, with potentially negative impact on the environment.

4.2.2 Ore processing

The purpose of this phase is to concentrate the original ore into copper-rich concentrate. The main steps consist of crushing and grinding the ore, concentrating it by flotation, dewatering, filtering and drying.

The mined ore lumps (400-1,500 mm in size) are crushed to 10-20 mm sized particles. A considerable amount of dust is generated at this stage. The ore is then ground in ball or rod mills using sprayed water to eliminate dust formation. Flotation then follows. Depending on the process, different floating agents are used. Most of these agents are potential pollutants. Two streams of solids emerge from the operation: the concentrated ore (rich in copper) and the tailings. Both contain large amounts of water (some 3 m^3 and 10 m^3 per ton of solids, respectively). While the tailing slurry is discharged to tailing ponds, the concentrates are dewatered by thickening, filtering, and thermally drying the solids. Dust is produced during the last step.

4.2.3 Ore concentrate roasting

The purpose here is to remove part of the sulphur from the concentrated ore, producing SO_2. This is done by heating the ore at about 850°C in multiple-hearth or fluidized bed furnaces with hot combustion gases. Fluidized bed furnaces are much more environmentally sound since off-gases with high SO_2 content (12.5-14 per cent)[100] are produced. These gases can be further processed to recover SO_2. Desulphurization at this stage can be as high as 70 per cent. SO_2 and dust are the two main environmental hazards.

4.2.4 Matte production (smelting)

While roasting involves the presence only of solid and gas phases, smelting involves the production of a so-called "matte", i.e. a molten stream of impure copper also containing sulphur, iron, and other impurities. Several smelting processes exist and will be examined.

99/ "Environmental Aspects of Copper Production", UNEP Workshop, Geneva, 13-16 April, 1981.

100/ Ibid.

Reverberatory smelting

This is the oldest method still in use. The roasted concentrate plus flux are fed to the reverberatory furnace, a horizontal chamber capable of processing 800-1,300 tons of ore per day. The flux is a mixture of silica, limestone and other minerals, which is fed to the furnace in order to react with the impurities originally present in the charge (such as iron), forming a slag. The slag then separates spontaneously from the copper-rich matte. The charge is exposed to a flame produced by burning fuel. The flame and combustion gases heat the charge producing complex chemical reactions which generate SO_2, a copper-rich liquid matte, and a molten slag floating on the matte.

During the process the iron oxidizes and goes into the slag, while the copper is partially desulphurized forming the matte. The copper content of the matte is about 45 per cent.

A typical charge to a reverberatory furnace is made of:[101/]

Ore concentrate	65 per cent
Converter slag	25 per cent
Hydrometallurgical precipitate	2 per cent
Flue dust	1 per cent
Flux	7 per cent

The second and third items are copper-rich by-products of other processing steps. The charge is converted to about 47 per cent matte and 53 per cent slag. The composition of the slag is given in table 4.1.[102/]

Some 20-45 per cent of the sulphur in the charge is converted to SO_2, which is released in the gas phase at low concentration (0.5-2.5 per cent), and high temperature (1,200°C). This makes the removal of SO_2 very difficult. The composition of this so-called off-gas is given in table 4.2.[103/] In addition, between 14 and 40 kg of dust are emitted with the off-gas per ton of copper produced. Therefore the off-gas stream is very polluting.

The slag is tapped, cooled, and then dumped or further processed. The matte is sent to the conversion step.

101/ "Compendium on Low-and Non- Waste Technology", Primary Copper Production Using the Outokumpu Flash Furnace, UN Economic and Social Council, 1 May 1984.

102/ Ibid.

103/ Ibid.

Table 4.1. Summary of slag analysis

Compound or element	Composition, weight per cent	Trace elements	Parts per million
Iron oxide (FeO)	34–40	Zinc	7,800
Silicates (SiO_2)	35–40	Manganese	450
Calcium oxide (CaO)	3- 7	Antimony	400
Manganese oxide (MgO)	0.5- 3	Lead	100
Aluminum oxide (Al_2O_3)	4.5-10	Chromium	100
Copper	0.4- 0.7	Selenium	20
Sulphur	1.0- 1.5	Nickel	25
		Cadmium	10
		Mercury	less than 1.0
		Arsenic	Trace
		Tellurium	Trace
		Cobalt	Trace

Source: "Compendium on Low-and Non- Waste Technology", Primary Copper Production Using the Outokumpu Flash Furnace, UN Economic and Social Council, 1 May 1984.

Table 4.2. Composition of off-gas stream from reverberatory furnace

Component	Green feed, weight per cent	Calcined feed, weight per cent
Carbon dioxide	8.4	10.2
Nitrogen	69.3	71.0
Oxygen	0.25 - 1.0	0.25 - 1.0
Water	18.8	17.7
Sulphur dioxide	1.5 - 2.5	0.6

Source: "Compendium on Low- and Non-Waste Technology", Primary Copper Production Using the Outokumpu Flash Furnace, UN Economic and Social Council, 1 May 1984.

Blast smelting

This type of process is rather flexible in that various sources of copper ore can be used. Two main types of blast smelting processes exist for primary copper production: copper-sulphuric (modified pyritic) and semi-pyritic.

The first method begins with pelletizing and sintering the ore concentrate to a suitable size. There are SO^2 emissions in this step. The ore is fed to the blast furnace together with quartzite (about 93 per cent SiO_2), lime and coke in an air stream. The heat generated by the partial oxidation of the ore melts the charge, which separates into an iron-rich silicate slag and a molten copper and iron sulphides matte. The advantages of this method are: a) practically no dust is emitted from the furnace, b) off-gases have an SO_2-concentration high enough for efficient removal (some 80 per cent of the initial sulphur can be removed from the charge), and, c) low copper ores (1-2 per cent) can be processed. The disadvantages are the high fuel consumption, some requirements on the ore quality, and the necessity of pelletizing the ore (with dust and fume generations).

The semi-pyritic method can be applied only to ores with low sulphur content. Moreover the off-gases have low SO_2 concentration (1-2 per cent) which makes SO_2 removal difficult. Therefore this method has few future prospects.

Electric smelting

This method is especially useful for processing ore concentrates with high copper and low sulphur contents, although conventional ores can also be treated. The main advantages of this method are the small volume of off-gases and dust generated (less than 1 per cent), and the high SO_2 concentration in the off-gases. No combustion air is required. However, this process has high energy requirements and can be used only where electricity is economically available.[104]

Flash smelting

This process combines roasting, smelting, and partial converting. The process takes place in the flash furnace shown in figure 4.2. Preheated air or oxygen-enriched air is blown into the furnace. If preheated oxygen in sufficiently high concentration is used (200°C; 30-40 per cent) no external heat is required and the process is energetically self-sufficient. Before being loaded to the furnace the ore concentrate is mixed with the flux and dried. The charge is then blown with the air into the furnace where it melts into slag and matte. The SO_2 formed goes into the gas stream. The slag has a relatively high copper content (up to 2.5 per cent) and is separated, cooled, ground, and further processed to recover the metal. The matte, containing from 45-75 per cent copper, is tapped and sent to a converter for blister copper production. The gas stream and the converter off-gas stream are rich in SO_2 (10-30 per cent and 7-13 per cent respectively).[105] Consequently these streams can be readily treated in an acid conversion plant.

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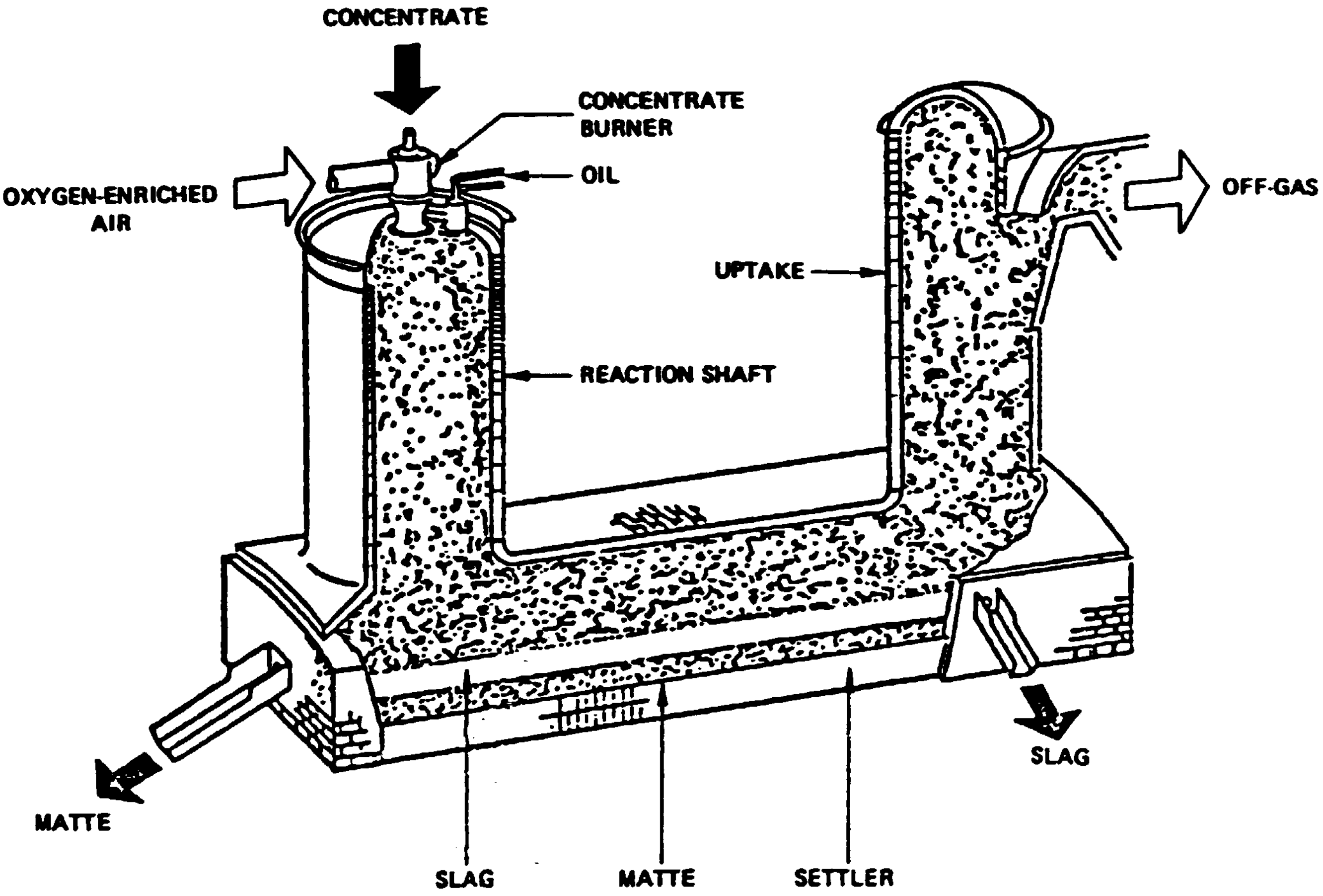
[104] Ibid.

[105] Ibid.

Figure 4.2. Outokumpu process furnace for copper production



Source: "Compendium on Low-and Non- Waste Technology", Primary Copper Production Using the Outokumpu Flash Furnace, UN Economic and Social Council, 1 May 1984.

The Outokumpu flash smelting process, originally developed in Finland, has gained wide acceptance and is now used in more than thirty plants all over the world. The INCO flash smelter is similar in principle and is used mainly in Canada. The main advantages of flash smelting are the efficient energy utilization (20-30 per cent of that required in a reverberatory furnace), the high sulphur conversion (from 50-80 per cent) and recovery, and the flexibility of ore concentrate compositions. A schematic flow diagram for the Outokumpu process is shown in figure 4.3.[106]

4.2.5 Matte conversion

The matte produced during the smelting operation must be converted in order to remove the iron and sulphur it contains. This is accomplished in horizontal converters with a production capacity of 40-100 tons/day of blister copper. In the first conversion stage air is blown and the iron sulphide is oxidized to oxide. It is removed as slag together with the silica flux. During the second stage the following reactions occur:

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$$

The overall reaction is:

$$Cu_2S + O_2 \longrightarrow 2Cu + SO_2$$

Blister copper is thus produced (98 per cent pure copper containing sulphur and other impurities).

SO_2 and dust are emitted during both phases. The main environmental problem here is associated with the fugitive emissions during the matte transfer, slagging, and emptying. Arsenic, lead, and cadmium are present in the dust. Efficient hooding and collection is essential. The SO_2 content is high enough for efficient removal, but conversion is a batch process and therefore difficult to adapt to a continuous gas cleaning process. A possible alternative exists in large plant where several converters operate in sequence, thus producing a more or less continuous off-gas stream.

4.2.6 Blister copper fire refining

This is the first step in refining and is carried out in rotary or reverberatory furnaces. Air is used to oxidize any remaining sulphur to SO_2. Other metals are also oxidized and enter the slag.

In the second step some hydrocarbons are injected into the melt until the oxygen content drops below 0.1-0.3 per cent. Copper is then cast into anode molds and is ready for electrorefining. The pollutants contained in the off-gases are SO_2 (0.1-0.3 per cent), solid particles (containing lead in concentrations from 0.5-1.5 per cent), and carbon monoxide

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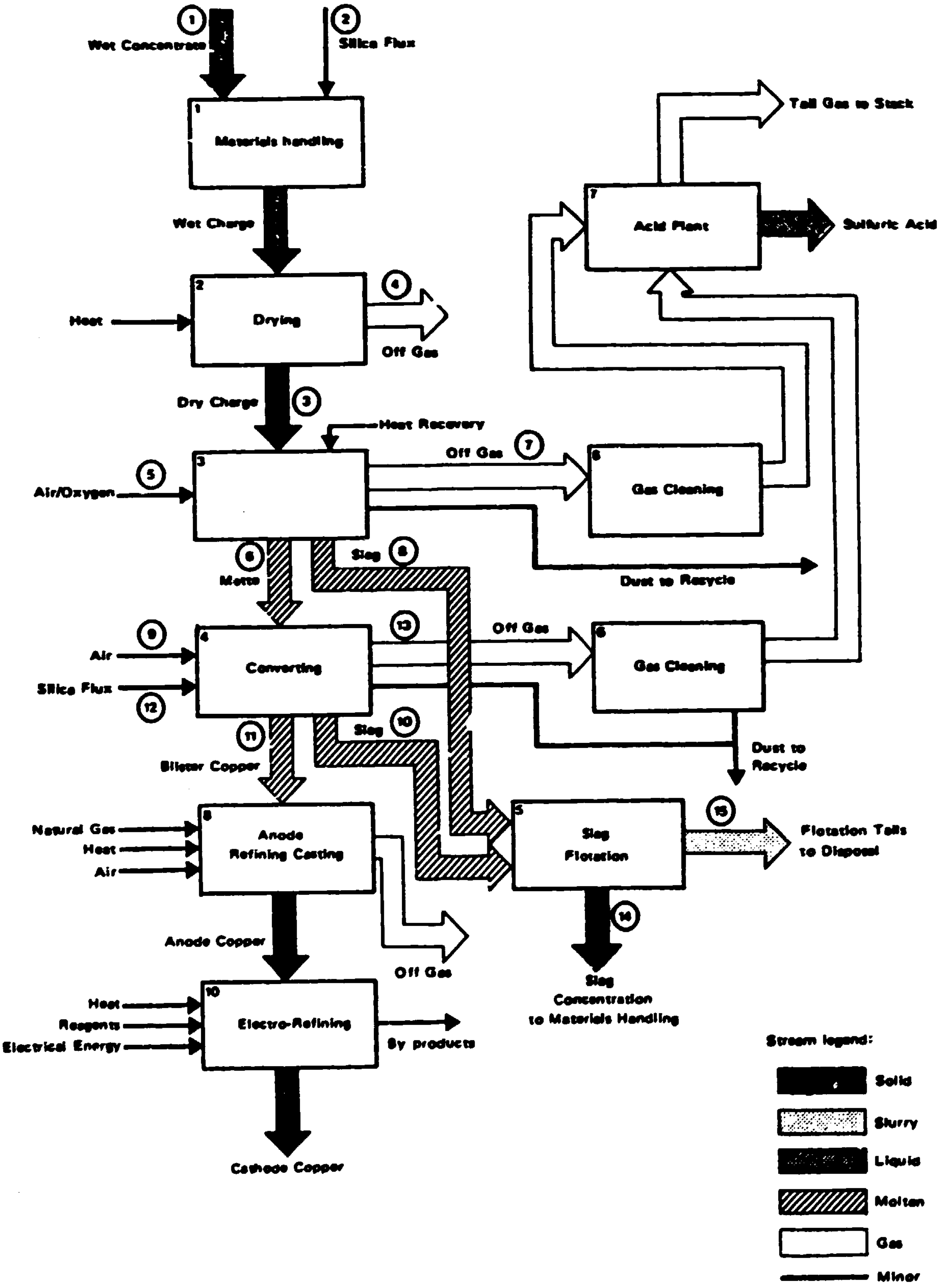
[106] Ibid.

Figure 4.3. Outokumpu process flow schematic



Source: "Compendium on Low-and Non- Waste Technology", Primary Copper Production Using the Outokumpu Flash Furnace, UN Economic and Social Council, 1 May 1984.

(0.5-1.0 per cent). Carbon monoxide cannot be removed since a reducing atmosphere must be maintained in the furnace. Heat energy (T = 1,200°C) is recovered in waste heat boilers which also trap most of the dust.

4.2.7 Electrorefining

The final purification step is carried out by electrolysis in an aqueous solution of $CuSO_4$ and sulphuric acid at 60°C. Anode copper from step 2.6 is used as the anode and the purified copper (99.98 per cent) is obtained at the cathode. During the process less active metals (such as gold, silver, selenium) do not dissolve and are recovered as anode slimes at the bottom of the cell. Other metals (such as iron, nickel, cobalt) dissolve into the solution which therefore must be periodically purified.

A potential pollutant is the acid mist which is formed during the operation. In addition, if arsenic is contained in anode copper then arsine, a poisonous gas, could be generated. In some refineries the electrolytic solution is periodically replaced in order to avoid too high a concentration of arsenic. The small amount of wastewater is normally treated to remove heavy metal contaminants. It is sometimes recycled and sometimes discharged.

4.2.8 Hydrometallurgy

Hydrometallurgical processes are used for oxidized ore bodies of copper. The processes are based on the dissolution of copper and other metals in sulphuric acid. Leaching in situ, dump leaching, heap leaching or vat leaching are used. The first three methods are rather slow since the acid is sprayed on the ore and the leachate is drawn off. Acid seepage into the ground can cause environmental problems. Vat leaching is environmentally more sound although the problem of acidic solid residue disposal remains.

Leaching produces a copper sulphate solution. To obtain the copper either cementation or solvent extraction is used. Cementation consists of displacing copper with iron. The copper precipitate powder is then pyrometallurgically refined. Since not all copper precipitates, the wash waters are contaminated and may constitute an environmental hazard.

Solvent extraction consists of contacting the copper sulphate solution with an organic immiscible solution which selectively removes copper. After phase separation, copper is precipitated by adding acid, and then electrolytically refined. This method is environmentally preferable to cementation since most liquids are recycled and little waste effluent is produced.

4.3 Pollution control technologies for copper production plants

4.3.1 Pollution control during mining

Dust is the main environmental problem at this stage. Dust generated by truck hauling can be reduced by employing trucks of greater capacity and covering the roads with a non-dusty upper layer. Emulsions can be used for this purpose. Additional advantages of this method are increases in both haulage speed and tire life by 10-15 per cent.[107] The amount of dust produced by blasting can be reduced by spraying a solution of calcium hydroxide or sodium sulphate (10 per cent) in blast holes. Dust formation at open pit mining sites can be reduced by creating a light mist with steam-air jets. Reforestation is important for both land reclamation and to create green buffer areas to prevent dust and harmful chemicals from spreading. One hectare of forest may collect up to 18 tons of dust.[108] Sowing of perennial cereals can be used to eliminate dust formation at spent open pit mining sites.

4.3.2 Pollution control during ore processing

Dust is again the main environmental problem. During crushing and grinding the most effective method to prevent dust formation is to sprinkle or spray water. In a closed room it is necessary to seal the dust generating equipment, provide good ventilation, and use dust collecting equipment. Dust collection efficiency at this stage can be as high as 95 per cent. Remote control of these operations is the rule.

The main environmental problem of ore flotation is water pollution caused by floating agents. This has been partially circumvented in recent years by replacing highly toxic cyanide salts with sulphides, and toxic phenolic foaming agents of the cresol type with non-phenolic agents. In addition, water recycling has been extensively introduced.

4.3.3 Pollution control during ore concentrate roasting

This operation can be the highest single-step desulphurization of the whole copper production process (50-70 per cent removal). Fluidized bed roasting produces SO_2 in concentrations high enough (up to 14 per cent) to allow high recovery rates (up to 99.5 per cent). This increases the overall sulphur recovery efficiency of the whole production process to some 75-85 per cent. Other low-SO_2 content streams generated by other operations can be diluted with the roaster off-gas stream. The resulting stream can still be efficiently processed (e.g. in a H_2SO_4 plant) for SO_2 removal. However, in multiple hearth furnaces the SO_2 content in the off-gas is only 7.5 per cent. This is still suitable for efficient SO_2 removal, but not for dilution with other gas streams. Roasting gases also contain dust which is usually removed in cyclones and electrostatic precipitators.

4.3.4 Pollution control during matte production

If reverberatory furnaces are used as smelters, off-gases have an SO_2 content which is too low for effective removal. Consequently no control exists at present. Waste heat recovery is practiced, then dust is removed from the off-gases in electrostatic precipitators (efficiency higher than 99 per cent). The collected dust is then recycled.[109]

107/ "Environmental Aspects of Copper Production", UNEP Workshop, Geneva, 13-16 April 1981.

108/ *Ibid*.

109/ *Ibid*.

If blast smelting is adopted the roasting step is replaced by a pelletizing-sintering step which generates a gas stream whose SO_2 content (about 7 per cent) is suitable for conversion to sulphuric acid. If the modified pyritic process follows SO_2 can still be removed from the gas stream although less efficiently. With the semi-pyritic blast smelting this is no longer possible since SO_2 content is too low (below 2 per cent).

In electric smelting, the concentration of SO_2 in the off-gases is very high. No air is admitted to the smelter (provided proper sealing exists, mainly near the electrodes), and the gas volume is low. The dust content is also low and this allows the use of smaller electrostatic precipitators.

Flash smelting also produces off-gases with high SO_2 content (up to 30 per cent) which may become even higher if nearly pure oxygen is used (85-95 per cent).[110] These gases can be diluted with other streams from other parts of the plant and are suitable for very efficient sulphur removal.

4.3.5 Pollution control during matte conversion

Beside SO_2 and dust, fume leakage is the main environmental problem. This can be effectively circumvented by proper hood design, operation, and maintainance. SO_2 concentrations in off-gas average 4-4.8 per cent and sometimes even higher values (provided some measures are taken, such as effective hood and gas duct sealing, hood water and evaporation cooling). These lower concentrations limit the SO_2 recovery efficiency to about 50 per cent (sometimes values up to 85 per cent can be obtained), in a sulphuric acid production plant.

4.3.6 Pollution control during fire refining

The furnace produces off-gases having an SO_2 content less than 0.3, which is too low for removal. Waste heat boilers may be fitted to the furnace for waste heat recovery and dust trapping. The gas is then released into the atmosphere without any further treatment because of its low content of pollutants. Sometimes further dust removal could still constitute a good practice.

4.3.7 Pollution control during electrorefining

Shop ventilation air is usually vented without treatment. As for waste water, its heavy metal content is removed by neutralization with lime, which precipitates the metals as salts. More advanced methods such as ion exchange or flocculation can also be employed.

4.3.8 Pollution control for hydrometallurgical processes

In hydrometallurgy liquids and sludges require disposal. There is also a potential for acid seepage. Whereas pyrometallurgical slags are solid and

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[110] *Ibid*.

inert, hydrometallurgical sludges may contain undissolved metals, acid, and large quantities of water. They are usually impounded in ponds, which must be water proofed.

4.3.9 Removal of sulphur dioxide from gas streams

Sulphur dioxide is present in all gaseous streams produced by smelters in concentrations ranging between 0.1 and 95 per cent. At present, industrial technologies exist to remove SO_2 provided that its concentration is above 4 per cent. Recovery of SO_2 and its subsequent conversion to H_2SO_4 not only eliminates the associated pollution problems, but also may improve the overall economies of the copper manufacturing process. Technologies exist also for streams with lower SO_2 concentrations, but they are not industrially used because of their cost. SO_2 can be converted to sulphuric acid, elemental sulphur, liquid sulphur dioxide, ammonium sulphate or gypsum. Table 4.3 shows the concentration requirements for the stream to be purified for each method.[111]

Table 4.3. Characteristics of gas streams required for optimum treatment in sulphur recovery plants

		Percentage SO_2	Percentage O_2	Flowrate and composition
Contact acid	- single	5-8	8-12	Can be variable[a]
	- double	5-8	8-12	Can be variable[a]
Liquid SO_2	- physical	70-80	Low as possible	Constant
	- chemical	10-11[b]	0	Constant
Elemental sulphur		10	1-3	Constant

a/ More economical when constant.

b/ Plant requires pressure or chemical absorption followed by treatment of strong regenerated stream.

Source: Lemmon, W.A., "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April, 1981.

Contact sulphuric acid process

This is the most common method for recovering SO_2. The process consists of contacting SO_2 and oxygen in the presence of a catalyst (vanadium pentoxide) to form SO_3, which is then converted to H_2SO_4 by

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[111] Lemmon, W.A., "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April 1981.

adding water. The reaction is exothermic and heat can be recovered. The process operates with SO_2 concentrations between 5 and 8 per cent and oxygen concentrations from 30-50 per cent higher than the SO_2 concentration. The conversion efficiency is 97 per cent and 99.5 per cent for single and double contact plants respectively.[112] A major economic drawback is that the acid must be transported to the market places which are usually far away from the production point.

Elemental sulphur processes

Several processes have been developed (Outokumpu Allied Chemical, ASARCO, Texagulf). They are all based on a two step process consisting of reducing the SO_2 to H_2S and then catalytically converting the hydrogen sulphide to sulphur, recycling the reactant. Only concentrated SO_2 streams (10-15 per cent) can be processed. The oxygen content must be rather low (below 3 per cent). The conversion efficiency is about 90 per cent. The main advantage of the process is that sulphur is easy to transport and store.

Liquid sulphur dioxide process

This process can operate only with an SO_2 concentration as high as 70-80 per cent and practically no oxygen. The off-gas must be clean. It is compressed and refrigerated until SO_2 liquifies. Alternatively, SO_2 can be removed from the original gas stream by absorption and subsequent regeneration in concentrated form, and then liquefied.

4.4 Potential for by-product re-use

Overburden rocks resulting from open pit mining can be effectively used as construction material. In underground mining the overburden material can be used as filling material for mining operations as well as embankment material for the construction of dikes, dams and roads.

Slags obtained from smelting operations can also be used. The amount of slag generated varies between 10 and 30 tons per ton of copper produced. The slag composition is also an important factor to assess the profitability of slag processing. Copper slag usually contains silica, aluminum, calcium, magnesium, and iron in different proportions, as well as lesser amounts of nickel, cobalt, zinc, lead, cadmium and rare metals. Typical slag processing involves three phases:

- non-ferrous metal and rare metal extraction
- iron removal
- manufacturing of construction material from the residue

Pelletized copper slags can be used as binders after autoclave solidification. The concretes so manufactured have mechanical properties comparable to clinker cements, and can be used to produce reinforced concrete

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112/ Ibid.

structures. Typical compressive strengths are from 400 kg/cm^2 for dense filling material (2,500 kg/m^3), to 80-100 kg/cm^2 for cellular concrete with a density of 400-1,000 kg/m^3.

4.5 Copper recycling (secondary copper production)

World secondary copper production accounts for a large share of total production, namely some 20 per cent. The reasons for such a high figure are that copper is only slightly degraded under normal service conditions and it is a valuable metal. Moreover, copper scrap can be easily remelted or reprocessed. In order to properly utilize scrap material it is important to know size and amounts, scrap composition, and contaminants. This information will determine the type of pretreatment, if any, and processing technology.

Scrap can be divided into two basic types. The first originates from the copper industry itself or related activities. This scrap usually has very well known characteristics and is, in general, uncontaminated. The second type comes from metal which was recovered after a period of use. A whole spectrum of such scrap exists. At one end there is copper in large amounts and relatively high grade (e.g. piping, electric wires and bar, boiler tubes). At the other end of the spectrum there is metal which is contaminated with other metals or oils and is more difficult to recover (e.g. car radiators, scrap from grinding operations, chromium plated parts, domestic appliances).

In processing copper scrap it is very important to be able to classify and isolate the scrap. A number of sorting techniques exist (hand sorting, magnetic sorting, gravity separation). A good example is provided by copper cables covered with insulating material such as PVC. Rather than burning the insulation, or charging the cable as such to melters (with evolution of chlorinated hydrocarbons, hydrochloric acid and phosgene), mechanical shredding followed by gravity separation or electrostatic separation is more effective for recovering the copper and, in some instances, even the insulator.

High-grade copper scrap is usually melted without refining, provided its composition is known and most alloying elements can be retained. Slightly contaminated scrap is commonly charged to reverberatory or rotary furnaces with the addition of flux. A slag containing most of the oxidized contaminant forms and is removed. A full cycle lasts from 24-48 hours depending on the scrap quality. Air or oxygen is blown. If the charge is contaminated with zinc, lead and other metals then oxides are formed and must be collected (as dust) by bag filters, Venturi scrubber or other devices.

Highly contaminated scrap and low grade copper residue undergo a more complex treatment. A blast furnace refining process is then used, as shown in figure 4.4.[113] The blast furnaces used in secondary copper refining have rather small capacities (some 10 tons/hour), but may constitute a significant pollution source unless fumes are purified. Some 100 kg/hour of dust can be generated, containing large fractions of zinc oxide (50 per cent) and lead

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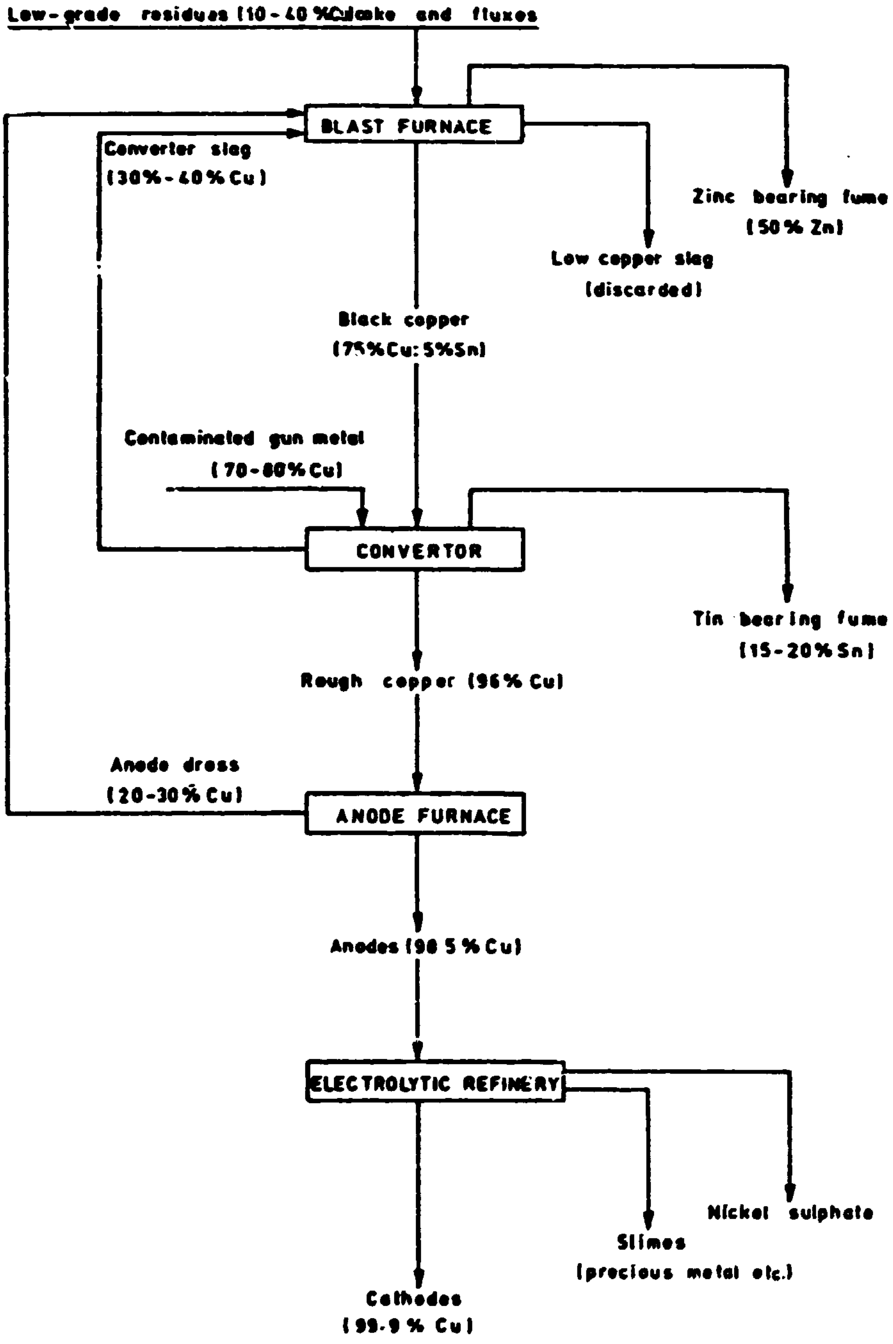
113/ Atkins, P.R. and J.F. Lowe, The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979, p. 109.

Figure 4.4. Secondary copper blast furnace refining flow sheet



Source: Atkins, M.H. and J.F. Lowe, The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979, p. 109.

oxide (10 per cent). Besides slag and fumes, a blast furnace produces so-called black copper (with a copper content higher than 80 per cent) which is then refined in a reverberatory or rotary furnace, and then in electrolytic cells. Depending on the charge, dust generation may range between one and several hundred kg/ton of copper refined. Consequently fume collection is usually imperative.

4.6 Retrofitting of existing plants to reduce pollution

In recent years major emphasis has been placed on increasing the efficiency of ore processing. In order to reduce energy consumption some plants have been retrofitted with systems capable of grinding the ore to a much finer product so that mineral recovery is enhanced. Process control has been upgraded by introducing on-stream analysis methods and automated control loops.

A promising technology to enhance flotation efficiency is the reverse flotation process. The gangue is floated rather than the copper-rich ore. This system has already been used at the CRA company's Woodlawn mine in Australia.[114]

As for smelting operations, the main environmental problem in old plants is the emission of SO_2. More often than not, SO_2 content in off-gases (especially from reverberatory furnaces or converters) is too low for removal. In principle, it is technically feasible to reduce such emissions to very low level. For example, low-concentration SO_2 in the off-gas could be absorbed and then released to give a more concentrated stream. In practice this technology is not yet economical. Therefore most old smelters keep releasing untreated SO_2. In order to minimize adverse effects on life and the environment in the neighborhood of the plant, a tall stack could be provided for efficient dispersion into the atmosphere. However long range transport of SO_2 has already caused acid rain in northern Europe and North America.

A more satisfactory approach consists of retrofitting old converters with oxygen-enriched air blowing systems. This results in a more energy efficient process which also means that smaller amounts of gases are produced, and SO_2 is more concentrated. An example of such a system comes from the "Teniente Modified Converter" developed by Codelco for smelting El Teniente ore concentrates (Chile). Here the basic configuration of the existing smelter was modified and oxygen-enriched fuel burners were introduced on the roof of the converter. This resulted in an increased production of 600 tons/day of copper without any additional fuel consumption, in a single smelting-converting operation.[115] Converters with side removal of gases can have similar advantages. These systems give higher copper and SO_2 recovery efficiency with limited capital investment for modernization.

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[114] "Impact of New Technologies on the World Copper Market - A Study Prepared for UNCTAD", Commodities Research Unit Ltd. (London) and CRU Consultants Inc. (New York), 1986.

[115] *Ibid*.

Retrofitting is possible in hydrometallurgy due to the adoption of new solvents. After leaching the copper from the ore with a sulphuric acid solution, this stream is contacted with an organic solution to recover copper. The most common reagent used during this solvent extraction step is General Mills' LIX 64 (Liquid Ion Exchange). This solvent (of proprietary composition) selectively reacts with copper. Since then the development of second generation reagents such as LIX 860 has enabled existing plants to reduce operating costs and increase recovery efficiency. The newest reagents are not too sensitive to pH variations and can therefore operate at higher loading capacity using more acidic copper solutions.

4.7 Innovative and emerging production technologies

Several processes have emerged in recent years or are under evaluation at present. These new developments are mainly aimed at improving the economics of copper production by:

(a) Concentrating several smelting steps into one or only a few steps

(b) Reducing energy consumption

(c) Producing waste streams more amenable for pollution control treatment (especially SO_2-containing off-gases)

(d) Increasing productivity

(e) Developing continuous processes

(f) Improving existing technologies

Most of these new processes are pyrometallurgical, but some important improvements have been made in hydrometallurgical technologies.

4.7.1 Noranda process

The first commercial application of this process started to operate at Noranda (Canada) in 1973. The process is continuous and combines three steps of copper production: roasting, smelting and converting. It is based upon the use of a single horizontal vessel, some 5 meters in diameter and 20 meters in length, as depicted in figure 4.5,[116] which is fed with the copper-rich material and flux at one end. Oil or natural gas are also fed to the vessel while oxygen-enriched air is blown from side ports. At high oxygen concentrations (up to 35 per cent) the process is nearly energetically self-sufficient and very little fuel is required. The molten slag and matte which form during the process are periodically tapped. The slag contains high amounts of copper (3-12 per cent) and is cooled, milled and floated to recover copper. This is then used as part of the feed. The matte contains copper in high concentrations (about 70 per cent). Conversion takes place in small converters and lasts only 2-4 hours due to the good quality of the matte. The off-gas produced by the process has a concentration of 16 per cent SO_2 and

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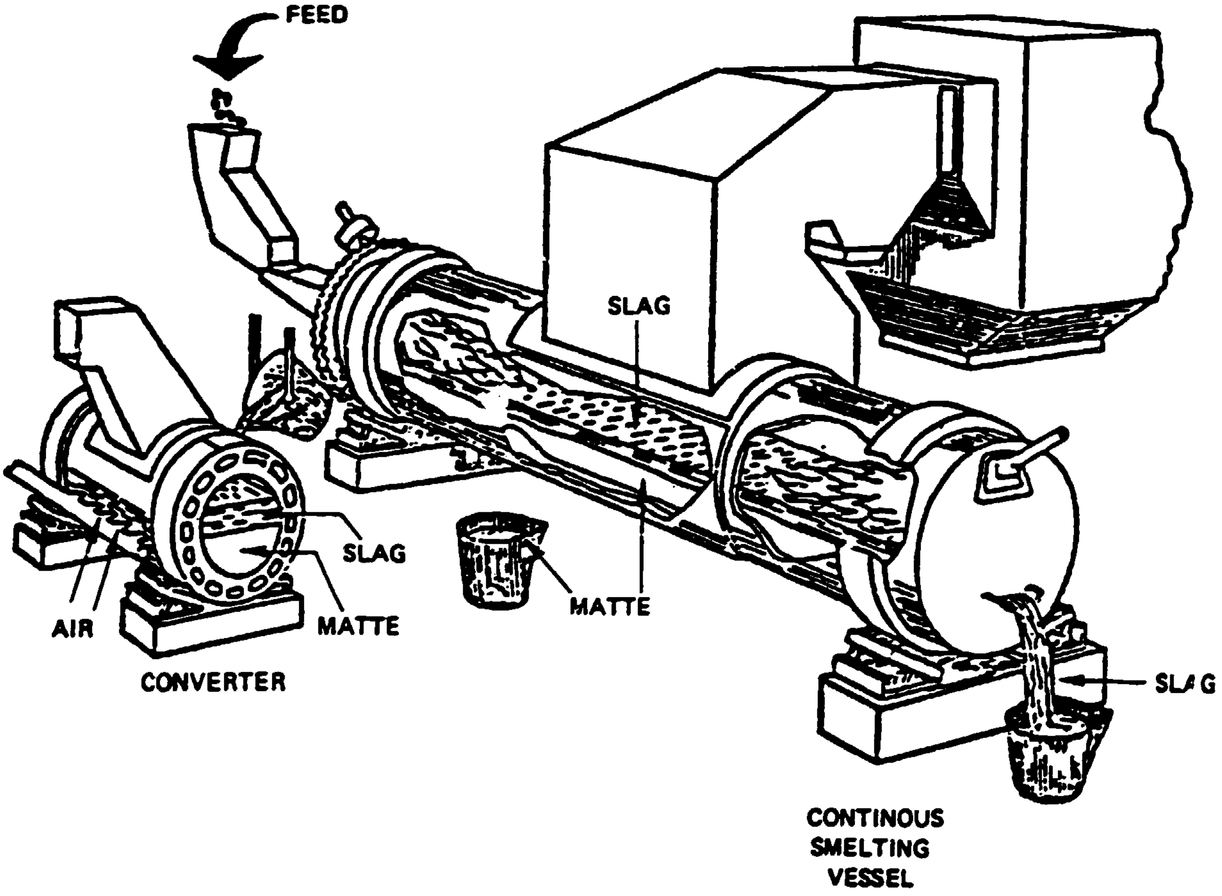
116/ "Compendium of Low- and Non- Waste Technology", Copper Production Using the Noranda Process, UN Economic and Social Council, 1 May 1984.

Figure 4.5. Typical Noranda process configuration



Source: Perera, N.P., "Environmental Problems of Copper Mining and Refining in Zambia", UNEP Industry and Environment, Vol. 5, No. 1, January, February, March 1982.

can feed an acid plant. The gases are first sent to a waste heat boiler and then to a particle removal system (cyclone plus electrostatic precipitator) before undergoing conversion to sulphuric acid. The process is described in figure 4.6.[117]

4.7.2 Molten metal pool smelting

This process was developed in the USSR where a 1,200-ton charge/day-plant exists. Smelting occurs in a molten bath. Specific output is claimed to be 6-8 times greater than that of a flash furnace, while dust production is only 1-1.5 per cent.[118] The process does not require external energy input, and produces SO_2-rich off-gases (20-40 per cent SO_2) which can be fed to a sulphuric acid plant. The process appears to be promising because of the almost complete elimination of emissions to the environment, low manpower requirements, and possibility of process automation.

4.7.3 Mitsubishi process

This is also a continuous process. In terms of operations it resembles flash smelting, but the smelting, converting, and slag processing steps are carried out separately in interconnected vessels between which transfer occurs by gravity flow. The first element of the system is a smelting furnace. The charge and the flux are fed through the roof whereas oil and air (or oxygen enriched air) are fed from lances. The resulting matte and slag flow into an electric slag cleaning furnace. Phase separation takes place here. The purified slag is continuously removed, granulated, and reprocessed, while the matte is sent to a converter producing blister copper. The off-gases from the three stages average 10 per cent SO_2 content, which is suitable for acid conversion. This process is relatively expensive in terms of capital expenditure and energy requirements but it operates continuously, requires little labour, and can be automated. The process has not yet found very wide application. The Kidd Creek plant in Ontario uses this process.

4.7.4 KIVCET process

This process has been developed in the USSR where a pilot plant now operates. It is best suited for charges containing relatively large amounts of zinc. The process consists of roasting and subsequently smelting the ore suspended in a cyclone chamber. No external fuel is required. The matte and slag produced are then separated in a settler and further processed. Off-gases contain 15-20 per cent of SO_2.

4.7.5 Bia-Yin process

This process has been developed in China. Its main feature is the use of a modified reverberatory furnace in two parts separated by a partition wall. In the first chamber roasting occurs. Smelting takes place in the second

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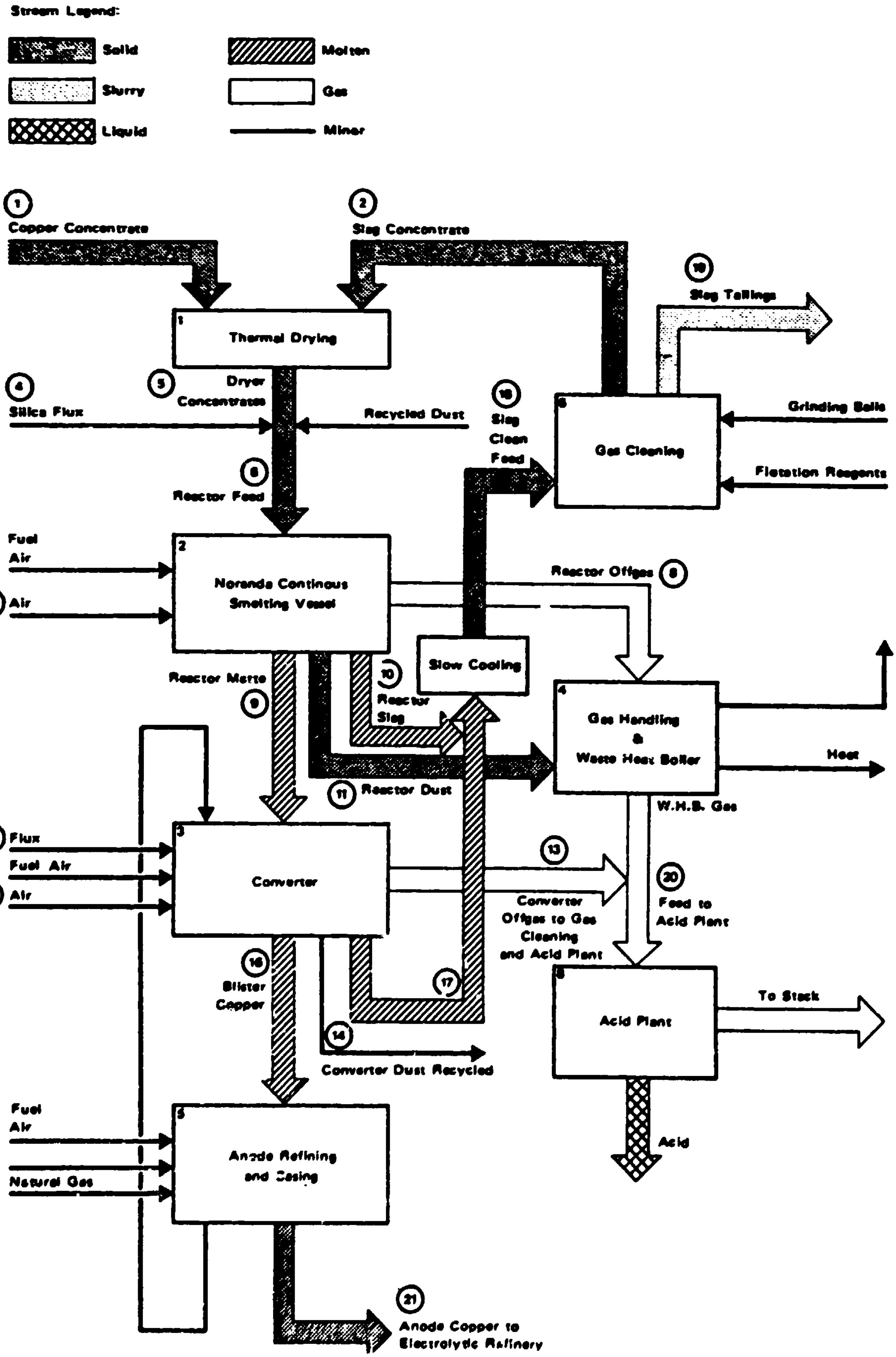
[117] *Ibid*.

[118] "Environmental Aspects of Copper Production", UNEP Workshop, Geneva, 13-16 April, 1981.

Figure 4.6. Materials flow schematic for the Noranda process



Source: Perera, N.P., "Environmental Problems of Copper Mining and Refining in Zambia", UNEP Industry and Environment, Vol. 5, No. 1, January, February, March 1982.

chamber. Air is blasted in the melt providing very good mixing and enhanced oxidation. It is claimed that this process has a smelting capacity twice as large as a conventional reverberatory furnace, under comparable operating conditions.[119]

4.7.6 Other smelting processes under development

The Amex Dead Roast/Shaft Blast Furnace process consists of dead roasting the copper ore concentrate in a fluidized bed More than 96 per cent of the initial sulphur is removed thus eliminating the need for a conversion step. The calcines are then added to the flux and coke, and charged to a shaft blast furnace from which slag and blister copper are produced. It has been claimed that this process can bring substantial savings (up to 72 per cent) compared to the capital cost required for a comparable traditional plant.[120]

Another promising process is the Queneau-Schumann Continuous Oxygen process consisting of charging the ore concentrate and flux into a molten metal bath where oxygen is injected through submerged lances. Highly SO_2-concentrated off-gases are generated. Crude copper is continuously produced and then further refined.

4.7.7 Hydrometallurgical processes

Considerable research has been carried out in recent years on hydrometallurgical processing of oxide ores. In addition, less successful efforts were devolved to the hydrometallurgical processing of sulphide ores. The latter technology will be applied only to small scale operations (less than 25,000 ton/year) or special sulphide ores.

Solvent extraction-electrowinning processes have gained wide acceptance and are expanding under the influence of new reactant development. Examples of such an operation are the Mineroperu's 33,000 tons/year plant at Cerro Verde, the 50,000 tons/year plants in Chile and Mexico, and the 80,000 tons/year Chingola plant by Nchanga Consolidated Copper Mines in Zambia.

The recently developed thin layer leaching process is based on a two-stage process consisting of curing the ore with sulphuric acid and then leaching it with dilute sulphuric acid. Standard solvent extraction then follows. The main advantage of this process (which was originally conceived by Sociedad Minera Pudahuel of Chile) is that there is no economy of scale, and is suited for small as well as large operations. This feature makes it very attractive for developing countries.

Another potential advantage of the process is that it can be adapted to treat sulphide ores as well. A commercial application of this process was developed at the Lo Aguirre mine in Chile (16,500 tons/year of copper), but other projects are carried out in Peru, Brazil, Chile, USA., and Jordan (where a 3,000 tons/year pilot plant exists).

119/ "Impact of New Technologies on the World Copper Market" A Study Prepared for UNCTAD", Commodities Research Unit Ltd. (London) and CRU Consultants Inc. (New York), 1986.

120/ Ibid.

Another method under development is the bacterial process. Thiobacillus Ferrooxidans, a microorganism, is employed for this purpose. It consumes CO_2 and oxidizes ferrous iron and sulphides during its life cycle. As a result, copper sulphide is converted to copper sulphate which can be processed electrolytically. The process is attractive because of its low cost, but it is very slow.

4.8 A case study

The plant is in the UK, produces 20,000 tons of refined secondary copper, and employs 250 people. The company under consideration has operated the plant since the 1950's.[121/] The plant consists of a blast furnace, a converter, a tin/lead refining plant, an anode furnace, and electrolysis cells. It processes scrap material containing at least 10 per cent copper as metal or oxide. The feed to the blast furnace consists of copper residues, oily scarf, coke and flux. The off-gases are cooled in a spray cooler and the dust is collected in a baghouse (99.99 per cent efficiency). Gases are dispersed from an 80 meters high stack. Some 2,700 tons/year of zinc oxide are recovered and sold. The electrolytic cells for refining copper contain 12 per cent sulphuric acid plus copper and nickel in solution. The hold-up of the system is 1,250 m^3.

In the converter, tin, lead and the remaining zinc are oxidized. The oxides are collected in a baghouse. The three existing bag filters have an efficiency higher than 99.9 per cent. If one breaks down it takes at most 15 minutes to isolate the defective filter and stop the undesired emission. The malfunction is noted by a change in the pressure drop across the filters. They are further processed in a reverberatory furnace producing 300 tons/year of relatively pure zinc oxide plus crude lead and tin (which are refined and cast into ingots). The off-gases are released from a 45 meter high stack.

The total capital expenditure for the pollution control equipment was £150,000 for the three baghouses and £100,000 for the stacks. Their operating and maintenance costs were £62,500 in 1975. The plant has much lower emission rates than those allowed by the inspecting authorities.

4.9 Pollution control costs

For a new reverberatory furnace (1,500 tons/day capacity) the smelting cost can be estimated to be 97.8 cents/kg of copper produced.[122/] This cost does not include SO_2 emission control or particulate matter recovery costs. On the other hand the smelting cost for a new flash smelter is only 61 cents/kg[123/] and this figure includes the cost for complying with existing air emission standards.

121/ Atkins, M.H. and J.F. Lowe, The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979, p. 109.

122/ "Compendium of Low- and Non- Waste Technology", Copper Production Using the Noranda Process, UN Economic and Social Council, 1 May 1984.

123/ "Compendium on Low-and Non- Waste Technology", Primary Copper Production Using the Outokumpu Flash Furnace, UN Economic and Social Council, 1 May 1984.

For those cases where SO_2 can be effectively removed from the off-gases (i.e. where SO_2 concentration is high enough) an estimate of the removal cost is given in table 4.4[124] for different methods. The table shows only order of magnitude costs and does not include hot gas cleaning systems (which could increase the cost by as much as 30 per cent). No modifications of or adaptations to the existing plant were considered.

Table 4.4. Cost of sulphur fixation per pound of copper produced*

	Single catalysis acid plant						Double catalysis	
	Continuous gases only		Variable gases only		Continuous and variable gases		Continuous and variable gases	
Sulphur fixation, percentage	50	45	95	97				
Production cost $US/ton S	59	92	54	58				
Neutralization cost $US/ton S	92	92	86	86				
Sulphur/metal ratio in concentrate	Low	High	Low	High	Low	High	Low	High
Sulphur fixation costs cents/lb Cu	1.07	2.14	1.50	3.01	1.86	3.73	2.05	4.10
Neutralization (total cost of making acid and neutralizing it) cents/lb Cu	2.75	5.50	3.02	6.03	4.67	9.64	5.07	10.14

(Canada - 1979)

* Gas cleaning costs not included

Source: Lemmon, W.A., "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April, 1981.

As for dust removal an idea of the costs associated with different technologies and removal efficiencies can be obtained from table 4.5.[125] Cost figures are from 1972.

124/ "Background Information for New Source Performance Standards: Primary Copper, Zinc and Lead Smelters", EPA-450/2-74-002 a.

125/ Stone, E.H.F., "Fume and Effluent Treatment Plant in the Non-Ferrous Metals Industry", Institute of Metals, Review 169, 1972.

Table 4.5. Efficiency and cost of control equipment for 1,000,000 m³/h dusty gases at 20°C

Equipment	Removal efficiency, standard dust (%)	Total running cost (£ per annum)	Total cost including capital charges (£ per annum)
Inertial collector	58.6	587	1,313
Medium-efficiency cyclone	65.3	1,233	1,693
Low-resistance cellular cyclone	74.2	480	1,380
High-efficiency cyclone	84.2	1,547	2,567
Tubular cyclone	93.8	1,360	2,467
Electrostatic precipitator	99.0	933	5,867
Shaker-type fabric filter	99.7	3,380	6,847
Low-velocity fabric filter	99.8	3,127	6,327
Reverse-jet fabric filter	99.8	6,640	11,507
Jet-impingement scrubber	97.9	2,807	4,807
Irrigated cyclone	91.0	1,900	3,153
Self-induced spray deduster	93.6	2,093	3,493
Spray tower	94.5	4,000	6,933
Fluidized-bed scrubber	95.0	3,067	4,180
Irrigated-target scrubber	97.9	2,513	4,247
Disintegrator	98.5	15,840	18,707
Irrigated electrostatic precipitator	99.0	1,320	7,653
Low-energy annular-throat scrubber	99.5	4,933	7,067
Medium-energy Venturi scrubber	99.7	7,293	9,560
Medium-energy annular-throat scrubber	99.8	7,466	9,733
High-energy Venturi scrubber	99.9	10,933	13,400

<u>Source</u>: E.H.F. Stone, <u>op.cit</u>.

4.10 Emission standards

According to The World Bank emission levels in off-gases should be maintained below the following figures:

Table 4.6. World Bank guidelines for emission levels in off-gases

Sulfur dioxide (SO_2)			
Inside plant fence	Annual arithmetic mean	100	g/m^3
	Maximum 24-hour peak	1,000	g/m^3
Outside plant fence	Annual arithmetic mean	100	g/m^3
	Maximum 24-hour peak	500	g/m^3
Particulates			
	Annual geometric mean	75	g/m^3
	Maximum 24-hour peak	260	g/m^3
Nitrogen oxides (as NO_2)			
	Annual arithmetic mean	100	g/m^3
Carbon monoxide (CO)			
	Maximum 8-hour average	10	mg/m^3
	Maximum 1-hour average	40	mg/m^3

Source: Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

The UK emission standards for the off-gases emitted by copper production plants have the following values: total particulates shall not exceed 0.46 g/m^3 for emission up to 700 m^3/min reducing to 0.23 g/m^3 for larger emissions. Copper and zinc shall not exceed the limit of 0.115 g/m^3. Other standards are set for cadmium and lead, depending on the size of the plant. For large emissions the limits are 0.012 g/m^3 and 0.7 kg/hr for cadmium, and 0.012 g/m^3 and 5.4 kg/hr for copper. The minimum stack height is fixed at 30 meters.[126]

For liquid effluents different standards are applicable to different plants.

126/ Butler, D.H., "Copper, Environmental Impact in Its Processing, Use and Disposal", UNEP, Industry and Environment Programme, Paris, 1 September 1982.

Table 4.7. Standards for liquid effluents

For primary copper smelting plants the limits are:
(mg/liter of effluent)

	Maximum 24-hour	Consecutive 30-day average
TSS	50	25
As	20	10
Cu	0.5	0.25
Pb	1.0	0.5
Cd	1.0	0.5
Se	10	5
Zn	10	5
pH	6-9 units	6-9 units

For electrolytic copper refining plants the limits are:
(kg/metric ton of product)

	Maximum 24-hour	Consecutive 30-day average
TSS	0.10	0.05
Cu	1.7×10^{-3}	0.8×10^{-3}
Cd	6×10^{-5}	3×10^{-5}
Pb	6×10^{-4}	2.6×10^{-4}
Zn	1.2×10^{-3}	0.3×10^{-3}

For secondary copper refining plants the limits are:
(mg/liter of effluent)

	Maximum 24-hour	Consecutive 30-day average
TSS	50	25
Cu	0.5	0.5
Zn	10	5
Oil and Grease	20	10
pH	6-9 units	6-9 units

Source: Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

4.11 Health protection for workers

Copper is a metal of fairly low toxicity. The paucity of literature on ill effects caused by exposure to it seems to confirm this.[127]/[128]/ Some occupational exposure limits for airborne copper, as recommended in selected countries, are reported in table 4.8.[129]/

Table 4.8. Occupational exposure limits for airborne toxic substances

					USA		
						ACGIH	
	Fed. Rep. Germany	Japan	Sweden	USSR	Occupat. stand.	TWA	Short term
Copper dust mg/m^3	1		1	1	1	1	2
Copper fumes mg/m^3	0.1				0.1	0.2	0.2

Source: ILO, Occupational Safety and Health Series No. 37, Geneva, 1977.

Copper melts and boils at relatively high temperatures. Consequently it does not release metal fumes as readily as other metals such as lead, cadmium or zinc. Furthermore, copper dust and fumes have a characteristic odor which gives a warning to the workers, thus limiting exposure before toxic intake can occur. Nevertheless workers can develop undesirable health effects if limit concentrations are exceeded. In extreme cases, metal fume fever, a 24-48 hour illness can result. Contact dermatitis has also been reported,[130]/ but observations of copper smelter and refinery workers over more than 25 years have failed to show any significant incidence of dermatitis. In copper smelting operations it is likely that more harmful metal fumes will be present

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127/ "Copper, Medical and Biological Effects of Environmental Pollutants", The National Research Council, National Academy of Sciences, Washington, D.C., 1977.

128/ Demayo, A., M.C. Taylor, and K.W. Taylor, "Effects of Copper on Humans, Laboratory and Farm Animals, Terrestrial Plants, and Aquatic Life", August 1982.

129/ Nordman, H., UNEP Workshop on the Environmental Aspects of Non-Ferrous Metals Industries, WHO UN Environmental Programme.

130/ Saltzer, E.I., and J.W. Wilson, "Allergic Contact Dermatitis Due to Copper", Arch. Derm. 98:375-376, 1968.

from lead, cadmium, antimony, selenium, berillium, and especially arsenic. All the authors who have reported increased incidence of lung cancer among workers in copper smelters have suggested that arsenic trioxide in dust and fumes was the culprit.131/132/133/134/

SO_2 can also be considered to be a potentially harmful chemical in the working environment. Its detrimental effect on human health appears at concentrations as low as 0.5 mg/m^3, although its odor can only be detected at 2.6-3 mg/m^3. Substantial irritant effects appear at 20 mg/m^3. Other chemicals and substances (such as humidity and dust) appear to have a synergistic effect in combination with SO_2.

131/ Kuratsune, M., S. Tokudome, T. Shirakusa, M. Yoshida, Y. Tokumitsu, T. Hayano, and M. Seita, "Occupational Lung Cancer among Copper Smelters", Int. J. Cancer 13:552-558, 1974.

132/ Lee, A.M. and J.F. Fraumeni, Jr., "Arsenic and Respiratory Cancer in Man: An Occupational Study", J. Nat. Cancer Inst. 42:1045-1052, 1969.

133/ Milham, S., Jr. and T. Strong, "Human Arsenic Exposure in Relation to a Copper Smelter", Environm. Res. 7:176-182, 1974.

134/ Tokudome, S. and M. Kuratsune, "Cohort Study on Mortality from Cancer and Other Causes among Workers at a Metal Refinery", Int. J. Cancer 17:310-317, 1976.

5. LEAD

5.1 Introduction

Lead has a wide variety of industrial applications. In 1979 lead was used in the western world for the manufacturing of batteries (48 per cent), cable sheathing (7 per cent), sheets and pipes (9 per cent), alloys (8 per cent), gasoline additives (8 per cent), and other products (20 per cent).[135]

In many countries lead additives for gasoline are still allowed. Consequently, in those countries, lead additives account for a higher percentage of total lead consumption (e.g. 18 per cent in the UK in 1976,[136] Programs for phasing out lead additives are underway in many countries. This factor has resulted overall in a relatively stagnant market for lead, even though lead is still vital for some technical applications for which no substitute materials yet exist. The overall refined lead production in 1985 was some 5.6 million metric tons. Only 63 per cent of this figure came from mining and subsequent extraction operations (primary lead) whereas the remaining 37 per cent came from recycling scrap material, mainly batteries, cables, and pipes (secondary lead).[137]

Lead is contained in a number of minerals such as galena (PbS), carrusite ($PbCO_3$) and anglesite ($PbSO_4$). Galena is by far the main source. The most important lead mines are located in the USA, Australia, Mexico, USSR, Peru, Canada, Yugoslavia, Bulgaria, Japan, Spain, China, Sweden, Morocco, and South Africa. Other mines and commercial deposits are known in more than fifty countries, although in some of them (such as in the UK, France and Belgium) the extracted ore is too low in lead content for smelting and must be mixed with imported concentrated ore prior to smelting.

5.2 Primary lead production processes and pollutants produced

Primary lead production includes mining, ore processing, smelting and refining. Not all operations are necessarily carried out by one single company, although the industry tends to be dominated by a few companies which are fully integrated from mining to marketing. Some 9 per cent of the total 18,000 tons/year of lead emissions generated in the USA is attributed to the primary lead production industry.[138]

135/ "Environmental Aspects of Selected Non-Ferrous Metals Industries", UNEP, Industry and Environment Overview Series, 1984.

136/ Atkins, M.H. and J.F. Lowe, The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979.

137/ Lead and Zinc Statistics, 1976-1979, Monthly Bulletin of the International Lead and Zinc Study Group, London SW1A 1LD, England, Vol. 20, No. 3, March 1980.

138/ Davis, W.E., Emission Study of Industrial Sources of Lead Air Pollutants 1970, United States Environmental Protection Agency, Document APTD-1543, 1973, pp. 1/123.

5.2.1 Mining

The main products of lead mine production are mixed ores and lead ores. Mixed ores are those ores which contain high percentages of other metals, mainly zinc. For example the Tochibore and Mozumi mines in Japan produce ore with a Zn/Pb ratio between 12 and 14. Worldwide, mixed ores are by far the most important accounting for 62.9 per cent of lead concentrate production in 1976. The corresponding figure in 1957 was 80.7 per cent, which shows the growing relevance of lead ores, possibly caused by the depression of the zinc market.[139/] Conversely, in the USA the lead ore production accounts for 86 per cent of the total. The lead content in the ore is normally between 3 and 8 per cent, but ores with lower lead content may be also economically processed.

Most primary lead is produced by underground mining methods (such as stoping systems, and cut-and-fill, room-and-pillar methods). The main environmental problem associated with this operation is ground or surface water pollution. This is caused by the water contained in the rocks or introduced during the mining operations. Water may contact some oxidized material and become contaminated with dissolved metals and acids. In addition this water may contain oil, grease, and residual organics from incomplete explosions, and dust. Air may also be contaminated with dust. Fortunately most mines are underground and this problem has usually limited environmental impact.

5.2.2 Ore processing

Ore processing consists of a series of operations for the physical separation of the ore into lead concentrate, zinc concentrate (for mixed ores), and tailings, as shown in figure 5.1.[140/]

After rough crushing (usually carried out at the mine site) the mined ore is wet ground in ball or rod mills to a fineness which depends on the degree of dispersion of the metal ore in the rock. After the addition of flotation agents the ore undergoes flotation. This operation may also consist of step-wise flotation, re-grinding, and addition of a different flotation agent if more than one metal ore must be recovered. Each different concentrated ore is separately floated off by air sparging in the presence of a specific flotation agent. Later, each metal concentrate is separated from the process water in settlers, recovered, and dried for further processing. One of the major environmental problems at this stage is the disposal of the process water and tailings, which consists of a slurry of finely divided material containing different reagents. This waste stream is usually impounded. An

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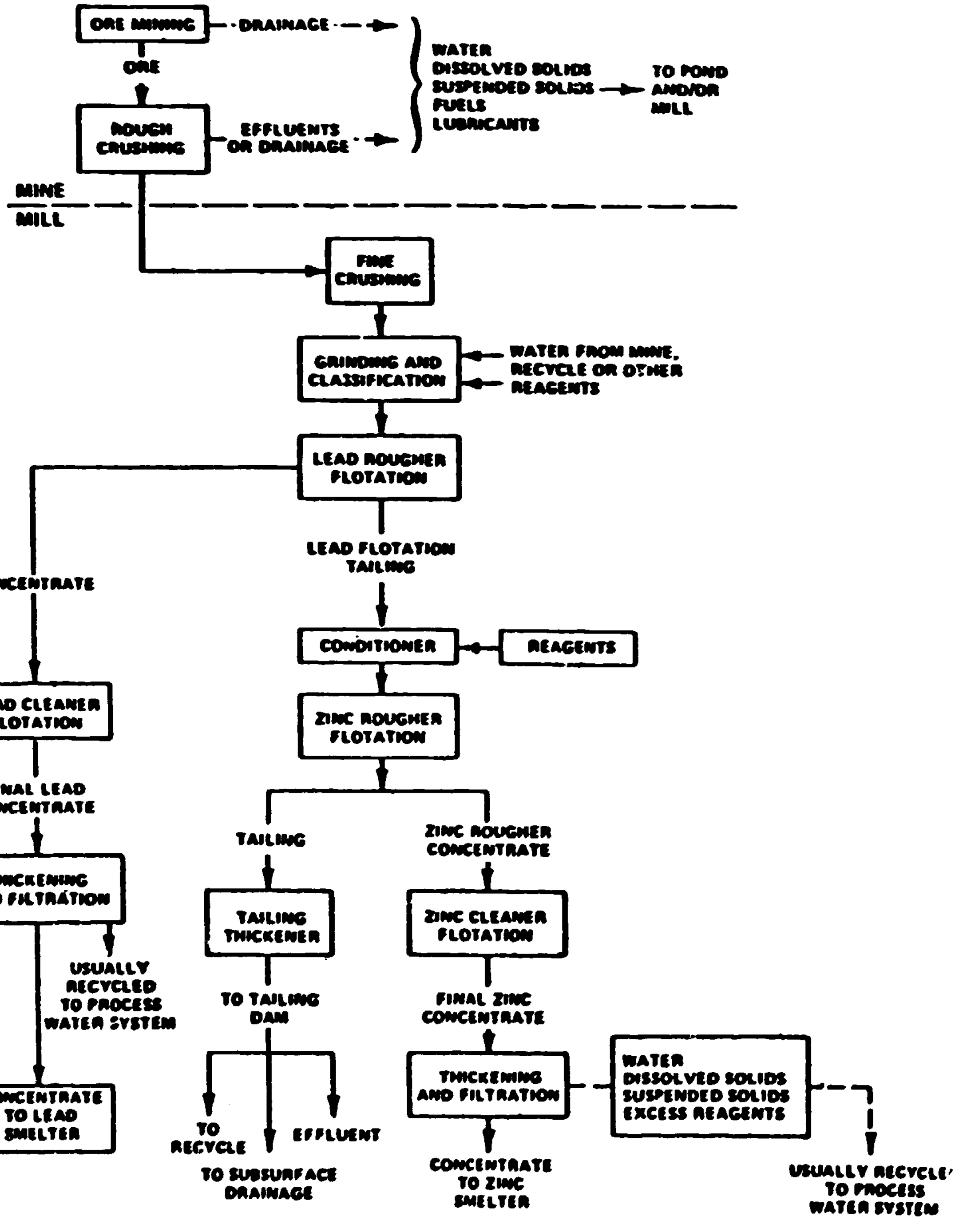
139/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy and Environmental Control, John A. Wright: Lead Industries into the 1980's, AIME, New York, 1979.

140/ "Development Document for Interim Final and Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry", United States Environmental Protection Agency, EPA 440/1-75/061, Vols. I and II, Washington, D.C., October 1975.

Figure 5.1. Typical lead zinc ore milling operation



Source: "Development Document for Interim Final and Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry", United States Environmental Protection Agency, EPA 440/1-75/061, Vols. I and II, Washington, D.C., October 1975.

environmental impact may be caused by the loss of ore concentrates during transportation. This operation is commonly carried out with trucks or barges. Some of the finely ground, dried ore may be blown as dust into the air.

5.2.3 Lead ore concentrate smelting

The lead concentrate which is obtained from the previous operation typically contains 66-70 per cent lead, 4-5 per cent zinc, plus various amounts of silver, antimony, copper, bismuth, and other metals.[141/] The moisture content of the concentrate is usually a few per cent in order to control dust formation, but not more than 12 per cent. The purpose of the smelting operation is to convert the PbS present in the concentrate to metallic lead, and remove part of the initially contained impurities. The almost universal smelting process adopted today is the roast sintering-blast furnace reduction process. It consists of the charge preparation, followed by roasting in sintering machines, and final PbO reduction in blast furnaces. A schematic diagram of the process is shown in figure 5.2.[142/] The earlier method consisting of roasting the galena to oxide, sulphate and the lead metal in reverberatory furnaces has been completely abandoned and will not be discussed.

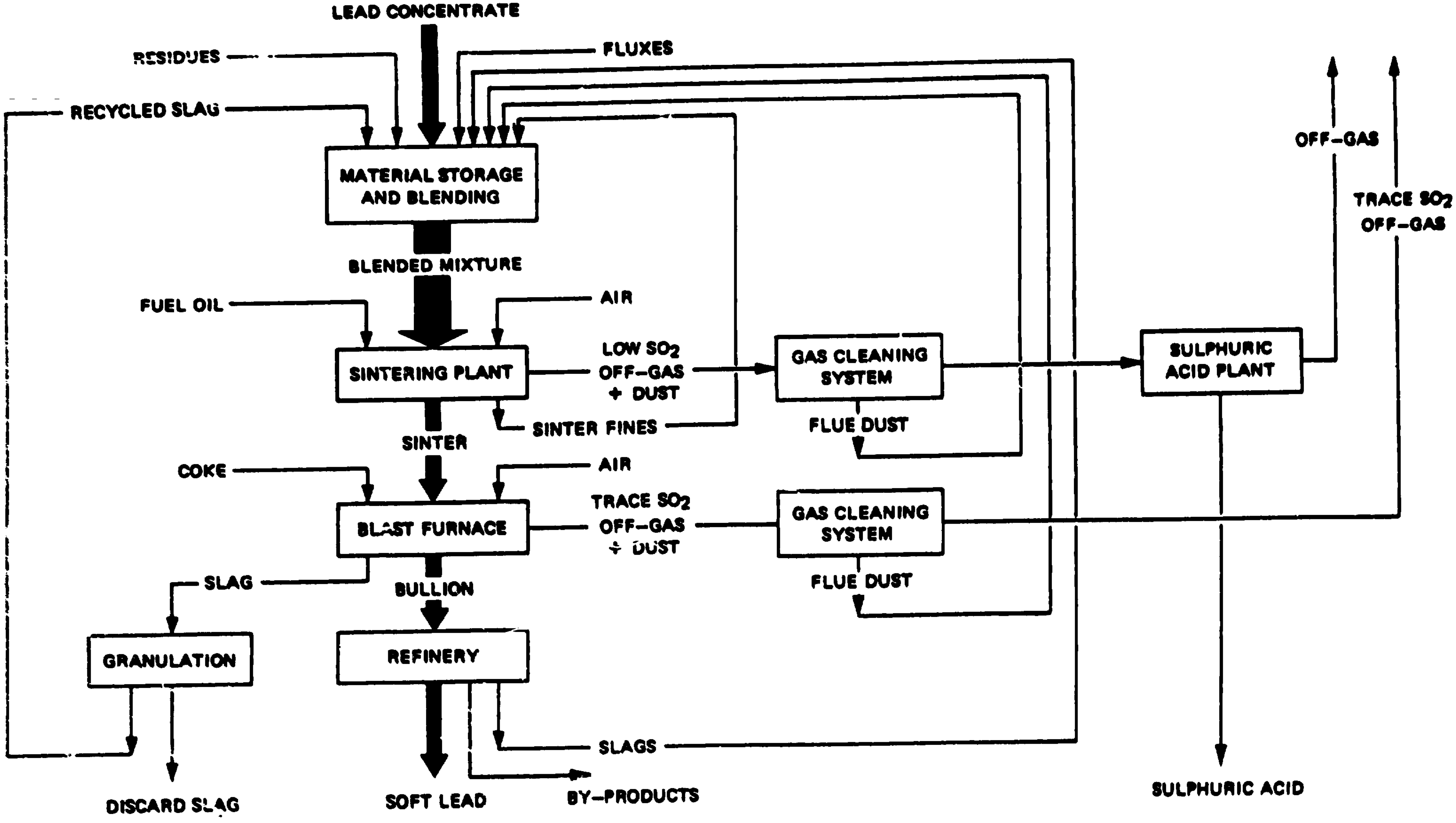
Charge preparation

The lead concentrate is added with fluxes (made of silica sand, iron ore, and limestone) plus other recycled material from subsequent operations (such as ground blast furnace slag, flue dust, refinery slag, sinter fines) and mixed in a mixing drum. This preparation will 1) lower the charge sulphur content so that during the following roasting operation the resulting product will have a sulphur content less than 3 per cent, 2) recover most of the lead otherwise lost during the subsequent operations, and 3) prepare a suitable feed for sintering.

141/ "Environmental Impacts and Controls in the Extraction and Production of Lead, Zinc and Cadmium", UNEP Workshop, Geneva, 13-16 April 1981.

142/ "Compendium on Low- and Non-Waste Technology", Continuously Operating Direct Lead Smelting Processes (QSL), United Nations Economic and and Social Council, 22 February 1984.

Figure 5.2. Flow diagram of conventional technology, blast furnace process



Source: "Compendium on Low- and Non-Waste Technology", Continuously Operating Direct Lead Smelting Processes (QSL), United Nations Economic and Social Council, 22 February 1984.

Roast sintering

This operation consists mainly of the oxidation of the lead sulphide ore. The physical chemistry of the process is rather involved.[143] An oversimplified reaction representing this step is:

$$Pb + 3/2\ O_2 \longrightarrow PbO + SO_2$$

Because of the dilution of the concentrated ore during the charge preparation step the feed to the sintering apparatus contains only 45-50 per cent lead and 5-7 per cent sulphur. For each ton of lead concentrate fed some 3,000-5,000 tons of slag, dust, and flux must be recycled.[144]

The sintering machine consists of a grated, travelling-belt conveyor, onto which the feed is loaded and ignited. Air is blown through the grate producing the oxidation (termed roasting) of PbS. During this whole operation the temperature is always kept below the melting point of the solid, which tends to agglomerate (sinter), and finally tumbles in a collection bin. The sinter product typically contains about 50 per cent lead and 1.7-2 per cent sulphur.

Two sintering machine designs are commonly employed: down-draft and up-draft. The former is older and is being slowly phased out by the up-draft type. Up-draft equipment can generate off-gases with a much higher average SO_2 content (between 4 and 5 per cent).[145] The main environmental problems associated with sintering are the emissions of SO_2, dust, and fumes. The problem is worsened by the presence of volatile heavy metals which may be entrained by the off-gases and later condense.

Blast furnace reduction

The sinter product is a lumpy, porous material. After being crushed to the desired size it is premixed with coke (as reducing agent) and fed to a blast furnace. Air is blown into the furnace. Lead and other nobler metal oxides are reduced to their metal form producing lead bullion. Zinc and iron remain in their oxide form and form the slag, together with the flux, which contains a low percentage of lead (1.5-2.5 per cent).

The off-gases contain mainly SO_2 as gaseous pollutant in a very low concentration (between 300 and 2,500 ppm).[146] These gases also contain fumes and dusts.

143/ "Lead-Zinc-Tin '80" TMS-AIME World Symposium on Metallurgy and Environmental Control, G. Wills: The Physical Chemistry of Lead Extraction, AIME, New York, 1979.

144/ Compendium on Low- and Non-Waste Technology", Continuously Operating Direct Lead Smelting Processes (QSL), United Nations Economic and and Social Council, 22 February 1984.

145/ *Ibid.*

146/ "Environmental Impacts and Controls in the Extraction and Production of Lead, Zinc and Cadmium", UNEP Workshop, Geneva, 13-16 April 1981.

5.2.4 Lead bullion refining

The molten lead tapped from the blast furnace has a temperature of about 1,150°C. At this temperature the molten phase is a very good solvent and many metals dissolve in it (such as Cu, Fe, Ni, Co, Zn, As, Sb, Sn, In, Ag, Au, Bi). The concentration of these impurities may vary from ppm to per cent levels. The impurities are usually removed from the lead bullion, because of their value. They are always removed in groups.

The first refining operation is carried out during the cooling of the lead bullion, producing the solidification and separation of Cu, Fe, Ni, Co and Zn in a floating solid which may be skimmed off. Because copper is the most abundant element this operation is called copper drossing.

A second group of elements (As, Sb, Sn and In) is removed during the subsequent softening operation (these elements are responsible for hardening lead). This operation is conducted in a reverberatory furnace by air injection at 600°C. These elements oxidize and are separated as slag. Metals nobler than lead (Ag, Au and Bi) are removed by precipitation as intermetallic compounds upon addition of reactants (such as zinc) which must be then removed by oxidation. The final purification step is carried out with caustic soda plus an oxidizing agent. A diagram of the refining operations is shown in figure 5.3.[147/] The main environmental hazard at this stage is created by the emissions containing heavy metals fumes. Electrolytic lead refining is an alternative refining process. It consists of using the impure lead as anode in an acid solution through which direct current is passed. In such a case the environmental hazard is created by the acid mist which may be generated during the refining operation.

5.3 Pollution control technologies for lead production plants

5.3.1 Pollution control during mining

Underground mines are always equipped with a ventilation system which must be capable of bringing fresh air from the outside and, at the same time, sufficiently diluting the spent air containing dust and fumes from mining operations. Dust formation may be limited by spraying water on the rocks or ore prior to each operation. Wastewater produced during mining can be processed in a treatment plant to remove at least the suspended solids and partially recycled. In arid regions the paucity of water may exacerbate the problem and a good water management plan is a must. A good example of this is provided by the Mount Isa Mines Ltd. in Australia. Here a complex system for

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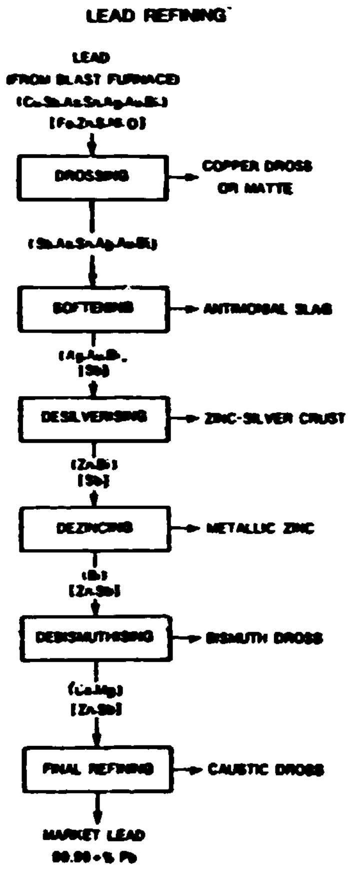
[147/] "Lead-Zinc-Tin '80" TMS-AIME World Symposium on Metallurgy and Environmental Control, T. Davey: The Physical Chemistry of Lead Refining, AIME, New York, 1979.

Figure 5.3. Lead refining



Source: "Lead-Zinc-Tin '80" TMS-AIME World Symposium on Metallurgy and Environmental Control, T. Davey: The Physical Chemistry of Lead Refining, AIME, New York, 1979.

water collection, pumping and distribution exists which supplies water to all individual demand points.[148] The opposite problem arises in those mines where water is present in rocks and must be pumped away. It is likely that this water will be acidic and contaminated with dissolved metal salts. Therefore water treatment must be provided. Water treatment in such a case consists of a pH adjustment with lime which precipitates the heavy metals. Upon the addition of coagulants a sludge is formed and then collected in thickeners. The thick sludge is then pumped away and disposed of in lagoons.[149]

5.3.2 Pollution control during ore processing

Air pollution during frothing operations is usually negligible. Dust may be a problem during all the remaining operations involving dry solids handling. Dusty solids may be stored in closed or protective structures to prevent blowing off. During transport on trucks or barges the concentrated ore should be covered in order to avoid the same problem. High concentrations of ore dust in the air (up to 100 meters in height) have been measured along the roads where there is a heavy traffic of loaded trucks.[150] In order to ease the problem the ore may be shipped with a 10-12 per cent moisture content to the smelting plant.[151]

Water pollution can be a serious problem because of the presence of flotation agents and tailings. Whenever possible recycling should be adopted. In many mines mine water is used for subsequent operations such as milling and flotation. Waster water slurries containing tailings can be disposed of in three possible ways: underground, in tailings ponds, and in seas. Underground disposal is adopted by many companies. This method consists of pumping the slurry back to the spaces left empty from mining operation, sometimes with the addition of cement. This method has the lowest environmental impact.

Impoundment in tailings ponds creates a potential environmental impact because of possible leaks of contaminated water into the ground. In practice, because of the potential acidic water leakage problem the lead/zinc industry in the USA has been rated second (exceeded only by the uranium industry) in

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148/ "Operations at Mount Isa", Mount Isa Mines Limited Australia, 1977.

149/ "Processes, Procedures, and Methods to Control Pollution from Mining Activities", United States Environmental Protection Agency, EPA 430/9-73-011, Washington, D.C., October 1973.

150/ Hemphill, D.D., "Lead Contamination Along Roadways", in Lead in the Environment, Boggess, W.R. and Wixon, B.G. (ed.), Natl. Sci. Foundation, NSF/RA-770214, Washington, D.C., 150, 1977.

151/ "Environmental Impacts and Controls in the Extraction and Production of Lead, Zinc and Cadmium", UNEP Workshop, Geneva, 13-16 April 1981.

terms of the toxic hazard rating for land disposed wastes.[152]/[153]/ Once the water has evaporated the tailings may be subjected to wind action and dust may be blown off. Consequently the area should be stabilized with some kind of vegetation. In some cases, such as arid regions, where this would be impossible the problem has been overcome by spreading rocks over the dried tailings. This system has been successfully used in Australia.[154]/

Marine disposal of tailings is seldom used. However one example is the Greenex Black Angel mine in Greenland. Here the tailings are stabilized with lime and then disposed of in a fjord nearby.[155]/

5.3.3 Pollution control during concentrate smelting

Pollution control during charge preparation

Fugitive dust emissions can be a serious problem because of the high lead content. They can be controlled by wetting the material, or use of effective dust collection devices. Moisture in the charge should never fall below 8 per cent. The collected emissions can be treated in a wet scrubber in order to recover the dust which can then be recycled.

Pollution control during roast sintering

SO_2 and dust emissions are the main problems at this stage. Most up-draft sinter machines are capable of producing off-gases with SO_2 concentrations of at least 4 per cent, suitable for conversion to H_2SO_4 in an acid plant (see chapter on copper for details). This concentration is achieved by recycling gases more dilute in SO_2 through the machine until a sufficiently concentrated gas stream is produced.

Off-gases from down-draft machines are too dilute for effective SO_2 removal. Consequently they are vented. The off-gases are cooled and processed through bag filters, electrostatic precipitators, or wet scrubbers to collect dust emissions. Cooling condenses the heavy metals. Otherwise condensation of heavy metals can occur within the stack or in the stack plume, with subsequent fallout and environmental pollution. If wet scrubbers are used water will also be contaminated with heavy metals and will require

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152/ "The Health and Environmental Impacts of Lead on an Assessment of a Need for Limitations", Office of Toxic Substances, United States Environmental Protection Agency, EPA-560/2-79-001, Washington, D.C., April 1979.

153/ "Environmental Impacts and Controls in the Extraction and Production of Lead, Zinc and Cadmium", UNEP Workshop, Geneva, 13-16 April 1981.

154/ Ibid.

155/ Greenland Fisheries Investigations, Recipient andersogeke ued Marmorilik, 1980, 1979, 198, 1977, 1976, Ostervaldgade 10, 1350 Kobenhaven, K. Denmark (In Danish with summary in English and Greenlandic).

treatment prior to discharge (such as lime addition for heavy metal precipitation). The concentration of the main pollutants in the wastewater stream produced by a smelting plant is given in table 5.1.[156]

Table 5.1. Pollutant concentration in waste water from lead smelting plant

	Number of		Concentration, mg/L		
Pollutant	Analyses	Times detected	Range	Median	Mean
COD	3	2	ND* - 170	3.7	58
TOC	1	1		3.3	3.3
TSS	1	1		26	26
Total phenol	2	2	0.012 - 0.050		0.031
Ammonia	2	2	0.43 - 3.8		2.1

*ND = not detectable

Source: EPA Treatability Manual, Vol. II, Industrial Descriptions, United States Environmental Protection Agency, July 1980.

Pollution control during blast furnace reduction

The gases from the furnace are usually passed through a boiler in order to recover waste heat. During this phase some metals may condense and be recovered. The gases can then be cleaned from the dust by passing them through bag filters. The collected dust can be recycled. The sulphur which was contained in the sinter material fed to the blast furnace also goes into the gas stream as SO_2, but the SO_2 concentration is too low for removal. Consequently the gases are diluted with fresh air (also used as ventilation air) before de-dusting and then sent to the stack. Some 10 per cent of the total potential SO_2 emissions come from this source.

The waste slag produced during this operation and the sintering process is usually disposed of in a land disposal site.

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[156] EPA Treatability Manual, Vol. II, Industrial Descriptions, United States Environmental Protection Agency, July 1980.

5.3.4 Pollution control during lead bullion refining

The refining operations are usually carried out at relatively low temperatures. The only environmental hazard comes from the fumes which may originate. They contain lead and, in some cases, metals such as bismuth, cadmium, hallium, and arsenic as the main pollutants. Large volumes of ventilation air are usually used. This air is passed through bag filters before venting.

In electrolytic lead refining the main hazard is arsenic trioxide evolving from the bath into the off-gases. Therefore cooling must be provided to condense the arsenic trioxide before the gases are sent to the bag filters.

5.4 Potential for by-product re-use

The waste rocks generated during ore processing are considered useless and constitute a major disposal problem, especially because of the quantity produced (the waste to metal ore ratio is some 56 per cent).[157] In addition, the slag from the smelting operations cannot be re-used (as is done for other metals) because of the high content of heavy metals. This makes it impossible to use this waste as road construction or snow and ice control material because of the potential dust generation and the associated environment problems. On the other hand the slag may contain zinc which can be recovered as zinc oxide. Zinc is also very often contained in the initial ore. It is recovered by flotation and then processed as described in the zinc chapter.

Several valuable metals are usually present in the lead ore in appreciable amounts. After the smelting operation the copper bullion contains copper in concentrations ranging from a few tenths of a per cent to several per cent. Silver is contained in the range of 0.1-0.5 per cent, sometimes as high as 1 per cent. The gold concentration is typically only a small fraction of the silver concentration.[158] All these metals are recovered during the lead bullion refining operations.

5.5 Lead recycling (secondary lead production)

Recycling is a very important source of lead, accounting for some 40 per cent of total lead production worldwide. The scrap material comes from a number of sources such as cable coverings, babbit (an alloy coming from machine bearing lining), discarded parts, pipes, low-grade drosses, and skimming from metal processing. However, the most important source of secondary lead is old batteries, accounting for 70-80 per cent of the total secondary lead production.

157/ "Environmental Impacts and Controls in the Extraction and Production of Lead, Zinc and Cadmium", UNEP Workshop, Geneva, 13-16 April 1981.

158/ "Lead-Zinc-Tin '80" TMS-AIME World Symposium on Metallurgy and Environmental Control, T. Davey: The Physical Chemistry of Lead Refining, AIME, New York, 1979.

Secondary lead smelting consists mainly of processing the scrap in reverberatory, rotary or blast furnaces. A block diagram for the process is given in figure 5.4.[159]

The scrap material is first sorted into clean lead, which requires little refining, and more impure lead which undergoes full processing. Batteries must be broken apart in order to remove the cases from the lead or lead oxide plates. During this phase sulphuric acid is released from the batteries and must be recovered. Mechanized plants now exist which break apart the cases and separate the lead material in fully sealed conditions. In some plants the batteries are directly loaded to a new type of furnace, thus eliminating the breaking phase altogether.

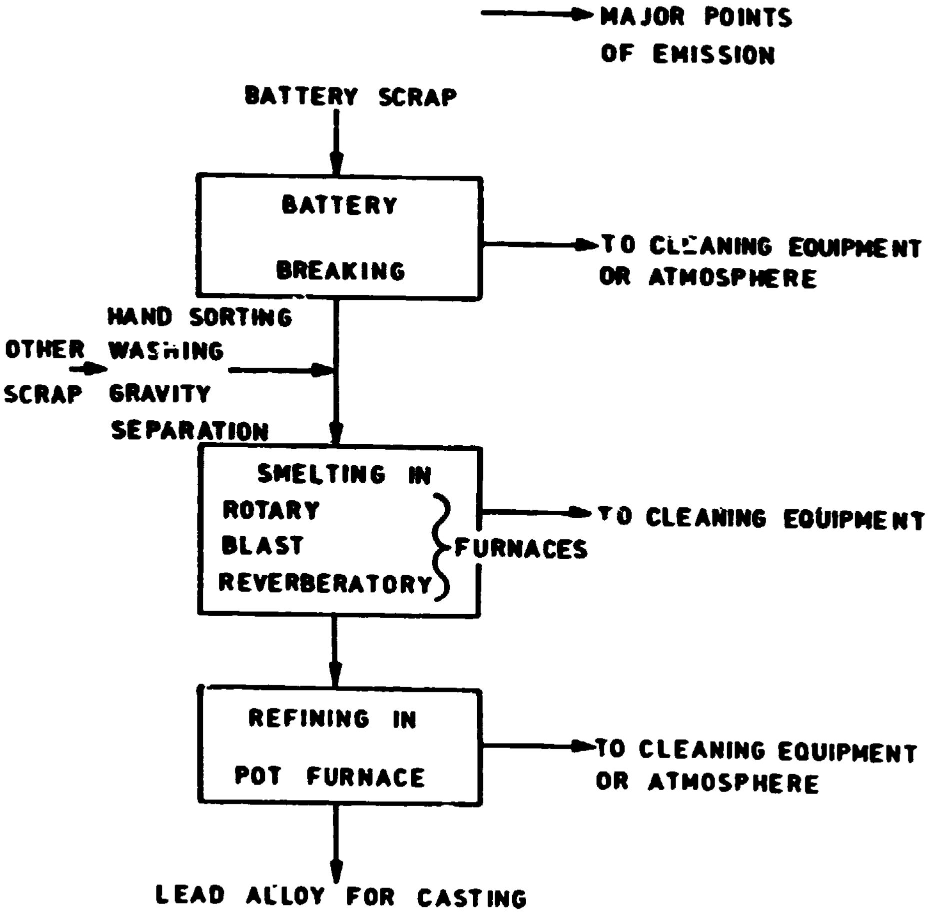
After sorting, the scrap is loaded to a suitable furnace. High-grade scrap is used for the production of soft lead (which does not contain antimony) using reverberatory furnaces. The antimony present in the scrap is oxidized and goes into the slag. Rotary and, more often, blast furnaces are used for low-grade scrap. Coke is charged as reducing agent. High temperatures are required not only for melting, but also for reducing the lead oxide present in the scrap. The product of this process is hard lead containing some 8 per cent antimony and other impurities. Hard lead then undergoes softening and impurity refining in reverberatory furnaces where antimony and other metals are oxidized. Further refining operations may follow, as described in the previous sections.

Several environmental problems are encountered during secondary lead production. During scrap washing or flotation operations water can be contaminated and must be recycled or treated before being discharged. Water may become contaminated during Venturi scrubber operations as well. The typical pollutant content in the wastewater from secondary lead production facilities is reported in table 5.2.[160] The water from the battery breaking process will also be contaminated with sulphuric acid and will require neutralization with soda or lime.

159/ Atkins, M.H. and J.F. Lowe, The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979.

160/ EPA Treatability Manual, Vol. II, Industrial Descriptions, United States Environmental Protection Agency, July 1980.

Figure 5.4. Secondary lead smelting



Source: Atkins, M.H. and J.F. Lowe, The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979.

Table 5.2. Conventional and nonconventional pollutants in the secondary lead subcategory

	Number of		Concentration, mg/L		
Pollutant	Analyses	Times detected	Range	Median	Mean
COD	3	3	65 - 220	150	145
TOC	3	3	4 - 130	70	68
TSS	4	4	0.06 - 3,700	760	1,300
Total phenol	4	4	0.004 - 0.012	0.010	0.009
Oil and grease	3	3	6.4 - 40	35	27
Ammonia	1	1		12	12
Chloride	1	1		79	79

Source: EPA Treatability Manual, Vol. II, Industrial Descriptions, United States Environmental Protection Agency, July 1980.

Plants where battery burning is carried out must be equipped with an afterburner to provide complete combustion of plastic materials. However some difficulties have been experienced with battery cases made of PVC or polypropylene.161/ Emissions from furnaces depend on type of scrap material charged, type of furnace, furnace temperature, and amount of air admitted. The emissions consist primarily of lead and lead oxide dust or fume. Antimony, arsenic, and cadmium dusts may also be generated. The incomplete combustion of battery cases may result in smoke evolution. Sulphur compounds may also be emitted as a result of the sulphuric acid present in the batteries.

Because of the heavy metal content, dusts and fumes must be removed almost completely. This is usually done in bag filters, electrostatic precipitators, or wet scrubbers. Baghouses are the most common choice. Sometimes off-gases are cooled prior to dust removal. The gases are then vented through a stack. SO_2 emissions, if any, go often untreated. If wet Venturi scrubbers are used then the water may absorb some sulphur dioxide. The slag formed in the furnaces must be disposed of and cannot be re-used

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161/ "Environmental Aspects of Selected Non-Ferrous Metals Industries", UNEP, Industry and Environment Overview Series, 1984.

because of the high heavy metal content. Large volumes of ventilation air are used throughout the whole process including refining (only low level emissions occur at this stage). This air can be processed through bag filters or cyclones prior to venting.

5.6 Retrofitting of existing plants to reduce pollution

The main environmental hazards posed by lead production facilities are SO_2 and dust emissions. Both can and have been successfully reduced in the past in existing plants. The first step in removing SO_2 from off-gases consists of changing the concentrated ore roasting technology by switching from down-draft to up-draft sintering machines. Then off-gases can be produced which are amenable to SO_2 removal. For those plants that are located in remote areas (sulphuric acid would be too costly to transport), it is possible to deliberately produce very diluted SO_2 gas streams which can then be dispersed by a tall stack. It is, however, well known that such lead smelters create pollution problems in the surrounding areas. For example, in one case air pollution extended for about five kilometers from the smelting site whereas soil pollution was detected for more than ten kilometers.[162/163/] Similarly, air and soil pollution around the Mezica mine and smelter (Yugoslavia) extended as far as ten kilometers and seven kilometers respectively.[164/165/]

In 1974 the United States Environmental Protection Agency examined the six major lead production plants in the USA. They estimated that the economic impact of bringing them within federal control standards was expected to be 51 million dollars (although three of the plants were already equipped with acid plants).[166/] This shows that also in this case pollution control is possible if sufficient resources are devoted to this purpose.

As for particulate emissions, existing plants can be relatively easily equipped with bag filters and other dust collecting equipment which can remove nearly 100 per cent of dust and fumes from off-gases.

162/ "Lead", Environmental Health Criteria 3, WHO, Geneva, 1977.

163/ Landrigan, P.J., S.H. Gelbach, B.F. Rosenblum, J.M. Shoults, R.M. Candelaria, W.F. Barthel, J.A. Liddle, A.L. Smrek, N.W. Staehling, and J.F. Sanders, (1975b) "Epidemic Lead Adsorption Near an Ore Smelter; The Role of Particulate Lead", New Engl. J. Med., 292:123-129.

164/ Djuric, D., Z. Kerin, L. Graovac-Leposavic, L. Novak, and M. Kop, Environmental Contamination by Lead from a Mine and Smelter; A Preliminary Report, Arch. Environ. Health, 23:275-279, 1971.

165/ Kerin, Z., Lead in New-Fallen Snow Near a Lead Smelter, Arch. Environ. Health, 26:256-260, 1973.

166/ The Cost of Clean Air, United States Environmental Protection Agency, 1974.

5.7 Innovative and emerging production technologies

Although the traditional smelting process in the lead industry is blast furnace smelting, several other new processes exist such as the QSL, the Outokumpu flash smelting, the Imperial smelting furnace, the Kivcet process and the Boliden electric furnace.

5.7.1 QSL process

This process has been developed for sulphide ores (such as galena) as well as sulphate ores, mixed ores, flue dusts, and other residues. The lead ore concentrate needs only a relatively simple preparation before being fed to the QSL smelter. The concentrate is mixed with flue dust and flux, and then pelletized. Very little dust is generated at this stage in comparison to the traditional feed preparation.

The QSL smelter consistsd of a horizontal cylinder lined with refractory bricks.[167] The charge is continuously fed to the oxidation zone where it rapidly dissolves in the molten bath kept at 950-1,000°C. The partial oxidation of the PbS is caused by the oxygen-enriched air injected into the smelter, producing primary lead bullion, lead oxide (which goes into the slag) and SO_2. The slag flows into the reduction zone of the smelter where pulverized coal (as reducing agent) is injected. The temperature here is higher (1,250°C), thus providing the conditions for reducing the lead oxide to secondary lead bullion. Both bullions are tapped as well as the slag. The SO_2 generated during the process has a concentration in the off-gases of about 15-25 per cent against the 5-6 per cent of a traditional up-draft sintering machine. The main advantages of this process over the conventional process are the following:[168]

- Low capital and operating costs;
- Continuous process;
- Reduced amount of flux required;
- Low volume of off-gases produced;
- High concentration of SO_2 produced.

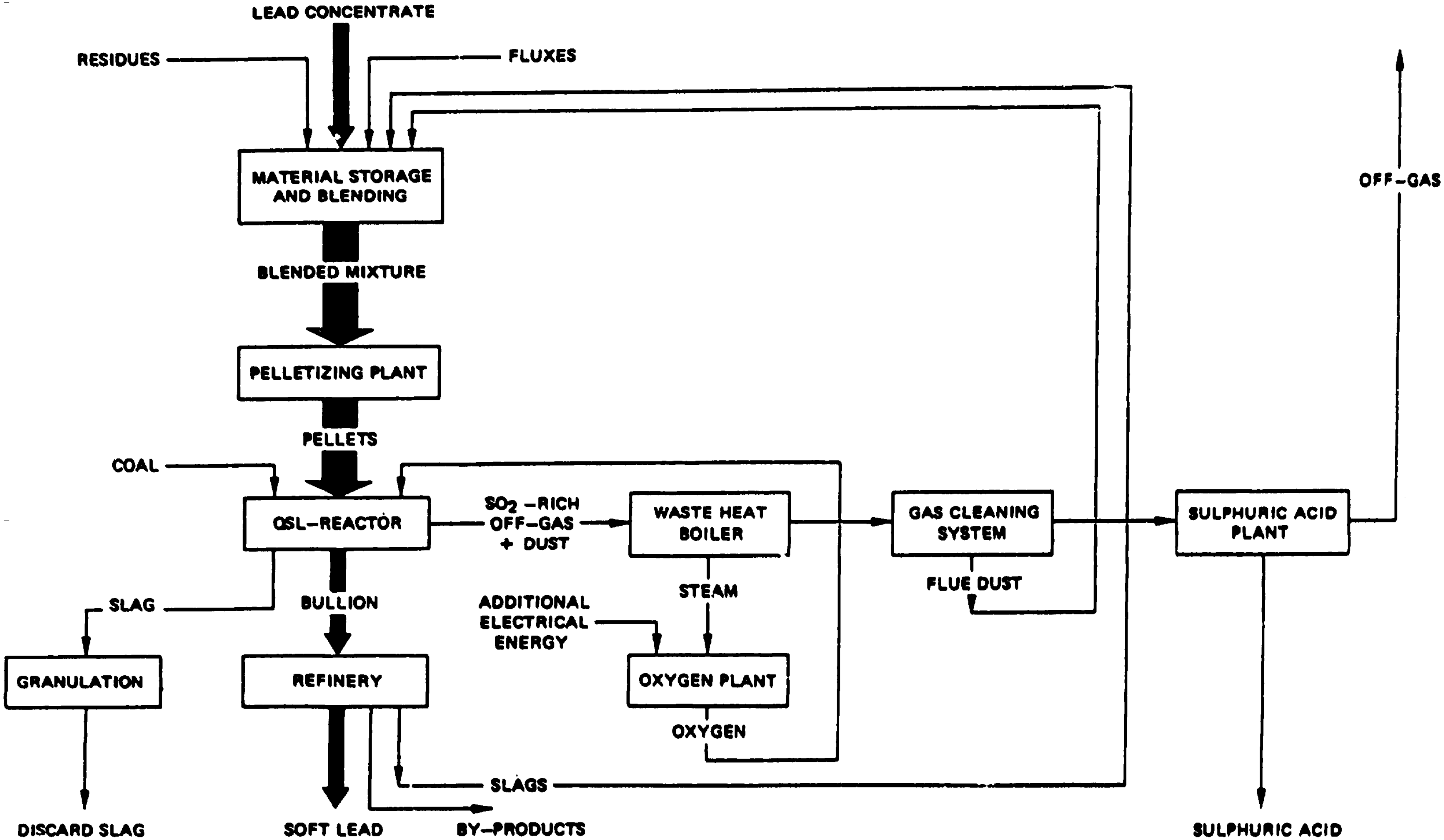
So far only a semi full scale plant with a capacity of 40,000 tons/year of lead bullion has been built. A block diagram for the process is given in figure 5.5.[169]

167/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy and Environmental Control, W. Schwartz, P. Fischer, P. Queneau and R. Schuhmann, Jr.: QSL - A Continuous Process for Environmentally Clean Lead Production, AIME, New York, 1979.

168/ Compendium on Low- and Non-Waste Technology", Continuously Operating Direct Lead Smelting Processes (QSL), United Nations Economic and and Social Council, 22 February 1984.

169/ Ibid.

Figure 5.5. Flow diagrams of low- and non-waste technology (QSL process)



Source: "Compendium on Low- and Non-Waste Technology", Continuously Operating Direct Lead Smelting

5.7.2 Outokumpu flash smelting

This process is the adaptation to lead smelting of the process originally developed for copper smelting. With this process the traditional separate roasting and smelting operations are replaced by one operation carried out in a single unit.

The ore concentrate is first premixed with flux, and recycled flue dust. Then it is dried and injected in the flash furnace together with oxygen-enriched air. Each particle is surrounded by hot gases and melts, producing lead bullion particles, slag particles and SO_2. Because of the rapid exothermic oxidation reaction the temperature can be maintained at 1,300-1,400°C without any addition of external heat. The particles then settle on the bottom of the furnace where separate lead bullion and slag layers are formed and continuously tapped. The furnace off-gases contain SO_2 in extremely high concentration (some 85 per cent). The gases are sent to a waste heat boiler and then passed on to de-dusting equipment. The dust is recycled back to the furnace.

Some 90 per cent of the lead input is recovered as lead bullion. The remaining 10 per cent goes into the slag, which has a lead content between 15 and 45 per cent. In order to recover this oxidized lead an additional electric furnace is used where powdered coal is injected. Lead bullion is produced and tapped. The slag formed contains only 2 per cent lead and is discarded.[170/] No commercial plants exist at the moment, but the process appears very promising.

5.7.3 Hydrometallurgical processes

Although no full scale industrial unit employing a hydrometallurgical process has been built as yet, research is under way and pilot plants exist which utilize this technology.[171/][172/] The processes are all based on the same principle, namely leaching of the galena with a strong oxidizing agent, ferric chloride, according to the following reaction:

$$2\ FeCl_3 + PbS \longrightarrow 2\ FeCl_2 + S$$

Leaching takes place at a low temperature (90°C) and low pH (0.3) in the presence of HCl. The gangue and the precipitated sulphur are removed by filtration. The saturated solution is cooled down to 20°C to precipitate

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170/ "Compendium on Low- and Non-Waste Technology", Outokumpu Lead Flash Smelting Process, United Nations Economic and Social Council, 22 February 1984.

171/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy and Environmental Control, J. Demarthe and A. Georgeaux: Hydrometallurgical Treatment of Lead Concentrates, AIME, New York, 1979.

172/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy and Environmental Control, M. Wong, F. Haver, and R. Sandberg: Ferric Chloride Leach-Electrolysis Process for Production of Lead, AIME, New York, 1979.

the lead chloride. After drying, the $PbCl_2$ is then loaded to an electrolytic cell containing LiCl and KCl as electrolytes. The electrolysis occurs at 400°C, producing molten lead at the cathode and chlorine gas at the anode. Lead is siphoned away and then further purified. The chlorine gas is fed to a chlorination tower together with the spent solution containing the ferrous chloride. The following reaction takes place:

$$2\ FeCl_2 + Cl_2 \longrightarrow 2\ FeCl_3$$

thus regenerating the oxidizing agent which can be fed back to the beginning of the process.

The main advantages of such a process are:

- Low temperatures involved;

- Limited environmental impact since no lead dust or SO_2 is generated;

- Limited investment costs.

5.8 A case study

The Mount Isa Mines Limited at Mount Isa (Australia) is considered here. The company extracts 2.6 million tons of silver-lead and zinc ore and 4.7 million tons of copper ore per year.[173] The lead smelting operation started in 1931 and presently produces 150,000 tons of crude lead per year. Smelting consists of roast sintering the concentrated ore and blast furnace reduction of the lead oxide from the sintering operation. Originally the plant operated with three (and later eight) down-draft sintering machines. In 1966 they were all replaced by a single up-draft machine which not only increased the plant capacity, but was also the first step in the upgrading of the plant environmental situation. The sinter off-gases were initially cooled and passed on an electrostatic precipitator. Eventually this system was replaced by a shaking baghouse. In 1974 the unit was expanded to two stages containing fourteen sections. These improvements have produced a considerable reduction of lead in the in-plant air, which is now below the 150 microgram/m^3 limit.

As for SO_2 emissions, the company has operated an intermittent control system since 1972. The Mount Isa smelter lies in an arid region, but the closest residential area is only 200 meters away. Consequently the company has allowed the smelting operations to be limited or shut down when the SO_2 concentration in the air in the nearby town exceeded set levels.[174] These levels were equivalent to the United States Environmental Protection Agency air standards for SO_2. In order to reduce the downtime the smelter was

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173/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy and Environmental Control, L. White and R. Marston: Developments in Lead Smelter Hygiene and Environmental Practices at Mount Isa, New York, 1979.

174/ Environmental Impacts and Controls in the Extraction and Production of Lead, Zinc and Cadmium", UNEP Workshop, Geneva, 13-16 April 1981.

equipped in 1978 with a 270 meter-high stack. This has minimized the environmental impact of SO_2 on the urban area, but the SO_2 is simply dispersed over the surrounding region (semi-desert). Evaluations of the various means of reducing SO_2 emissions have indicated that there is no other economically practicable route which the company could follow.[175]

5.9 Pollution control costs

An estimation of the economic impact on primary lead smelters caused by the compliance with strict environmental standards was made by the United States Environmental Protection Agency in 1974.[176] Both dust and SO_2 emission were considered and acid plant costs were included in the estimates. The results for model size plants are given in table 5.3.[177]

Table 5.3. Costs of control for selected model plants in the United States primary lead industry

Model size (tons)	Investment ($US m)			Annualized cost ($US m)			Cost per ton of annual capacity		
	expected	min	max	expected	min	max	expected	min	max
107,000	8.9	4.3	12.5	2.1	1.0	3.0	17.8	8.8	26.3
131,000	9.9	5.1	13.8	2.5	1.2	3.4	17.4	8.3	23.6

Source: Atkins, M.H. and J.F. Lowe, The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979.

The costs are estimated for secondary smelters to be much lower since those plants were in a much more favorable situation from an environmental standpoint. The corresponding figures are given in table 5.4.[178]

175/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy and Environmental Control, L. White and R. Marston: Developments in Lead Smelter Hygiene and Environmental Practices at Mount Isa, New York, 1979.

176/ The Cost of Clean Air, Environmental Protection Agency, 1974.

177/ Atkins, M.H. and J.F. Lowe, The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979.

178/ Ibid.

Table 5.4. Costs of control for selected secondary lead plants

Model tons/day	Investment ($US 000)			Annualized cost ($US 000)			Unit cost $US 1000/ton/day		
	expected	min	max	expected	min	max	expected	min	max
109	305	171	434	68.9	26.3	108.1	0.63	0.24	0.99
54	148	79	218	34.3	11.3	54.4	0.64	0.21	0.99
15.8	59	37	82	15.3	9.3	21.7	0.97	0.59	1.31

Source: Atkins, M.H. and J.F. Lowe, The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979.

A study carried out by Charles River Associates and the Research Corporation of New England for the Lead Industry Association estimated the impact of new air quality standards promulgated by the EPA in 1978 on the lead industry.[179] Proposed compliance with the EPA 1.5 microg/m^3 (90 day average) standard for lead concentration in air was considered economically devastating.[180]

Table 5.5. Impact of attempting to meet EPA ambient air lead standard

Industry sector	Costs ($US)		Plant closings
	Capital	Annual	
Primary smelting	190 million	35 million	All seven
Secondary smelting	285 million	60 million	40 of 50 (90 per cent loss of capacity)

Source: "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy and Environmental Control, J. Cole: United States Environmental Laws and Regulations as Applied to the Lead and Zinc Industries, AIME, New York, 1979.

179/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy and Environmental Control, J. Cole: United States Environmental Laws and Regulations as Applied to the Lead and Zinc Industries, AIME, New York, 1979.

180/ Ibid.

5.10 Emission standards

The World Bank guidelines on pollutant concentrations in the gaseous effluents produced by lead smelters are as follows:[181]

Table 5.6. Presumptive limits for lead works

Sulfur dioxide		
Inside plant fence	Annual arithmetic mean	100 micro/m^3
	Maximum 24-hour peak	1,000 micro/m^3
Outside plant fence	Annual arithmetic mean	100 micro/m^3
	Maximum 24-hour peak	500 micro/m^3
Particulates		
	Annual geometric mean	75 micro/m^3
	Maximum 24-hour peak	260 micro/m^3
Arsenic (as As)		
Inside plant fence	24-hour average	0.006 mg/m^3
Outside plant fence	24-hour average	0.003 mg/m^3
Cadmium (as Cd)		
Inside plant fence	24-hour average	0.006 mg/m^3
Outside plant fence	24-hour average	0.003 mg/m^3
Lead (as Pb)		
Inside plant fence	24-hour average	0.008 mg/m^3
Outside plant fence	24-hour average	0.004 mg/m^3

Source: Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

The limits imposed in the UK depend on the size of the plant, and consequently the amounts of gases emitted. Three classes are considered. The corresponding limits are reported in table 5.7.[182]

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[181] Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

[182] "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy and Environmental Control, A. Barbour: European Economic Community Laws and Regulations as Applied to the Lead and Zinc Industries, AIME, New York, 1979.

Table 5.7. Air pollution limits for lead works, UK

Works category	Gas volume		Individual stack concentration*		Total mass emission*	
	cu.ft./min.	m^3/min.	grains/ cu.ft.	g/m^3	lbs/hour	kg/hour
Class I	>7,000	200	0.05	0.115	0.6	0.27
Class II	7,000-140,000	200-4,000	0.01	0.023	6.0	2.7
Class III	>140,000	>4,000	0.005	0.0115	12.0	5.4

* Measured as elemental lead

Source: "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy and Environmental Control, A. Barbour: European Economic Community Laws and Regulations as Applied to the Lead and Zinc Industries, AIME, New York, 1979.

World Bank guidelines on pollutant concentrations in liquid effluents for primary lead smelters are as follows:183/

Table 5.8. Guidelines for permissible water pollutants from a primary lead smelter (kg/ton product)

	Maximum 24-hour	Consecutive 30-day average
TSS	4.2×10^{-2}	2.1×10^{-2}
Cd	8.0×10^{-4}	4.0×10^{-4}
Pb	8.0×10^{-4}	4.0×10^{-4}
Zn	8.0×10^{-3}	4.0×10^{-3}
pH	6-9 units	6-9 units

Source: Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

183/ Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

For secondary lead smelters the corresponding figures are:[184]

Table 5.9. Guidelines for permissible water pollutants from a secondary lead smelter (kg/ton product)

	Maximum 24-hour	Consecutive 30-day average
TSS	5×10^{-2}	2.5×10^{-2}
Cd	4×10^{-5}	2.0×10^{-5}
Pb	1×10^{-3}	0.5×10^{-3}
As	1×10^{-4}	0.5×10^{-4}
pH	6-9 units	6-9 units

Source: Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

5.11 Health protection for workers

Lead is well known to produce acute and long-term poisoning, especially in workers in the lead industry. Smelting and refining operations have the greatest potential for hazardous exposure. In recent years lead poisoning has decreased noticeably among those workers due to safer handling procedures, better worker protection at the workplace, and automation which has reduced the need for the worker's presence during some production phases.

Lead poisoning occurs by inhalation, ingestion, or absorption through the skin. On the average, 30 ± 10 per cent of inhaled lead is absorbed by the organism. About 5-10 per cent of the ingested lead is also absorbed.[185] The lead so metabolized can cause long term effects since the biological half-time of lead is generally accepted to be longer than ten years.[186] The nervous system is especially affected by lead. Health effects can be correlated to lead concentration in the blood. The present no-detect-effect level for subclinical neuropathy is 40-50 microg/100 ml. Noticeable brain

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184/ Ibid.

185/ "Environmental Health Aspects of Non-Ferrous Metals: Cadmium, Copper, Lead, Nickel and Zinc", UNEP Workshop on the Environmental Aspects of Non-Ferrous Metals Industries, WHO, United Nations Environment Programme.

186/ "Lead", Environmental Health Criteria 3, WHO, Geneva, 1977.

dysfunctions start at a concentration of 60-70 microg/100 ml.[187] In evaluating health effects the following guideline may be useful: if the blood lead level is used as a measure of lead absorption then continuous exposure to 1 microg/m^3 of lead in air would contribute to lead levels of about 1-2 microg/100 ml of blood.[188] For this reason the occupational exposure limit for airborne lead is rather low in most countries. Table 5.10 presents some of these values.[189]

Table 5.10. Occupational exposure limits for airborne toxic substances

					USA		
	Fed. Rep. Germany	Japan	Sweden	USSR	Occupational standard	TWA	ACGIH Short term
Lead and inorganic compounds, mg/m^3	0.2	0.15	0.1	0.01	0.2	0.15	0.45

Source: ILO, Occupational Safety and Health Series No. 37, Geneva, 1977.

Hazards to workers can nevertheless be very serious. For example, the lead concentration in the air was measured for different operations in a typical lead ore smelter in Salt Lake City, Utah, (USA). These data are reported in table 5.11.[190] They clearly indicate that lead concentrations were extremely high with potential health hazards to the workers who were, in fact, required to use respirators.

187/ Ibid.

188/ "Lead, Executive Summary", Environmental Health Criteria 3, WHO, Geneva, 1983.

189/ "Environmental Health Aspects of Non-Ferrous Metals: Cadmium, Copper, Lead, Nickel and Zinc", UNEP Workshop on the Environmental Aspects of Non-Ferrous Metals Industries, WHO, United Nations Environment Programme.

190/ "Lead", Environmental Health Criteria 3, WHO, Geneva, 1977.

Table 5.11. Air lead concentrations in three primary lead smelters (microg/m^3)[a]

Smelter	Year	Location[b]	Means[c]	Mean of means	Range (all values)
A	1972-75	(1)	610, 1930, 2860	1800	250-3670
		(2)	970, 470, 450	630	250-1380
		(3)	860, 950, 320	710	200-1700
		(4)	1220, 350, 950	840	260-1640
B	1973-74	(1)	1310, 2330, 4720	2790	370-5160
		(2)	2740, 3460, 770	2320	310-7570
		(3)	860, 140, 530	510	120-1560
		(4)	1270, 540, 5730, 4050	2900	60-7220
C	1973-74	(1)	—	—	—
		(2)	3850, 8740, 830	4470	10-31 200
		(3)	1320, 230	780	90-1340
		(4)	80	80	

[a] Data provided by M. Varner, American Smelting and Refining Co., Salt Lake City, Utah, USA.

[b] Locations: (1) Ore proportioning; (2) nodulizing and sintering; (3) blast furnace; (4) drossing and reverberation.

[c] Determined with personal monitors on separate occasions. Each sampling period was 5-7 hours.

Source: "Lead", Environmental Health Criteria 3, WHO, Geneva, 1977.

Similar data are not available for secondary smelters, but some studies seem to indicate that workers are indeed exposed to high lead levels in air which then results in increased blood lead levels.[191]

191/ Ibid.

6. ZINC

6.1 Introduction

Zinc is the fourth most widely used metal in the world. Its industrial importance derives from its characteristics. Zinc has a low melting point and can be cast in fine detail into complex shapes.[192] Because of its excellent castability it has been extensively used in die casting, especially in the automotive industry. In addition, zinc is resistant to corrosion under normal atmospheric conditions. It is also strongly electronegative, which makes it anodic to steel. Hence, in the presence of steel and electrolyte it dissolves preferentially, affording corrosion protection. For this reason it is extensively used in metal coating (galvanizing). Zinc is also used as alloying metal with copper to produce brass, and as oxide in white wall tires (as filler) and in paints. In 1979 zinc was consumed in the western world for galvanizing (40 per cent), brass production (21 per cent), die casting (19 per cent), zinc oxide production (8 per cent), sheets and strips (8 per cent) and other uses (3 per cent).[193] In recent years the zinc consumption in the industrialized countries has grown at a rate below that of the growth of national outputs.[194] The main reason for this is the competition and substitution, in some applications, with other materials such as plastics or aluminum. In 1985 the overall world slab zinc production was some 6.7 million tons. Only about 6 per cent came from secondary slab zinc (zinc recycling). Zinc can be recycled also in forms other than slab metal (e.g. as zinc oxide). If this zinc recycling is also included then secondary zinc production totals about 25 per cent of the overall production.[195]

Zinc is mined in more than 40 countries in the world. The most important mines are located in Canada, Peru, Australia, the USA, Nicaragua, the Republic of Korea, Ireland, Sweden, Spain and the Federal Republic of Germany.

6.2 Primary zinc production processes and pollutants produced

Mining and ore concentration are common operations in any primary zinc production process. The subsequent smelting operation is carried out following either one of the two major classes of processes: the roasting-electrolytic process or the pyrometallurgical process. A purely hydrometallurgic process can be used but only for less common oxidized zinc ores. After smelting, zinc is refined from impurities.

192/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, J.L. Broadhead: Zinc in the 1980's, AIME, New York, 1979.

193/ "Environmental Aspects of Selected Non-Ferrous Metals Industries", UNEP Industry & Environment Overview Series, 1984.

194/ Atkins, M.H. and J.F. Lowe, "The Economics of Pollution Control in the Non-Ferrous Metals Industry", Pergamon Press, 1979.

195/ "Environmental Aspects of Selected Non-Ferrous Metals Industries", UNEP Industry & Environment Overview Series, 1984.

6.2.1 Mining

Zinc is contained as ZnS in minerals such as blende (spherosite), as $ZnCO_3$ in smithsonite, or as ZnO in calamine. Spherosite is by far the most common. Zinc is mined from mixed ores or zinc ores. Mixed ores usually contain recoverable amounts of other metals, epecially lead. Mining is conducted mainly underground using standard mining methods. Open cast pit mining is also used with overburden material layers varying typically between 3-12 meters, as in the Indian Rajastan mines.[196] The main environmental problem associated with mining is mine drainage caused by the water (either contained in the rocks or pumped in) leaching some metal compounds from the rock. Furthermore, this water is often very acidic. The United States Environmental Protection Agency published a study which reports that the mine water in most mines in the USA has a pH of about 3.3, and is discharged at a rate of 10,000 liters/minute.[197] Additional environmental problems are the physical disturbance of the natural ground during excavation and dumping of overburden material, and air pollution caused by dust contamination.

6.2.2 Ore processing

This phase consists of a series of physical operations aimed at concentrating the zinc mineral from the ore. The main operations are crushing, grinding, mixing with flotation agents, the actual flotation, the recovery of the concentrated streams rich in the metal ore, the recycling of the flotation solutions, and the disposal of the tailings and excess process water. Additional details are given in the lead chapter which also contains a diagram for mixed ore (lead-zinc) processing.

6.2.3 Smelting process

This process is based on two steps. The first step consists of converting the initial zinc compound (either ZnS or $ZnCO_3$) to zinc oxide according to the simplified reactions:

$$2\ ZnS + 3\ O_2 \text{ ---> } 2\ ZnO + 2\ SO_2$$

$$ZnCO_3 \text{ ---> } ZnO + CO_2$$

This step is called roasting and is similar, at least in principle, in any zinc smelting process.

The second step is a reduction of the oxide to zinc metal. This step can be carried out either electrolytically or pyrometallurgically. The electrolytic smelting process is now adopted in about 67 per cent of the existing smelters. The pyrometallurgical process is used in the remaining cases.

196/ Dave, J.M., "Environmental Pollution from the Zinc Industry in India: A Case Study", UNEP Industry and Environment, Vol. 5, No. 1, January, February, March 1982.

197/ "Processes, Procedures, and Methods to Control Pollution from Mining Activities", United States Environmental Protection Agency, EPA-430/9-73-011, Washington, D.C., October 1973.

The roasting-electrolytic process

The first step, roasting, can be carried out using several types of roaster. Air is blown into the roaster and SO_2 is produced. In some old multi-hearth roasters the SO_2 concentration in the off-gases is too low for effective removal. Modern practice is now oriented toward the use of fluidized bed roasters which not only produce rich sulphur dioxide streams (amenable for acid plant treatment), but also are more energy efficient and do not require additional fuel.

During the roasting phase some mercury and arsenic, initially present in the ore, may evaporate in the gas stream. They must be removed and collected from the gas stream before it enters the contact acid plant. Dust may also be present and must be removed.

After roasting, the resulting calcine is leached with sulphuric acid. Zinc dissolves in the solution as sulphate. The solution is neutralized by adding more calcine or lime until the iron and other impurities precipitate as salts. The pulp is filtered. Then dust is added to the solution causing zinc cadmium precipitation. After thickening and filtering the clear saturated solution is sent to an electrolytic cell where the zinc is reduced to metal on an aluminum cathode while sulphuric acid is produced at the lead anode and then recycled.

The main environmental hazard at this stage is created by the filtered coke. It contains all the impurities left from the calcine. Some valuable impurities are collected during further purification stages, but the residue, containing heavy metals and acid, must be treated and disposed of.

The pyrometallurgical process

The first step of this process is also roasting, but the operation resembles the sintering process used in lead production. The zinc-lead concentrate is first premixed with previously desulphurized recycled calcine to obtain a desired overall sulphur content and then fed to an up-draft sintering machine. The resulting off-gases have an SO_2 concentration in the range of 6-7 per cent, which is higher than that achieved in lead sintering, and therefore even better suited for conversion in an acid plant. The gases also contain mercury, lead, cadmium, and dust, which must all be removed before SO_2 conversion. The main environmental problems at this stage are connected to potential fugitive emissions which contain lead and cadmium as main pollutants.

During sintering, the newly formed zinc oxide agglomerates into hard porous lumps which are then mixed with coke (as reducing agent) and charged to the blast furnace. Air is blown into the furnace. The reducing reaction producing metallic zinc and carbon monoxide takes place at about 1000°C. This temperature is higher than the boiling temperature of zinc, which immediately vaporizes upon formation. In order to prevent the reverse reaction from occurring (giving ZnO) the zinc vapor must be condensed and removed.

Formerly, the reduction process took place in vertical or horizontal retorts. Some are still in use. These suffer from conversion problems, are very energy intensive, and have serious emission problems. These disadvantages have been overcome by the Imperial Smelting Process (ISP), consisting of a blast furnace fed with the charge from the top and preheated air from the bottom. The reactions taking place are quite complex. If mixed ores are used, lead bullion is tapped at the bottom together with slag (later removed). The gases produced in the furnace contain 7 per cent zinc vapors, 20 per cent CO and 12 per cent CO_2. The problem of zinc reoxidation is solved by using a lead splash rotor, i.e. a device spraying molten lead into the gas stream. The zinc vapors dissolve into the lead.198/ The mixture is then cooled and the molten zinc separates out (its solubility decreases with temperature) and is recovered. Lead is recycled back. The efficiency of the process is high (95 per cent).199/ The off-gases are scrubbed in Venturi scrubbers to remove the "blue powder" containing zinc and other impurities, which are removed and reprocessed. The exhausted CO is used as fuel to preheat the blast air. The main environmental problems of the blast furnace process are connected to the potential dust emission containing heavy metals and CO.

6.2.4 Zinc refining

The zinc which separates from the lead in the lead circuit can be cast directly or is further refined. Refining is carried out by distillation. Cadmium is more volatile than zinc and distills first. Since cadmium is toxic, the main environmental hazard here is fugitive emissions.

6.2.5 Hydrometallurgy

In alternative to the smelting process a hydrometallurgical process can be used to recover zinc, but only from oxidized ores. After ore processing, if any, the ore is leached with sulphuric acid in agitated tanks at room temperature. Zinc recovery often exceeds 90 per cent.200/ The rest of the process is very similar to the electrolytic process, but without any roasting step. Several purification steps then follow in order to remove impurities such as silica, iron, arsenic, antimony, copper and cadmium. The main environmental problem here is the disposal of the waste sludge containing heavy metals and acid.

198/ Barbour, A.K., J.F. Castle and S.E. Woods: "Production of Non-Ferrous Metals", in Industrial Air Pollution Handbook, A. Parker (ed.), McGraw Hill, UK, 1978.

199/ Temple, Derek: "Zinc-Lead Blast Furnace - The Key Developments", The 1980 Extractive Metallurgy Lecture, The Metallurgical Society of AIME, Metallurgical Transactions B, Vol. 11B, September 1980.

200/ Atkins, M.H. and J.F. Lowe, "The Economics of Pollution Control in the Non-Ferrous Metals Industry", Pergamon Press, 1979.

6.3 Pollution control technologies for zinc production plants

6.3.1 Pollution control during mining

Treatment and disposal of mine water is the main problem at this stage. This water is muddy and contaminated with particulate matter with potentially large fluctuations in its density and quality. Since mine water is usually acidic, its pH can be raised by adding limestone. This is especially beneficial if the water is going to be recycled to the ore processing plant, since the flotation operation for zinc and lead-zinc ores is typically run at elevated pH values (between 8.5 and 11). In this case, though, the suspended solids must first be removed. The water which cannot be recycled can be disposed of after treatment.

A good example of such a technology is given by the Tochibora Mine. Since the original lead/zinc-containing rock is rich in limestone, the pH value of the groundwater is already somewhat in the alkaline range (7-8). Moreover, it contains few dissolved ions. By removing the suspended solids the mine wastewater can be used as industrial water at the nearby Shikama lead-zinc plant. Some 60 per cent of the Shikama plant is supplied by the Tochibora mine.[201/]

6.3.2 Pollution control during ore processing

Dust emissions during grinding operations can be reduced by wetting the ore and encasing the grinding equipment. A much more serious problem during ore processing is caused by tailings and water disposal from the flotation operations. The tailing slurry is first sent to thickeners where the solids settle. These solids are then sent as a thick slurry to lagoons or impoundment areas. The thickener overflow can be recycled and used again for bulk flotation. The overflows from other flotation/thickening steps can also be recycled. However, some amounts of harmful impurities, consisting mainly of flotation agents, are contained in these streams and must be removed. Methods to remove these contaminants have been devised. For example, the Ion, Precipitation, and Ultra Fine (IPU) flotation process utilizes sulphuric acid, sodium sulphide, acofloc (a flocculant) and methyl-isobutyl-ketone additions to precipitate the impurities, which are then separated by filtration. The water can be recycled. This system has been used at the Shikama plant, resulting in a remarkable improvement of the total effluent quality, substantial savings of floatation reagents, and additional recovery of zinc and even copper (as by-product) from the wastewater.[202/]

6.3.3 Pollution control during smelting

Pollution control during the roasting-electrolytic process

During the roasting step the main environmental hazard comes from the roaster off-gases, which contain SO_2, dust and fumes, and also vapors from heavy metals such as mercury, cadmium, and arsenic (originally present in the

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[201/] Matsui, N., "Pollution Preventive Measures in a Lead-Zinc Mine in Japan", UNEP Industry and Environment, Vol. 8, No. 1, January, February, March 1985.

[202/] *Ibid*.

ore concentrate). In relatively modern plants a waste heat boiler is used to recover energy and cool down the roaster off-gases. Dust and fumes are then removed by passing them through cyclones and then, for a more complete removal, also through an electrostatic precipitator. In older plants utilizing low-efficiency roasters (such as the multi-hearth roasters) the SO_2 concentration in the gases is too low for removal and the gases are sent directly to a stack. In modern plants using fluidized bed roasters the SO_2 can be as high as 9.5 per cent, as in the new (1979) Jersey Miniere Zinc Company plant at Clarksville, Tennessee (USA).[203] Then the SO_2 can be converted efficiently to sulfuric acid.

Before SO_2 removal, the off-gases from the electrostatic precipitator must be cleaned from their heavy metal content. The gases are first scrubbed in Venturi scrubbers and then passed in a mercury-removal Boliden-Norzink tower where a mercuric chloride solution flows counter current. Mercury in the gas reacts with the solution forming mercurous chloride, which precipitates and is later removed by flotation. The heavy-metal free gas stream can then be treated in a sulphuric acid plant where conversion to H_2SO_4 takes place. The clean gases are usually vented through a stack.

In the second part of the process the potential environmental hazards come mainly from the zinc leaching operation. The leach residue produced during this operation contains all the insoluble solid materials present in the calcine plus some electrolyte solution. The residue is collected at the bottom of the thickeners as a slurry, after flocculation. It is then treated with lime to remove the excess acidity, washed and filtered. The final washed acid leach residue cake is then sent to an impoundment area or a lagoon. The environmental problems are complicated by the presence of heavy metal residues.

Pollution control during the pyrometallurgical process

The roasting operation is, in principle, similar to that used in the electrolytic process. Consequently it poses the same type of environmental problems. However, in the pyrometallurgical process the roasting phase is also a sintering phase, i.e. the end product must not only be fully calcined, but also have a minimum lump size in order to meet the requirements for the subsequent reduction step. This implies that about 80 per cent of the product from the sintering machine must be recycled as dust.[204] Therefore, in addition to standard off-gas cleaning, a very large volume of ventilation air must also be extracted and cleaned from dust. Bag filters, cyclones or Venturi scrubbers can be used for this purpose.[205] The off-gases should then undergo heavy metal removal before being sent to the sulphuric acid plant for SO_2 removal.

203/ "Lead-Zinc-Tin 80", TMS-AIME World Symposium on Metallurgy & Environmental Control, L. Painter: The Electrolytic Zinc Plant of Jersey Miniere Zinc Company at Clarksville, Tennessee, AIME, New York, 1979.

204/ Atkins, M.H. and J.F. Lowe, "The Economics of Pollution Control in the Non-Ferrous Metals Industry", Pergamon Press, 1979.

205/ "Processes, Procedures, and Methods to Control Pollution from Mining Activities", United States Environmental Protection Agency, EPA-430/9-73-011, Washington, D.C., October 1973.

The environmental problems associated with the next phase, i.e. sinter reduction, depend strongly on the type of equipment used. The Imperial Smelting Process is much more environmentally sound than horizontal retorts. The zinc contained gases produced during the reduction phase are almost completely recovered by the lead splash rotor. The escaping zinc vapors are condensed by passing the gases through wet scrubbers. During this operation the other heavy metals are also removed. The gases can then be vented.

The liquor obtained from the scrubber contains the heavy metals from the gases. Upon addition of lime to the liquor these metals are precipitated, settled in thickeners, dewatered and then reprocessed for recovery. The liquor is mostly recycled to the scrubber. Only a part is discharged after treatment. The slag produced from the ISP is granulated and dumped or used as an aggregate in concrete.[206/]

6.3.4 Pollution control during zinc refining

At this stage the main environmental hazard consists of potential fume emissions containing heavy metals, especially cadmium. Provided that a good fume collection system exists, removal of heavy metals is carried out using scrubbers as described in the previous section.

6.3.5 Pollution control during the hydrometallurgical process

As in the electrolytic process, sludge disposal after leaching constitutes a potential environmental problem. Effluent production is minimized by recycling.[207/] The excess is treated to remove heavy metals prior to discharge. The sludge can be impounded in leak-proof areas.

6.4 Potential for by-product re-use

The heavy metals which constitute a major environmental problem during the various operations described above can be effectively recovered for further purification and marketed. Cadmium is probably the most important by-product metal. In fact cadmium is not recovered from primary sources (i.e. it is not mined), but comes almost exclusively from zinc processing. If the electrolytic process is used, most of the cadmium originally present in the ore is solubilized with H_2SO_4 together with the zinc, after the roasting operation. Cadmium is then removed from the saturated solution by precipitation upon addition of zinc metal dust, which acts as a reducing agent. Cadmium can also be recovered as a by-product of the pyrometallurgical process during the sintering operation, or in the fumes contained in the off-gases from the ISP furnace. Whatever the collection method is, the cadmium-rich slurry or dust is solubilized with sulphuric acid and then recovered electrolytically. Another by-product of zinc smelting is selenium, which is recovered with cadmium from the sinter fumes.[208/]

206/ Anon., "Imperial Smelting Process - Britain's Contribution to Lead-Zinc Production", E & M Journal, November 1973.

207/ "Environmental Aspects of Selected Non-Ferrous Metals Industries", UNEP Industry & Environment Overview Series, 1984.

208/ Ibid.

Lead is also produced as a by-product of zinc in the ISP. In this case, lead is directly tapped from the furnace. Copper is also recovered from the lead dross. The ISP also produces a vitreous solid slag containing lime, silica, iron oxide zinc (around 6 per cent) and lead (some 0.7 per cent).[209] This slag can be dumped or is granulated and used as an aggregate in concrete.

6.5 Zinc recycling (secondary zinc production)

Zinc metal is not as extensively recycled as other metals. This is due to the fact that zinc is not normally used in metal parts which can be easily collected (such as plates or pipes), but is mainly used for coating. Secondary zinc comes primarily from zinc base alloys or copper base alloys. Not all the recycled zinc scrap is processed to recover zinc metal. Appreciable amounts are recycled as brass. Some galvanized residues are converted to zinc oxide or zinc dust.[210]

In spite of the low contribution of secondary zinc to the overall slab zinc production (about 6 per cent of the total) the production of zinc metal from scrap requires less than 30 per cent of the energy of primary smelting.[211] This and other factors, such as the gradual reduction of the quality of zinc ore in the developed countries, and tax credits for recycling (e.g. the 10 per cent Recycling Investment Tax Credit voted in 1978 by the United States Congress) should help to increase the production of secondary zinc. Stricter emission regulation and improved emission control technologies should also contribute to recover more zinc dust and fumes produced during operations such as smelting, refining and galvanizing.

Zinc scrap reprocessing starts from scrap collection and sorting. A mechanical pretreatment (such as shredding) usually follows. The scrap material is then charged to a reverberatory furnace or distilled in kettles. Fume emissions vary from 0-15 kg per ton of reclaimed zinc,[212] depending on the type of feed and the pollution control equipment used (if any). Baghouse filters and Venturi scrubbers can be effectively used to control emissions.

6.6 Retrofitting of existing plants to reduce pollution

For those plants which utilize obsolete or older production technologies, remedial actions are difficult. These plants may also suffer from low efficiency and high production costs and are destined to be phased out with

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[209] Anon., "Imperial Smelting Process - Britain's Contribution to Lead-Zinc Production", E & M Journal, November 1973.

[210] "Environmental Aspects of Selected Non-Ferrous Metals Industries", UNEP Industry & Environment Overview Series, 1984.

[211] Ibid.

[212] Atkins, M.H. and J.F. Lowe, "The Economics of Pollution Control in the Non-Ferrous Metals Industry", Pergamon Press, 1979.

time. As an example, in the USA between 1969 and [illegible] six out of eight primary zinc smelters utilizing the horizontal or vertical retort smelting process closed down. One was converted to the electrolytic process and the other one was still in operation in 1979.[213]

Replacing technologies, at least in some parts of the plant, may be beneficial from both an economic and environmental standpoint. For example, modern roasters not only do not require any supplementary fuel for their operation, but also produce rich SO_2 streams which can be much more effectively converted to sulfuric acid. Technologies now exist to control heavy metal emissions, especially mercury. Boliden-Norzink columns have been proved to perform very satisfactorily.[214] In pyrometallurgic smelting the ISP is already environmentally sound provided that pollution control devices are utilized to control final gaseous emissions. Additional pollution control equipment can be considered to be independent from the furnace and can be retrofitted to existing plants.

6.7 Innovative and emerging production technologies

Unlike other metals such as copper or lead, no new processes have emerged in the past decade for zinc.[215] Some possibilities have been developed, but not tested in practice on a full scale. We expect that, over the next decade, the major developments in this field will come from the application of process control and automation technologies to existing production processes and equipment, and from refinements of the existing processes.

In the last years the electrolytic process has greatly benefitted from the adoption of the fluidized bed roasting process. In addition, noticeable improvements were made in the recovery of zinc during the leaching phase. By using the jarosite, goethide, and haemotite processes it is now possible to separately precipitate iron from the zinc-rich solution, thus allowing the recovery of an additional 10-15 per cent of zinc.[216] As for the pyrometallurgical process, it is now possible to recover selenium and cadmium from the sinter flue dust.

Gradual but noticeable advances were also made in the ISP. For example, the lead-splash condenser efficiency has been improved to the point where water vapor can be tolerated, thus permitting the use of oil as fuel, in partial substitution for the more expensive coke. A promising new technology is a flash furnace capable of recovering up to 97 per cent zinc and still being able to tolerate up to 8 per cent SO_2.[217]

213/ "Environmental Aspects of Selected Non-Ferrous Metals Industries", UNEP Industry & Environment Overview Series, 1984.

214/ "Processes, Procedures, and Methods to Control Pollution from Mining Activities", United States Environmental Protection Agency, EPA-430/9-73-011, Washington, D.C., October 1973.

215/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, T.R.A. Davey: Advances in Lead, Zinc, and Tin Technology - Projections for the 1980's, AIME, New York, 1979.

216/ Ibid.

217/ Ibid.

As for the hydrometallurgical process, pressure leaching of sulphide ores has been carried out at the pilot plant stage. The advantage of this process is that it produces elemental sulphur which can be easily separated from the solution rich in zinc sulphate. Electrolysis is then used to recover the zinc metal.[218/]

The Kivcet process provides an alternative to the processing of mixed lead-zinc ores. Similarly to the copper process by the same name, the process consists of the roasting-smelting in one step of the ore by using enriched oxygen. The Kivcet furnace combines several advantages which can be found in other modern metallurgical technologies such as the Outokumpu method of combusting fine sulphide concentrate in an enriched oxygen atmosphere, and the lead-splash condenser to produce zinc, as in the ISP.[219/] Major advantages of the process are that desulphurization approaches 100 per cent and that an SO_2-rich stream is produced. The reduction takes place in a different part of the furnace producing lead bullion and raw zinc.[220/]

Some authors have predicted that the pyrometallurgical process will eventually take over from the electrolytic process because of the inherent inefficiency of converting fossil fuel to electricity and then using that to extract zinc.[221/] It is also claimed that pyrometallurgical processes have lower capital costs, can more easily treat complex ores, and do not suffer from the environmental problems of disposing of the leach residue. Because of the lack of need for a substantial industrial infrastructure, pyrometallurgical processes may be more suited for developing countries. On the other hand, the adoption of these processes may be inhibited by the need for compliance with stricter environmental standards, and the cost associated with the use of coke as a fuel.

6.8 A case study

The Electrolytic Zinc Plant of Jersey Miniere Zinc Company at Clarksville, Tennessee (USA) was chosen for a case study.[222/] The plant has a capacity of 81,670 tons of electrolytic zinc per year and went on stream in 1978. Concentrated ore can be received from nearby company-owned mines or from other sources via trucks, railroad cars, or barges. Storage capacity is provided for some 23,000 tons of concentrate.

218/ Atkins, M.H. and J.F. Lowe, "The Economics of Pollution Control in the Non-Ferrous Metals Industry", Pergamon Press, 1979.

219/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, T.R.A. Davey: Advances in Lead, Zinc, and Tin Technology - Projections for the 1980's, AIME, New York, 1979.

220/ "Environmental Aspects of Selected Non-Ferrous Metals Industries", UNEP Industry & Environment Overview Series, 1984.

221/ *Ibid*.

222/ "Lead-Zinc-Tin 80", TMS-AIME World Symposium on Metallurgy & Environmental Control, L. Painter: The Electrolytic Zinc Plant of Jersey Miniere Zinc Company at Clarksville, Tennessee, AIME, New York, 1979.

The Lurgi roasting plant is designed to process 423 tons/day of concentrate and recycled dross, producing 363 tons/day of calcine containing less than 1.75 per cent sulphur. The roaster is a fluidized bed having a grate area of 65 m^2. Calcine leaves the roaster as either bed overflow or carry over into the off-gases waste heat boiler. Some 18,000 tons/hr of steam at 38 bars are produced in the boiler. The off-gases are then cleaned in two parallel cyclones before entering an electrostatic precipitator where the dust content is reduced below 460 mg/m^3. A Venturi scrubber is used to remove some of the heavy metals before the gas enters a Norzink tower for mercury removal. The SO_2-rich cool gas is dried over sulphuric acid and then sent to a double-contact sulphuric acid plant. Vanadium pentoxide is the catalyst for the conversion from SO_2 to SO_3. The clean gas containing less than 300 ppm of SO is vented through a 61 meter tall stack. About 340 tons/day of sulphuric acid are produced.

The calcine leaching operation is carried out in 80 m^3 tanks. Most zinc is solubilized at this stage. The solid residue from this operation is repeatedly washed, settled, and filtered. The final cake is repulped and sent to a residue pond lined with an acid resistant material. The pond is designed for about eight years of storage.

The purification stage consists of several steps during which cobalt, copper and cadmium are selectively precipitated by adding zinc dust. The resulting cobalt cake and copper cake are stored and then sold. The cadmium cake is solubilized with sulphuric acid, purified from iron and arsenic impurities and then sent to the electrolysis section consisting of eight concrete PVC-lined cells operating at 60 amperes/m^2. The cadmium is recovered at the cathode, and later melted and cast for shipment.

After purification the zinc saturated solution is electrolyzed in 208 cells similar to those used for cadmium. The cells operate at about 450 amperes/m^2. Aluminum cathodes and lead-silver anodes are used. The spent electrolyte is recycled to the leaching tanks. Cathode handling and zinc stripping are done automatically. Cells and anodes are cleaned on a 50-day cycle.

6.9 Pollution control costs

One important source of information on pollution control costs in the zinc industry is a publication of the United States Environmental Protection Agency concerning the situation in the USA.[223/] In 1971 the EPA estimated that all the United States primary zinc smelters (producing over one million tons/year) emitted 263,000 tons of SO_2 and 18,600 tons of particulate. At that time no emission control existed for SO_2 and only 90 per cent of the total particulates produced in the smelting operation were collected prior to off-gas discharge into the atmosphere. By 1979 the EPA forecast that the corresponding figures would be 1,900 tons for SO_2 and 31,000 tons for particulate emissions, thanks to the adoption of control technologies. The associated investment costs were estimated to be

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223/ Atkins, M.H. and J.F. Lowe, "The Economics of Pollution Control in the Non-Ferrous Metals Industry", Pergamon Press, 1979.

$US 32.4 million with total annual operating costs of $US 8.15 million (1974 prices). More detailed information is reported in table 6.1 for different plant sizes.[224]

Table 6.1. Costs of pollution control for United States primary zinc producers

Model size (tons)	Investment ($US million)			Annual operating cost ($US million)			$US/t/year	Unit cost	
	expected	min	max	expected	min	max	expected	min	max
91,000	8.67	6.66	11.1	2.17	1.65	2.77	23.8	18.1	30.4
139,000	11.6	8.82	15.0	2.91	2.23	3.76	20.9	16.0	27.1
149,000	12.2	9.42	15.6	3.09	2.37	3.97	22.2	17.1	28.6

Source: The Cost of Clean Air, Environmental Protection Agency, Senate Document No. 93-122, 1974.

For the secondary zinc industry, the estimated investment costs for various model plant sizes are given in table 6.2.

Table 6.2. Costs of pollution control for United States secondary zinc producers

Model size capacity (tons)	Investment ($US 000)			Annualized cost ($US 000)			Unit cost $US/t/year		
	expected	min	max	expected	min	max	expected	min	max
4,990	138	80.4	195	43.2	22.5	64.4	7.85	4.09	11.7
10,990	225	131	345	12.3	386	113	6.03	3.22	9.42

Source: The Cost of Clean Air, Environmental Protection Agency, Senate Document No. 93-122, 1974.

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[224] Ibid.

6.10 Emission standards

According to reference[225] the maximum acceptable emissions into the air for zinc plants are the same as for lead plants. These standards have already been given in the lead chapter section 5.10. For liquid effluent standards, the limits set by the United States Environmental Protection Agency are reported in table 6.3.[226] The standards for primary zinc production plants are reported in table 6.4 in terms of kg of pollutant per ton of metal produced.

Table 6.3. Guidelines for permissible water pollutants from a primary zinc smelter (mg/l)

	Concentration (mg/l) in effluent	
	30-day average	24-hour maximum
pH	6-9 units	6-9 units
TSS	20	30
Cyanide	0.01	0.02
Cd	0.05	0.1
Cu	0.05	0.1
Hg	0.001	0.002
Pb	0.2	0.4
Zn	0.2	0.4

Source: "Development Document for Interim Final and Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry", United States Environmental Protection Agency, EPA 440/1-75/061 Vol. I and II, Washington, D.C., October 1975.

225/ "Development Document for Interim, Final and Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry", United States Environmental Protection Agency, EPA 440/1-75/061 Vol. I & II, Washington, D.C., October 1975.

226/ "Processes, Procedures, and Methods to Control Pollution from Mining Activities", United States Environmental Protection Agency, EPA-430/9-73-011, Washington, D.C., October 1973.

Table 6.4. Guidelines for permissible water pollutants from a primary zinc smelter (kg/ton zinc)

	Maximum 24-hour	Consecutive 30 day average
TSS	0.42	0.21
As	1.6×10^{-3}	8×10^{-4}
Cd	8.0×10^{-3}	4×10^{-4}
Se	0.08	0.04
Zn	0.08	0.04
pH	6-9 units	6-9 units

Source: "Environmental Guidelines", Office of Environmental Affairs, The World Bank, July 1984.

6.11 Health protection for workers

Zinc is relatively non-toxic. The most common worker intoxication from zinc is by fume inhalation during operations such as smelting or galvanizing or in any other where zinc is heated at high temperature. The result is metal fume fever, a disorder from which the worker usually recovers within 24 to 36 hours. It has been shown that occupational exposures to zinc oxide fumes in the range of 3-15 mg/m^3 for 2 to 35 years did not produce detrimental effects.[227/] In some workplaces concentrations up to 100 mg/m^3 and even higher have been found.[228/] Adequate ventilation should be provided to reduce these values below the occupational exposure limit adopted in each country. Some selected values are reported in table 6.5.

More serious toxic effects can be produced on the workers by exposure to cadmium, a by-product of zinc manufacturing. Cadmium can produce acute and long-term effects, especially on the lungs and kidneys. Exposure for eight hours to air containing 5 mg/m^3 may be lethal.[229/] Toxic effects may result from exposure to cadmium levels in air of 1 mg/m^3. For this reason the occupational exposure limits adopted in many countries are rather low. These limits are reported in table 6.6.

227/ Occupational Exposure Limits for Airborne Toxic Substances, ILO, Occupational Safety and Health Series No. 37, Geneva, 1977.

228/ Ibid.

229/ Ibid.

Table 6.5. Occupational exposure limits for airborne zinc, mg/m^3

					USA		
	Fed. Rep. Germany	Japan	Sweden	USSR	Occupational standard	ACGIH	
						TWA	Short term
Zinc chloride (fumes)			1		1	1	2
Zinc oxide (fumes)	5	5	1	6	5	5	10

Source: Occupational exposure limits for airborne toxic substances, ILO, Occupational Safety and Health Series No. 37, Geneva, 1977.

Table 6.6. Occupational exposure limits for airborne cadmium, mg/m^3

					USA		
	Fed. Rep. Germany	Japan	Sweden	USSR	Occupational standard	ACGIH	
						TWA	Short term
Cadmium dust and soluble salts (as cadmium)			0.5			0.5	0.15
Cadmium oxide (fumes as cadmium)	0.1	0.1	0.02	0.1	TWA/M[a] 0.1/3	M[a] 0.05	0.05

[a] M = ceiling value

Source: Occupational exposure limits for airborne toxic substances, ILO, Occupational Safety and Health Series No. 37, Geneva, 1977.

7. TIN

7.1 Introduction

Tin is an essential metal for industry, but is also relatively rare. The main applications of tin are in the production of tin-plate, solder, babbit (an alloy used for lining bearing shells), alloys such as brass, bronze, pewter, printer's type alloy, plastics and tin chemicals.[230] Tin-plating is by far the most important application, utilizing about 40 per cent of the world tin production. Some 90 per cent of the tin-plate production goes to the food and drink packaging industry.[231] In tin-lead solder the tin content varies from 2 per cent for container seaming to 63 per cent for electrical connections. Antimony, silver, zinc, and indium are used as alloying metals with tin in lead-free solders. The largest amounts of solder are used in air conditioners, car radiators, heat exchangers, plumbing fixtures, and electronic and computer equipment. Bronzes are mainly used in marine and railway applications because of their corrosion resistance. They contain between 5 and 10 per cent tin. Pewter contains about 90 per cent tin.

A growing market for tin is represented by the organotin compounds. About 70 per cent of the total production of organotin goes into polyvinylchloride (PVC) production where it is used as heat stabilizer. Organotin compounds are also used as antioxidants and anticracking agents in rubber, as antioxidants for textile oils, as catalysts for polyester, silicone elastomer, and olefin polymerization, and as hydrochloric acid scavengers in electric equipment (such as transformers or capacitors).[232] A special use of organotin compounds consists of exploiting their biocidal properties. To this purpose, they are used, among the others, as antifoulant agents in underwater coating (e.g. ship paints), as herbicides, as disinfectants in hospitals, as agricultural fungicides, and as rodent repellents.[233]

In spite of the multiple uses of tin, its annual production in 1985 was limited to 210,000 tons.[234] Only 8 per cent of this figure comes from recycling. Primary tin, which undergoes the whole production process from mining to final refining, is produced in relatively few countries. An interesting aspect of the known tin deposits is that they are mainly concentrated in the Pacific region, although recent discoveries have shown

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230/ "Tin and Organotin Compounds", Environmental Health Criteria 15, WHO, Geneva, 1980.

231/ The International Tin Council, London, Fourth World Conference on Tin, Kuala Lumpur, 1974.

232/ "Tin and Organotin Compounds", Environmental Health Criteria 15, WHO, Geneva, 1980.

233/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, J. Long: Innovations in Tin Use, AIME, New York, 1979.

234/ World Metal Statistics Yearbook 1986, World Bureau of Metal Statistics, May 1986.

that the Atlantic Ocean may also contain tin on the borders.[235] In 1975 six countries produced 72 per cent of the overall world tin production: Malaysia (35 per cent of the total), China (8 per cent) Indonesia (8 per cent), Thailand (7 per cent), the USSR (6 per cent), and the United Kingdom (6 per cent). Other important mines exist in Bolivia, Zaire, Nigeria, Burma, Brazil, South Africa, and Australia.

7.2 Primary tin production processes and pollutants produced

The current tin production technology consists of several steps, similar to those encountered in other non-ferrous metal processes: mining, ore processing, smelting and refining. Several specific technologies exist depending on the type of ore, impurities content and smelting equipment used. An overall block diagram for tin production is shown in figure 7.1.[236]

7.2.1 Mining

Nine different tin-bearing minerals can be found in the earth's crust, but only a few of them have some commercial importance. Cassiterite (SnO_2), an oxidized ore, is by far the most important. Small amounts of tin are also extracted from complex sulphide ores such as stannite ($Cu_2S.FeS.SnS_2$), frankeite ($5PbS.2SnS_2Sb_2S_3$), teallite ($PbSnS_2$) and canfieldite (Ag_8SnS_6). Cassiterite is often mined from low-grade deposit. More than 80 per cent of the world tin deposits contain less than 240 grams of metallic tin per cubic meter. The associated extraction problems are self-evident. Tin ores can be found in hard rocks (where cassiterite is usually a minor mineral), soft rocks, or tin placers. Different mining techniques are employed depending on the type of tin mineral, associated impurities, and location. Underground mining of hard rock tin ores does not differ from the traditional system used for other ores. Unfortunately cassiterite is a very brittle mineral and is easily shattered by explosion. This creates difficulties during the ore processing phase since particles below 10 microns in size are difficult to recover. Besides the typical, but limited, environmental problems associated with underground mining, a specific problem encountered in some tin mines comes from the emission from the granitoid of radon gas, which is slightly radioactive.[237]

Open-pit mining of hard rocks is rare. This technique is usually associated with soft rocks. Excavation is then carried out by power shovels or excavators. The associated environmental problems consist mainly of the physical disturbance of the ground with consequent destruction of the local vegetation, air pollution caused by dust, disposal of the overburden material,

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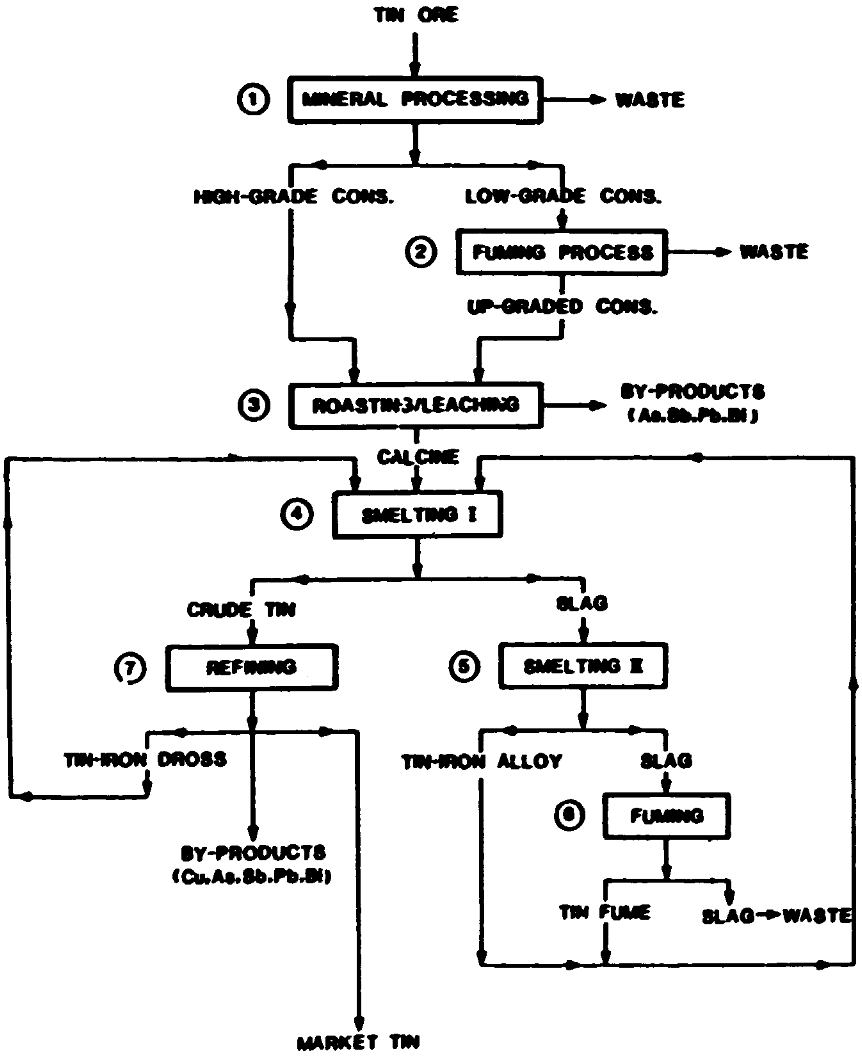
235/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, J. Harris: The Problems of Tin, AIME, New York, 1979.

236/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, T.R.A. Davey: Advances in Lead, Zinc and Tin Technology-Projections for the 1980's, AIME, New York, 1979.

237/ Dungey, C.J., et.al., An Investigation into Control of Radon and Its Daughter Products in Some Cornish Mine Atmospheres, Trans. Instn. Min. Metall., 88, April 1979.

Figure 7.1. Generalised tin flowsheet



<u>Source</u>: "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, T.R.A. Davey: Advances in Lead, Zinc and Tin Technology-Projections for the 1980's, AIME, New York, 1979.

and potential leaching process caused by rain water on the exposed mineral bed. Alluvional tin placers are a very important source of tin-rich ore. They are usually mined by dredging or hydraulicking. In the former case the mineral is first collected by the dredge with buckets, coarsely concentrated (discarding oversized material by means of screens), and then sent to the ore processing plant. In the latter case the ore is disagregated in the pit by high-pressure water jets. The slurry is then pumped to the ore processing plant. Water run-off is the main environmental problem at this stage.

7.2.2 Ore processing

About 75 per cent of the world tin supply comes from alluvional tin placers where cassiterite is present as distinct particles not chemically combined with other minerals.[238] These particles can be relatively easily separated from the surrounding material using gravity methods, provided that the cassiterite particle size is rather small (typically below 150 mesh). The pulp produced during the mining phase is passed through screens to remove coarser material and then sent to jigs where gravity separation occurs. the supernatant slurry, containing mainly cassiterite particles, is then de-watered, giving clean concentrates with a tin content of up to 75 per cent. The tailings from the process are discarded. Much more serious problems are encountered during the processing of ore from hard rocks. In this case, the cassiterite is often associated with quartz, wolframite, fluorite, topaz, scheelite, molybdenite, bismuthimite and lithium micas. In addition, sulphides, such as FeS_2, ZnS, PbS, Bi_2S_3, Sb_2S_3, and tungsten (as $FeMnWO_4$ or $CaWO_4$) are also contained in the mined ore.[239] Most of this material must be removed prior to smelting in order to bring the tin content from 0.5-1 per cent in the mined ore, to at least 5 per cent (which is the lowest acceptable tin concentration for present smelters). Currently there is no real specific method to recover casseriterite from the gangue minerals. Cassiterite is not hydrophobic, it is insoluble in or inert to the most common industrial chemicals, and does not adsorb flotation agents.[240] Consequently gravity separation is one of the few methods available to separate cassiterite from its impurities. However, this does not provide a clean separation, especially if cassiterite particles are very small, thus reducing the settling time differential with respect to the undesired gangue particles. Recovery rates can be rather low (about 50 per cent), yielding a 60 per cent tin concentrate.[241] Flotation of the gangue minerals, especially sulphides, is also used.

238/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, S. Pearce: Development in the Smelting and Refining of Tin, AIME, New York, 1979.

239/ Ryan, W., "Non-Ferrous Extractive Metallurgy in the United Kingdom", The Institution of Mining and Metallurgy, London, 1968.

240/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, J. Harris: The Problems of Tin, AIME, New York, 1979.

241/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, T.R.A. Davey: Advances in Lead, Zinc and Tin Technology-Projections for the 1980's, AIME, New York, 1979.

The main environmental problems associated with ore processing are those of tailings disposal. This problem is more serious for low-grade ores because of the sheer amount of waste material generated and because of the chemicals used during the more complex separation processes.

7.2.3 Smelting process for higher-grade tin concentrates

The conventional smelting process has been known for centuries, but it can be used only for concentrates with a high tin content (not less than 50 per cent).[242/] It is based on the reduction of tin oxide by carbon monoxide according to the reaction:

$$SnO_2 + 2CO \longrightarrow Sn + 2CO_2$$

This reaction typically takes place in smelting furnaces of the reverberatory types (rotary or stationary), or in electric furnaces. The furnace is fed with concentrates, different tin-containing materials (such as dust or hardhead, a tin-iron alloy) produced during the subsequent purification operations, reducing agents (coke or similar), and fluxes. The reducing action of the coke is produced on the tin oxide in a two-step reaction. The overall process can be roughly represented by the reaction:

$$SnO_2 + C \longrightarrow Sn + CO_2$$

The molten metals coalesce, settle, and can be finally tapped from the furnace and then sent to the tin refinery.

A major constituent of most tin ores is iron. During the smelting process the iron goes into the slag as ferrous silicate. At the end of each smelting cycle an equilibrium between the iron and the tin in both the slag and the metal matte establishes. The equilibrium can be represented by the following relationship:[243/]

$$\%\text{ iron in metal} = \text{constant} \times \frac{\%\text{ tin in metal} \times \%\text{ iron in slag}}{\%\text{ tin in slag}}$$

The value of the constant varies as a function of parameters such as temperature, composition, and impurity content. The relationship shows that if the iron content in the final product is to be low (and consequently its tin content, which is the remainder, must be high) then a slag rich in tin must be also produced. This is precisely what is done in the common industrial practice. In order to recover the tin contained in the slag a second smelting furnace is used for slag processing. This slag smelting step produces a final reject slag containing less than 1 per cent tin and a product consisting in a hardhead with about 30 per cent of iron and 70 per cent tin. The hardhead is then fed back to the primary smelting furnace. In addition, both furnaces produce dust-laden gaseous streams, which may also contain CO,

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[242/] "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, S. Pearce: Development in the Smelting and Refining of Tin, AIME, New York, 1979.

[243/] Ibid.

and SO_2 from the oxidation of the pyrites contained in the concentrates. The dusts have a high tin content and their recovery is therefore extensively practiced. Untreated gases from the furnace are a potential source of pollution. The rejected slag contains mainly CaO (typically 15-50 per cent), SiO_2 (25-40 per cent), Al_2O_3 (6-13 per cent), FeO (0.1-25 per cent) and tin (below 1 per cent). Lead can also be contained, but in very small percentages (less than 0.02 per cent).[244] A block diagram of the process is given in figure 7.2.[245]

7.2.4 Smelting processes for lower-grade tin concentrates

Because of the gradual depletion of the alluvial tin ore deposits more and more tin is coming from "lode" deposits (i.e. ore of complex composition) containing high levels of iron and other impurities (as pyrites). Because of the inefficiency of the ore concentrating processes these ores cannot be sent directly to the smelting furnace, but require an additional preliminary step. In practice, when the tin content in the concentrate falls in the 30-50 per cent range ore roasting becomes a necessary pretreatment to the actual smelting step.

Roasting takes place in oil-fired furnaces with a typical capacity of 50 tons per day of mixed charge (concentrate plus recycled dust).[246] During this operation a large fraction of the impurities is converted from solid sulphides or oxides to salts, with associated generation of SO_2. The charge can also contain NaCl which is added to it in order to chloridize some of the impurities, which can then be removed from the calcine by washing. In such a case the calcine is dumped into tubs containing either water or an acidic solution (HCl). The whole operation results in the partial removal of arsenic, lead, bismuth, sulphur, antimony, copper, and iron from the calcine.[247]

From an environmental standpoint the introduction of the roasting/leaching operation results in the generation of a gas stream containing variable amounts of SO_2, fumes, dust, and an acidic liquid stream containing dissolved metal salts.

The subsequent smelting process is similar to that described in the previous section and entails the same environmental problems. In some plants the slag smelting step may be substituted by or followed by an additional fuming step. Slag fuming is a process by which tin is volatized as SnO_2

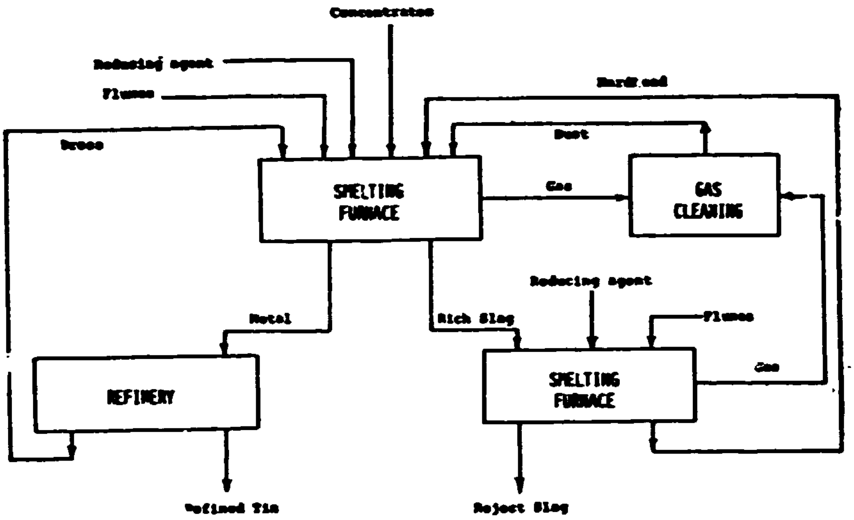
244/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, F. Oberbeckmann and M. Porten: Tin Smelting at Berzelius, Duisburg, AIME, New York, 1979.

245/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, S. Pearce: Development in the Smelting and Refining of Tin, AIME, New York, 1979.

246/ Ryan, W., "Non-Ferrous Extractive Metallurgy in the United Kingdom", The Institution of Mining and Metallurgy, London, 1968.

247/ Ibid.

Figure 7.2. The conventional tin smelting circuit



<u>Source</u>: "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, S. Pearce: Development in the Smelting and Refining of Tin, AIME, New York, 1979.

from the slag and then recovered. The process takes place in a fuming furnace consisting of an internally-lined brick furnace fitted with special tuyeres made of concentric tubes through which air, oil and pyrite (FeS_2) are fed. The furnace is filled up with molten slag from the smelting furnace. As pyrite is fed to the bath in the fuming furnace it dissociates rapidly into iron sulphide and sulphur. The strong agitation brought about by the combustion gases enhances a number of chemical reactions which result in the production of iron silicate and iron oxide (FeO), which remain in the furnace, and SnO_2 and SO_2 which are volatized.[248/] Tin oxide can then be recovered and fed back to the smelting furnace. A reject slag is also obtained from the fuming furnace and is discarded.

The fuming step results in an increase in the amount of tin recovered, but it also creates some potential environmental hazards, which can be rectified only by proper cleaning operations. The fuming furnace contains considerable amounts of dust (up to 3 per cent) (F3) and SO_2 (about 8 per cent in the more advanced type of furnaces). The reject slag contains only trace amounts of tin and heavy metals. A block diagram for the whole process is given in figure 7.3.[249/]

7.2.5 Crude tin refining

Some of the impurities originally present in tin concentrates (such as zinc, titanium, tungsten, tantalum, and niobium) tend to collect into the slag phase and are not found in crude tin. Others, such as iron, copper, arsenic, antimony, nickel, lead, bismuth, gold, and silver remain in the metallic tin phase and must be removed. Tin refining consists of several steps, each associated with the removal of one metal impurity. Iron is removed first as dross by air injection in the molten metal or by drossing (differential cooling and dross removal). Tin with an iron content as low as 0.005 per cent can be obtained.[250/]

Copper is removed by adding elemental sulphur to the molten tin and skimming off the dross so produced. Arsenic, antimony, and nickel are removed by the addition of aluminium dust which forms AlAs, AlSb, and AlNi. This may create some environmental and health hazards. In fact, if AlAs is accidentally contacted with water, arsine (AsH_3), an extremely poisonous gas, is produced.

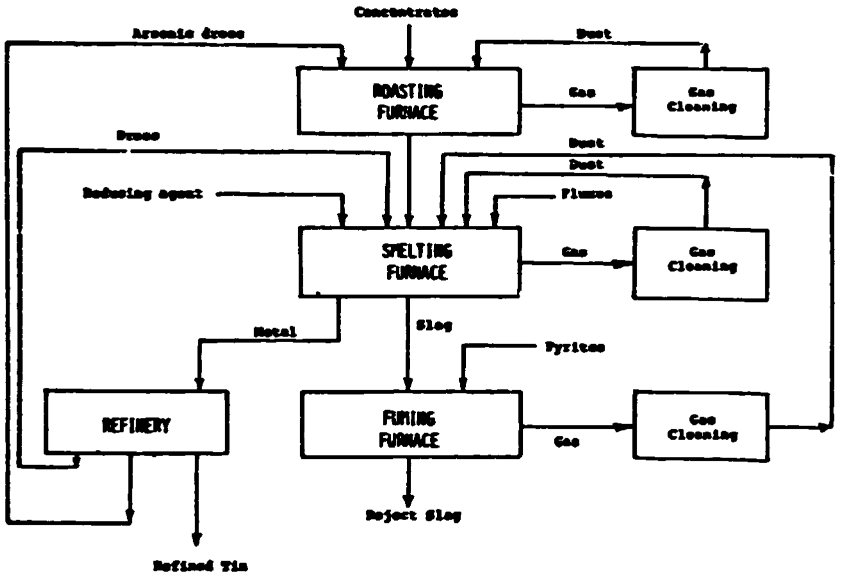
Removal of small amounts of lead and bismuth is accomplished by using chlorine and calcium (or magnesium) respectively. Alternatively, if large quantities of lead and bismuth are present, then removal is accomplished by electrolysis, using either acidic or alkaline baths.

[248/] Wright, P.A., Fourth World Conference on Tin, Kuala Lumpur, 1974, Vol. 3, p. 33.

[249/] "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, S. Pearce: Development in the Smelting and Refining of Tin, AIME, New York, 1979.

[250/] *Ibid*.

Figure 7.3. Smelting circuit for medium-grade concentrates



Source: "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, S. Pearce: Development in the Smelting and Refining of Tin, AIME, New York, 1979.

7.3 Pollution control technologies for tin production plants

7.3.1 Pollution control during mining

Because of the different types and locations of tin mines the environmental implications of the mining operations can be rather various. Underground mining of hard rock has a limited impact in comparison to open-pit mining. The problems associated with open-pit mines are mainly dust generation from blasting and earth moving operations, and deforestation. They can be partially circumvented by water spraying the dust generating areas, and by implementing an appropriate program of land reclamation and revegetation.

More serious problems are encountered in alluvial tin placers especially in southeast Asia where mine areas compete for land with other activities such as agriculture, forestry, and husbandry. So far the mined areas have not been extensively reclaimed. In principle it is feasible to put the tailings back into the mine and start immediate fertilization and revegetation (legumes are an optimal choice) with consequent full reclamation of the mined areas. A major obstacle in this direction is the fact that the alluvional placers are never completely worked out and further expolitation may continue in different periods, according to the fluctuation of the tin prize and the overall world tin supply.[251/]

7.3.2 Pollution control during ore processing

For the case of alluvial tin deposits the separation of cassiterite ore from gangue is just a physical operation. Consequently no major chemical pollution problems arise, but a large amount of tailings must be disposed of. This creates unsightly waste piles, tailings areas, and muddy rivers. This problem cannot be fully overcome, but can be partially circumvented by an appropriate land use and management plan coupled with reclamation programs.

The disposal of tailings is also the major problem encountered during hard rock ore processing. In addition to simple gravity separation the ore may sometimes be processed by flotation of the gangue. In such a case the process water has not only a high content of suspended solids, but may become contaminated by chemical agents. Water should then be recycled and the excess water should be treated with lime in order to neutralize the potentially hazardous dissolved chemicals, before discharge into the environment.

7.3.3 Pollution control during smelting of higher-grade tin concentrates

The gases evolving from the concentrate smelting furnace and from the slag smelting furnace contain large amounts of dust (e.g. 50-150 g/Nm^3 of gas in electric smelting).[252/] These gases are either cooled with cooling

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251/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, J. Harris: The Problems of Tin, AIME, New York, 1979.

252/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, F. Oberbeckmann and M. Porten: Tin Smelting at Berzelius, Duisburg, AIME, New York, 1979.

water or by passing them through waste heat boilers. They are then sent to dust collecting equipment usually consisting of Venturi wet scrubbers or multi-compartment baghouses where most of the dust is removed. Final dust removal may be accomplished with electrostatic precipitators. Traditionally, tin smelters have always made sure that the off-gas particulate emission is very low. In fact the dust contains a large fraction of the total tin processed (as high as 10 per cent of the charge for both furnaces) which can be conveniently recovered and recycled.

Smelter off-gases are also rich in CO and H_2 since a reducing atmosphere must be maintained in the furnace at all times. Therefore, the gases are flared off rather than simply being released through a stack. Depending on the charge composition the gases may also contain variable amounts of SO_2. In most circumstances this concentration is too low to permit conversion to sulphuric acid and the SO_2 is released into the environment.

7.3.4 Pollution control during smelting of lower-grade tin concentrates

Processing lower-grade ore often means processing hard rock ore containing large amounts of pyrites. Most of their sulphur content is then released during the preliminary roasting operation. If multiple-hearth roasters are used the SO_2 generated is not amenable to sulphuric acid conversion. This may create the typical environmental problems associated with SO_2 emissions. Higher SO_2 concentrations can be obtained only using modern roaster design or using ore fuming processes. In this case H_2SO_4 conversion plants can be successfully operated.

The leaching operation, often associated with roasting, may result in the contamination of the leaching liquor with elements such as arsenic, lead, and bismuth. These elements are recovered from the liquor by precipitation with lime and then reprocessed. The environmental problems and control technologies associated with the actual smelting operaton are similar to those described in the previous section. The slag fuming operation is also a potential source of emissions. The fumes and dusts evolved have a high economic value because of their metal content (about 50 per cent tin).[253/] The exhaust gas may also contain recoverable amounts of SO_2 (e.g. 8 per cent in the modern SIROSMELT type of furnace)[254/] which can be treated in sulphuric acid conversion plants.

7.3.5 Pollution control during crude tin refining

Most tin refining operations present minimal environmental hazards. A noticeable exception is the removal of arsenic using aluminum. Although arsine is formed only if the resulting AlAs is contacted with water, many smelters now prefer to use sodium instead of aluminum during this operation, in order to rule out any possibility of incidents. In acid electrolysis the

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253/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy & Environmental Control, K. Foo and J. Floyd: Development of the Matte Fuming Process for Tin Recovery from Sulphide Materials, AIME, New York, 1979.

254/ Ibid.

electrolytic bath contains phenol or cresol-sulphonic acids which may give rise, in principle, to hazardous emissions and fumes. This problem is usually minimized by the use of low temperatures and good ventilation. If alkaline baths are used the process is more efficient, since a higher impurity content in the crude tin is accepted. On the other hand, the electrolysis must be carried out at a temperature of 80°C and the emission problems may become more important. Good ventilation and hooding is then required.

7.4 Potential for by-product re-use

Some of the metals associated with tin minerals have a commercial value and are therefore recovered and sold. Separation of these metals (as salts or oxides) occurs during different stages of the tin production process. In particular, the metal by-product separation occurs during the roasting-leaching operation, during the fuming operation, and at the refining stage. As an example, the new SIROSMELT slag fuming process also produces a small amount of liquid matte (10 per cent of the charge) containing about 40 per cent copper and 30 per cent iron.[255/] Copper, lead, silver, and different alloys containing antimony, lead, and bismuth are commonly produced by tin smelters and are sold to specific metal refiners for further purification. For example the Copper Pass and Son Ltd. company in North Ferriby (UK) produces three different grades of tin, 99.9 per cent pure copper, 99.98 per cent pure lead, non-antimonial solders, Doré bullion (containing 92.25 per cent silver, 7.5 per cent copper, and 0.25 per cent gold), a bismuth-lead alloy (75 per cent bismuth), and two different lead-antimony alloys.[256/]

The slag does not have, in general, any commercial value and is therefore dumped. However, in some instances, it is not possible to free the cassiterite mineral from some impurities such as niobium and tantalum which are then carried into the smelter and end up in the slag. If the slag has a high enough concentration of such metals it becomes marketable for the hydrometallurgical extraction of these elements.[257/]

7.5 Tin recycling (secondary tin production)

Over the decade 1970-80 the amount of tin recovered from secondary sources has been roughly constant, amounting to about 20,000 tons per year.[258/] This figure corresponds to about 8 per cent of the total world tin production, but it is expected that secondary tin production will increase to about 30 per cent of the total production in the near future.[259/]

[255/] Ibid.

[256/] Ryan, W., "Non-Ferrous Extractive Metallurgy in the United Kingdom", The Institution of Mining and Metallurgy, London, 1968.

[257/] "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, J. Harris: The Problems of Tin, AIME, New York, 1979.

[258/] United Nations Yearbook of Industrial Statistics: Commodity Production Data 1966-1975, Vol. II, United Nations, 1977, pp. 498-500.

[259/] MacIntosh, R.M., Tin and Tin Alloys, in Kirk Othmer Encyclopedia of Chemical Technology, 2nd ed., New York, Interscience, 1968, pp. 273-325.

The most important sources of recycled tin scrap are plate clippings from can manufacturing, dross from tinning pots, bronze rejects and other tin-containing parts, babbit from used bearing, and type metal scrap.[260/] Surprisingly, only a small fraction of tin is recovered from used cans. Reclamation is hindered by several problems, mainly collection costs, and cleaning costs prior to recovery.[261/] Because of the fluctuation in the tin content of the scrap supply most reprocessing plants adopt flexible processes. In general, a reprocessing plant consists of a presmelting scrap treatment plant where the scrap is ground, mixed, dried, and then roasted in order to eliminate most contaminants (especially organic matter). Actual smelting takes place in blast or reverberatory furnaces and includes slag smelting. The final refining operations permit recovery of pure tin as well as the metal impurities it orginally contained (such as lead, copper, and antimony). The environmental problems associated with the whole process are similar to those found during primary production, but the SO_2 problem is minimal.

7.6 Retrofitting of existing plants to reduce pollution

Plants processing higher-grade concentrates have limited emission problems since nearly 100 per cent of the dust and fumes is already recovered in order to recycle their tin content. Moreover, SO_2 emissions are usually very low. Plants processing lower-grade tin concentrate (from ore processing to final metal) have been faced with the need to boost their productivity and decrease the amount of discarded waste material. Because of the inefficiency associated with the traditional cassiterite ore concentration process the general trend has been to retrofit existing plants with tin concentrate fuming furnaces which can produce a medium-grade concentrate (40-50 per cent tin) at high recovery rates (over 90 per cent). By comparison, mineral processing can give slightly better concentrates (about 60 per cent tin), but much lower recovery rates (about 50 per cent).[262/] This has not only economic implications, but also environmental consequences, since the amount of tailings to be disposed of is much lower. In some cases, fuming may even replace ore processing altogether.[263/] A disadvantage of the concentrate fuming process is that SO_2 is generated. On the other hand, if the proper technologies are employed the SO_2 generated will have a concentration in the

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260/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, J. Harris: The Problems of Tin, AIME, New York, 1979.

261/ "Tin and Organotin Compounds", Environmental Health Criteria 15, WHO, Geneva, 1980.

262/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, T.R.A. Davey: Advances in Lead, Zinc and Tin Technology-Projections for the 1980's, AIME, New York, 1979.

263/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, S. Pearce: Development in the Smelting and Refining of Tin, AIME, New York, 1979.

off-gases which is high enough for sulphuric acid conversion.[264] An interesting solution has been proposed, which would permit the reutilization of the SO_2 during the tin concentrate fuming or roasting operation.[265] The SO_2 could be fed to the slag fuming furnace in substitution for the pyrites which are now employed at this stage, thus reducing the overall amount of SO_2 generated during tin smelting.

7.7 Innovative and emerging production technologies

Because of the problems connected with the cassiterite separation from the gangue material, extensive research work has been carried out in recent years on cassiterite flotation.[266] Several hundred references can be found in the literature.[267][268][269] Despite these efforts cassiterite flotation has been employed with limited success only in a few cases, by using succinamates, arsenates and phosphonates as flotation agents. Unfortunately these agents are effective only on cassiterite particles characterized by a certain size range. Coarse and fine particles will not float causing a consequent loss in efficiency. It has been stated that, to date, flotation is not a better alternative to gravity separation since the flotation concentrate is very low-grade (about 20 per cent in tin).[270] Moreover, these methods introduce pollutants (e.g. arsenates) in the process water with potential negative environmental impacts.

The different fuming processes developed for ore concentration and slag processing can be considered to be the most important recent contribution to tin smelting. By this method it is now possible to economically process concentrates with tin content as low as 5 per cent, without even roasting the concentrate. Figure 7.4 shows a block diagram for such a[process.[271] Other applications of the fuming process were discussed in the previous sections.

264/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy & Environmental Control, K. Foo and J. Floyd: Development of the Matte Fuming Process for Tin Recovery from Sulphide Materials, AIME, New York, 1979.

265/ King, E.B., and L.W. Pommier, International Symposium on Tin, La Paz, 1977.

266/ "Lead-Zinc-Tin '80, TMS-AIME World Symposium of Metallurgy & Environmental Control, J. Harris: The Problems of Tin, AIME, New York, 1979.

267/ Perkins, S.R.J., Ore Treatment at Renison Ltd., in Papers Presented at the Tasmania Conference, 1977, Australas, Inst. Min. Metall., Parkville, May 1977, pp. 129-139.

268/ Goldman, R.H., et al., A Study of Competing Process Requirements in a Complex Tin Concentrator, pp. 141-154.

269/ Moncrieff, A.G., and P.J. Lewis, Treatment of Tin Ores, Trans. Instr. Min. Metall., A, Vol. 86, April 1977, pp. A56-A60.

270/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, J. Harris: The Problems of Tin, AIME, New York, 1979.

271/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, S. Pearce: Development in the Smelting and Refining of Tin, AIME, New York, 1979.

Some smelters (such as William Harvey & Co. Ltd., Bootle, UK)[272] have been effectively using a three-stage smelting process. Three smelting furnaces are used in cascade. The first furnace produces crude tin and a slag with a 15 per cent tin content. This slag is then processed to give a hardhead (70 per cent tin, 30 per cent iron) and a second slag with 5 per cent tin, which is then finally smelted giving a second hardhead (30 per cent tin, 70 per cent iron) and a reject slag with about 0.5 per cent tin.[273]

A submerged combustion smelting process has also been successfully tested. This process is based on the smelting of the tin-rich slag by using the submerged combustion produced by the violent mixing of air and oil beneath the surface of the molten slag coupled with the reducing action provided by coal dust injected into the bath.[274] Other new furnace designs have also appeared, such as the top-blown rotary converter,[275] and the supersonic top blowing converter, which will eventually replace the traditional reverberatory furnaces in the treatment of low grade concentrates.

Considerable advances have also been made in tin refining. Centrifuges (first adopted in the USSR) have been successfully employed in the separation of drosses during the several stages of the refining process. Vacuum distillation is also used for the removal of impurities from crude tin. Elements such as antimony, lead, bismuth, and arsenic are nearly completely removed by distillation at 1,200°C under very high vacuum. This refining method looks very sound from an environmental standpoint since all emissions to the environment are virtually eliminated.

7.8 A case study

The tin smelting plant owned by Berzelius Metallhütten, GmbH, in Duisburg, Federal Republic of Germany, was chosen as a case study.[276] The company built the plant in 1917. Since then the plant was modified several times. The smelting plant produces soldering tin in the form of blocks, bars, wires, and sheets, and refined tin. Its current production capacity is about 6,000-8,000 tons per year of soldering tin and 5,000 tons per year of refined tin.

272/ Ryan, W., "Non-Ferrous Extractive Metallurgy in the United Kingdom", The Institution of Mining and Metallurgy, London, 1968.

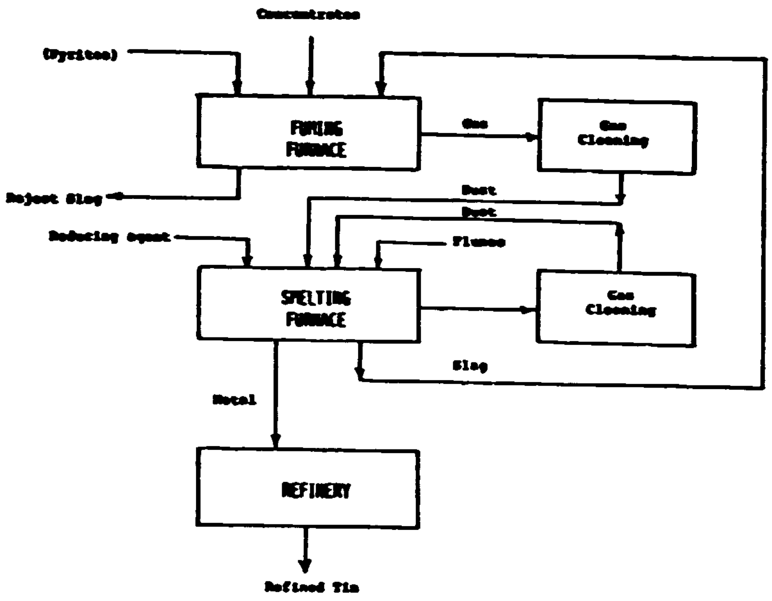
273/ *Ibid.*

274/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, T.R.A. Davey: Advances in Lead, Zinc and Tin Technology-Projections for the 1980's, AIME, New York, 1979.

275/ King, E.B., and L.W. Pommier, "The Future of the Texas City Tin Smelter", in International Tin Symposium, La Paz, November 1977 (microfiche available from Centro de Documentación, P.O. Box 8686, La Paz, Bolivia.

276/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, F. Oberbeckmann and M. Porten: Tin Smelting at Berzelius, Duisburg, AIME, New York, 1979.

Figure 7.4. Smelting circuit for low grade concentrates



Source: "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, S. Pearce: Development in the Smelting and Refining of Tin, AIME, New York, 1979.

Three brands of refined tin are produced, each with a different level of tin purity. These are termed M standard, M special, and Rose Tin. A block diagram for the smelter is reported in figure 7.5.[277]

The soldering tin smelter utilizes a 24 meter-long rotary kiln to produce a tin-lead alloy starting from a mixture of Sn-Pb-Zn metal oxides. the zinc is vaporized as oxide and then recovered from the kiln off-gases by electrostatic precipitators. The Sn-Pb alloy is then refined by electrolysis or kettle refining. Depending on the market demand, short rotary furnaces may also be used for the smelting operations. The refined tin smelter mainly processes Bolivian tin concentrates. Since 1976 the plant has been equipped with a 2-Mega-volt electric furnace. The choice of such a smelting technology was made after the shaft furnace, reverberatory furnace, and rotary furnace were considered. The main factors which were taken into account were the type of concentrate used, throughput, waste gas rate and pollutants produced, dust formation rates, attainable temperatures, energy requirements, and carbon consumption. A flow diagram of the electric furnace smelting plant is given in figure 7.6.[278]

The charge to the furnace consists of tin concentrates, recycled flue dust, ashes, coke, and fluxes. These components cannot be fed directly to the furnace because of the potential problems they would generate during the smelting operation (such as dust generation and incomplete tin reduction). They are firstly mixed together in predetermined concentrations (which may vary according to the tin composition in the concentrates) and then pelletized. After drying for 48 hours at 110°C the pellets acquire sufficient strength for charging to the electric furnace. The furnace consists of two interchangeable crucibles with an outside diameter of 4 meters and a height of 3 meters. They are internally lined with magnesite bricks. The furnace operates continuously. Heat is provided by suspended electrodes placed at about 1 meter from the bottom of the furnace floor. A molten metal phase and a slag phase are formed. They are intermittently tapped every 1.5-3 hours and 0.5-2 hours respectively. The metal phase separates into hardhead (containing up to 25 per cent iron) and crude tin. The hardhead is subsequently smelted in a rotary furnace in order to concentrate the iron and recover the tin.

The solidified crude tin metal is then refined in pots with a capacity of 10 tons of melt. The metal is liquified and then the separation of copper, antimony, arsenic, and lead is carried out by slowly decreasing the temperature, and centrifuging. Alternatively, these impurities are removed by electrolysis in a sodium sulphide electrolytic bath. The slags from the electric and rotary furnaces are smelted in another electric furnace or fumed.

The furnace off-gases are firstly cooled in a heat exchanger, in which partial dust removal also takes place, and then passed through a wet scrubber where the remaining dust is collected. The scrubber can handle up to 1,000 Nm^3/hr of gas with a dust content of 150 g/Nm^3. The removal efficiency is about 99.99 per cent using a water flow rate of 40 m^3/hr. The cooled waste gases (38°C) contain up to 30 per cent CO and 5 per cent H_2.

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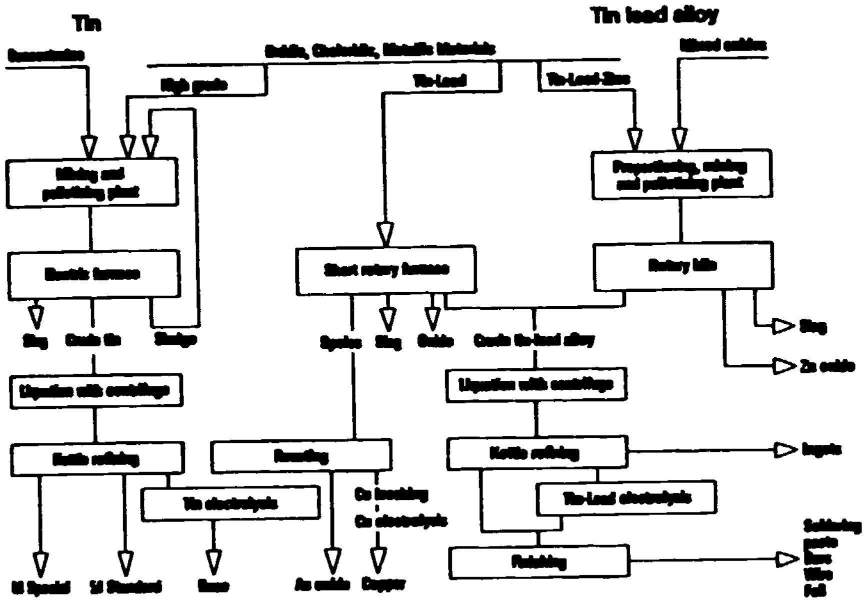
[277] *Ibid*.

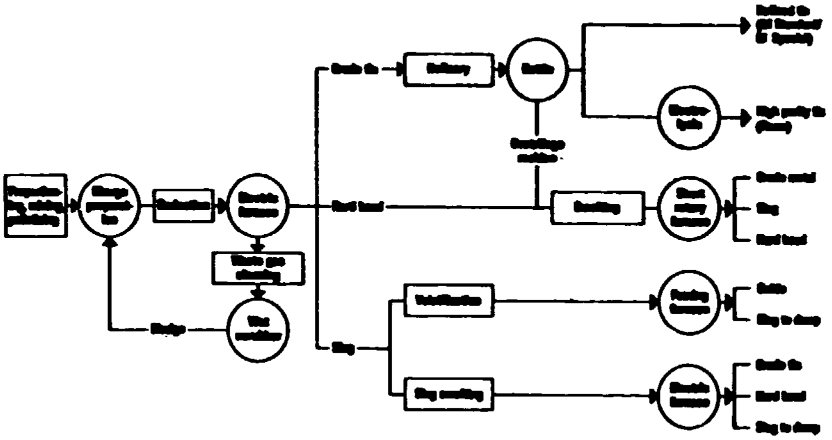
[278] *Ibid*.

Figure 7.5 Flow sheet of the Berzelius tin smelter.



Source: "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, F. Oberbeckmann and M. Porten: Tin Smelting at Berzelius, Duisburg, AIME, New York, 1979.

Figure 7.6. Process flow diagram of electrical furnace tin smelting



Source: "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, F. Oberbeckmann and M. Porten: Tin Smelting at Berzelius, Duisburg, AIME, New York, 1979.

Traces of SO_2 are also present (about 0.01 per cent). Therefore the gases are flared off before being released into the atmosphere. The dust collected is rich in tin and is recycled.

7.9 Pollution control costs

For the case of tin smelters, the equipment used for dust removal from off-gases can be considered as either pollution control equipment or process equipment, because of the valuable tin content of the dust. Data concerning the cost of dust collecting units have already been presented in the copper chapter. Data concerning the cost of SO_2 removal were also given there.

A comparison of the main characteristics of the different tin smelting furnaccs is given in table 7.1.[279] The information contained in this table can be used to evaluate the performance of each type of furnace and hence the associated environmental costs (based on a first estimation of the size of the gas cleaning devices and their operating costs).

7.10 Emission standards

The types of pollutants released by tin smelters vary depending on the technology used and the pollutant concetration in the tin concentrate processed. The gaseous emission limitations for some of the potentially relevant pollutants for this case (such as SO_2, CO, As, Pb and particulates) are given in table 7.2.[280]

7.11 Health protection for workers

Inhalation of elemental tin does not produce any effect in man.[281] Prolonged exposure to tin oxide dust and fumes can result in stannosis, a benign pneumoconiosis which is characterized by small shadows in the pulmonary x-ray picture. This disorder may develop after extensive exposure (at least 3-5 years), but does not produce any impairment of the pulmonary function, provided that other agents, such as silica, are not present in the inhaled dust. More than 200 cases of stannosis have been described in the literature.[282][283][284] Worker exposure to tin or tin oxide fumes is mainly associated with operations such as bagging of concentrate, mixing of furnace charge components, furnace tapping, and periodic cleaning of bag

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[279] Ibid.

[280] Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

[281] "Tin and Organotin Compounds", Environmental Health Criteria 15, WHO, Geneva, 1980.

[282] Schuler, P., E. Cruz, C. Guijon, V. Maturana, and A. Valenzuela, Stannosis, Benign Pneumoconiosis Owing to Inhalation of Tin Dust and Fume, II, Clinical Study, Ind. Med. Surg., 27:432-435, 1958.

[283] Robertson, A.J. and P.H. Whitaker, Radiological Changes in Pneumonconiosis due to Tin Oxide, J. Fac. Radiol., 6:224-233, 1957.

[284] Pendergrass, E.P. and A.W. Pryde, Benign Pneumoconiosis due to Tin Oxide, J. Ind. Hyg., 30:119-123.

Table 7.1. Comparison of tin reduction furnaces

	Rotary furnace	Reverbatory furnace	Electric furnace
Smelting time (h/t charge)	0.7	0.48	0.48
Temperatures (°C)	1100	1350	1580
Throughput (t/m^2d)	1.36	1.0	6.6
Furnace operation (days/year)	300	300	330
Refractory life (months)	8	8 2 years: walls and roof	>36
Fuel oil (l/h)	200	200	---
Reductants (kg/t metal)	330	370	220
Power consumption (kWh/t metal)	208	126.9	1580
Cooling water (m^3/t metal)	5.88	0.2	18
Tin recovery (percentage)	98.5-99.0	99.0	99.5
Waste gas (m^3/t charge)	6500	16,000	250
Dust, max. (percentage)	10	10	5

<u>Source</u>: "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, F. Oberbeckmann and M. Porten: Tin Smelting at Berzelius, Duisburg, AIME, New York, 1979.

filters. Some refining operations may also result in exposure to tin fumes. It has been reported that no cases of stannosis were observed in workers exposed to tin oxide dust concentrations of 10 mg/m^3 for ten years. Nevertheless, the generally accepted maximum allowable concentration of SnO_2 in the working environment is considered to be 2 mg/m^3 of air.[285]

285/ "Tin and Organotin Compounds", Environmental Health Criteria 15, WHO, Geneva, 1980.

Table 7.2 Guidelines for emission levels in tin smelter off-gases

Sulfur dioxide (SO_2)		
Inside plant fence	Annual arithmetic mean Maximum 24-hour peak	100 microg/m^3 1000 microg/m^3
Outside plant fence	Annual arithmetic mean Maximum 24-hour peak	100 microg/m^3 500 microg/m^3
Particulates	Annual geometric mean Maximum 24-hour peak	75 microg/m^3 260 microg/m^3
Carbon monoxide (CO)	Maximum 8-hour average Maximum 1-hour average	10 microg/m^3 40 microg/m^3
Lead (as Pb)		
Inside plant fence	24-hour average	0.008 mg/m^3
Outside plant fence	24-hour average	0.004 mg/m^3
Arsenic (as As)		
Inside plant fence	24-hour average	0.006 mg/m^3
Outside plant fence	24-hour average	0.003 mg/m^3

Source: Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

8. CONCLUSIONS AND RECOMMENDATIONS

(a) The non-ferrous metal industries considered in this work are a major source of environmental pollution. The extent of the environmental impact produced by these industries depends largely on the type of metal processed, the location of the plant and/or mine, the process technology adopted, and the pollution control system used.

(b) Mining activities are likely to have a detrimental impact on the environment especially if they are located near populated areas. During open-cast mining the overburden material is often piled up in dumping areas near the mine. Whenever possible this material should be re-used as infill or stockpiled for later rehabilitation of the mined area followed by reforestation.

(c) Strip mining and exploitation of alluvial tin placers especially in Southeast Asia should be immediately followed by backfilling procedures aimed at reclaiming the strip-mined areas while the mining operation advances further. Revegetation eventually followed by agricultural and other husbandry activities can then begin within a few years.

(d) Underground mining is likely to have a more limited environmental impact than other types of mining operations. The problem associated with the disposal of gangue material still exists, but it can sometimes be solved by backfilling operations.

(e) Mining activities are also likely to produce dust, noise, and noxious emissions of blasting fume residues. Dust emissions should be controlled by water spraying the dust generating areas (such as broken ore at mining stopes, or blast holes), building paved haulage roads, and using appropriate methods to reduce the dust produced by blasting (such as using steam-air jets for mist generation). The noise and dust levels near the mine can be effectively reduced by tree belts or artificial screens built with waste rocks and material. When feasible, ventilation should be provided, or predominant winds should be taken into consideration when choosing the blast points, in order to promote the dispersion of the noxious fumes resulting from blasting operations.

(f) In non-arid regions contamination of mine water can be a serious environmental problem. The water used during mining operations (such as the water used in drilling in underground mines) or the mine run-off water (especially in open-pit mines) may become contaminated with chemical species originally present in the ground. This may result in highly acidic water in open-pit mines or alkaline water in underground mines. Dissolved metals may also be present. Provisions should be made to (a) estimate in advance the type and amount of pollutants contained in the mine water, (b) estimate the water flow produced, (c) collect the water before it escapes into the environment, and (d) build water treatment plants capable of removing suspended solids, neutralizing the excess acidity of alkalinity, and precipitating the dissolved metals prior to the discharge of the water into the environment.

(g) Dust is generated also during some ore processing operations such as loading, unloading, transporting, crushing and grinding the ore. Provision should be made to reduce the amount of dust produced, by water sprinkling. During transportation the humidity content of the ore should be kept at a level which hinders dust formation. In order to decrease the dust concentration in the processing areas the dust generating operation should be identified and confined in appropriate rooms or spaces, the equipment should be sealed, and local ventilation should be provided. These recommendations should be even more strictly followed if the ore contains heavy metals such as lead or cadmium and antimony which constitute a health hazard by themselves.

(h) Concentrating metals in the sulphide ores (nickel, copper, lead, zinc, and tin) involves flotation. This practice requires very large amounts of water which becomes contaminated with variable amounts of flotation agents. These agents are often very toxic and contain cyanides. Consequently, the greatest efforts should be made in order to recycle the largest amount of flotation water (after tailings separation). Whenever possible less toxic flotation agents should be used, and research efforts should be directed toward their development.

(i) Tailings disposal after ore concentration can create a very negative environmental impact because of the amount of tailings produced by the industry, and because of their pollutant content resulting from previous operations (such as flotation). The safest way to dispose of these tailings consists of their impoundment in carefully selected areas, followed by revegetation. The impoundment areas should be located away from water sources, and should be impervious to seepage (i.e. the basin floor should be made of natural clay or artificial sealants).

(j) The concentration of most oxide ores and especially bauxite for alumina production requires a leaching operation. Both alkali (as in bauxite, and some nickel ore processing) and acids (as in some other nickel, copper and zinc ores) are used. The gangue material which is not solubilized during the process is removed and must be disposed of. This often creates an environmental impact, because of the residual alkali or acid content of the tailings. Impoundment in sealed basins is again the most acceptable disposal method which may or may not be followed by neutralization with lime, for the acid tailings case. Many alumina plants already utilize the method of total impoundment of the tailings, where the process and bauxite residues (red mud) lakes are integral parts of the process. Whenever possible this technology should be adopted. It has been proven that the practice of red mud disposal at sea is very detrimental to aquatic life. This practice should be replaced in the shortest time possible by more environmentally sound disposal methods.

(k) The pyrometallurgical smelting process used to produce the crude metal (such as nickel, copper, lead and zinc) from the sulphide ore concentrate involves the removal of the sulphur, originally contained in the concentrate, in the form of gaseous sulphur dioxide (SO_2). If released into the atmosphere SO_2 is eventually converted into sulphuric acid with the well known environmental consequences produced on human health, vegetation, and building by the phenomenon of the acid rain. The concentration of sulphur dioxide in the metal ore smelting furnace off-gas stream, and the amount of off-gases produced depends widely on the technology used. Older plants tend to produce more abundant gaseous emissions characterized by a low SO_2 concentration. Sulphur dioxide removal from such emissions is not economically viable. More modern plants produce SO_2-rich off-gases. In such a case it is possible to remove SO_2 from the off-gases and convert it into sulphuric acid, which is then sold. It is therefore recommended that smelters which produce off-gas streams with a high enough SO_2 concentration be retrofitted (if not already equipped) with an SO_2 conversion plant for sulphuric acid production. Older plants should be eventually either phased out or revamped with more modern equipment capable of producing off-gas streams amenable to sulphuric acid conversion.

(l) Smelters also produce large amounts of dust and fumes which may escape with the off-gases. It is recommended that new plants be equipped with high efficiency dust collecting equipment and that older plants be retrofitted with similar equipment. This move may prove to be advantageous also from an economic point of view since the dust collected often contains metal oxides which can be recycled to the smelting furnace.

(m) Emissions from electrolytic aluminum smelters contain fluorides as pollutants. Similarly, plants for the electrolytic production of other metals (such as tin or copper) may also emit mists which contain pollutants. It is recommended that such plants be equipped with appropriate ventilation systems fitted with particulate collection equipment.

(n) In recent years several new processes have emerged for the pyrometallurgical smelting of nickel, copper, lead, zinc and tin. These processes offer several advantages such as higher metal recovery rates, higher concentration of sulphur dioxide in the off-gases (and consequent amenability to its conversion to sulphuric acid), reduced amounts of dust and fumes produced, higher energy efficiency, and the potential for smelting complex ores. The environmental aspects should play a decisive role in the choice of the smelting process for new plants. Countries are recommended to implement more stringent and better enforced environmental standards.

(o) Recycling and re-smelting of several metal scraps is already extensively practiced for lead, aluminum, copper, and to a lesser extent, tin, zinc and nickel. The percentage of metals produced by reprocessing scrap is expected to grow appreciably in the near future as a consequence of the cost increase of the primary metal production and the reduced energy cost associated with the secondary production.

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SOMMAIRE

Cette étude traite de la production de six des métaux non-ferrugineux les plus importants, à savoir l'aluminium, le nickel, le cuivre, le plomb, le zinc et l'étain. Le document se concentre sur les principaux problèmes qui se rattachent à cette production et sur les moyens efficaces de les résoudre. Les développements techniques de production les plus modernes y sont passés en revue avec une attention particulière aux technologies qui existent déjà et à celles qui seraint utilisées en cas d'urgence tout en étant le moins nuisibles possible à l'environnement.

L'étude examine aussi les sous-produits principaux provenant de chaque métal, spécialement leur utilisation. Elle considère le recyclage des métaux qui peuvent être extraits de la poussière ou des boues de pollution obtenues dans les équipement de contrôle. Une attention spéciale est accordée aux frais de contrôle de pollution qui viendraient s'ajouter aux coûts de fabrication. Des normes environnementales y sont recommandées pour les différents poluants émis. On y décrit les mesures à prendre pour protéger la santé des ouvriers, leur sécurité et leur protection. Une étude de cas porte sur chaque métal à partir d'exemples pratiques obtenus dans des usines sur le terrain.

EXTRACTO

Los principales problemas del medio ambiente y como controlarlos efectivamente son presentados en este estudio sobre la producción de los seis metales no ferrosos más importantes: aluminio, níquel, cobre, plomo, cinc y estaño. Los desarrollos técnicos más modernos en los procesos de producción han sido también examinados. Se ha puesto especial énfasis sobre las tecnologías de producción existentes y las de emergencia que menos impacto causan en el medio ambiente.

Los sub-productos más importantes de cada metal fueron discutidos, enfatizando su utilización. El reciclaje del metal proveniente del polvo o sedimento retenido en el equipo de control de contaminación del medio ambiente fue discutido. Se presentaron los costos del control de la contaminación que se suman a los costos de producción. Se hicieron recomendaciones sobre los estándares del medio ambiente para los diversos contaminantes emitidos. Se explicaron las medidas necesarias para la salud, seguridad y protección del trabajador. Para cada metal se presentó un estudio utilizando la práctica concreta en un lugar de producción.

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