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37 p.
Tables
Annexes

Pollution Prevention and Abatement Guidelines

for the

Copper and Nickel Industries

This document is one of the chapters prepared for a forthcoming set of pollution guidelines jointly prepared by the World Bank, UNIDO and UNEP. The purpose is to give a succinct overview of the main issues affecting the subject industry sector, and of the best technologies and techniques available to avoid undue environmental impact. The regulatory framework within which the industry operates is briefly described by examples, and target discharge limitations that are economically achievable with currently available technology are suggested. The intended readership includes project personnel in investment and development institutions as well as anyone who wish to familiarize themselves with the key aspects of the industry concerned. The information is not sufficient by itself for detailed project design. For this more elaborate advice can be obtained from the references quoted or from other specialized sources of information. Comments on the document should be submitted to Mr. Anil Somani, the World Bank, IFC/M.I.G.A., Headquarters, 1818 H Street, NW, Washington D.C. 20433, U.S.A., with copy to UNIDO, Att. Mr. Ralph Luken, P.O. Box 300, A-1400 Vienna, Austria.

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1 EXECUTIVE SUMMARY

In the production of primary copper or nickel from either oxide or sulfide ores, the processes employed in the mining, mineral beneficiation and early stages of manufacturing are essentially the same for each metal. It is in the latter stages of manufacturing, primarily refining, where the process technology differs significantly. It is the scope or purpose of this document to provide a simple outline of the various commercially proven technologies, the major environmental problems to be considered, and some typical environmental regulations currently in force. Guidelines which are reasonable, based on experience in the industry, are proposed to provide guidance in cases where there are no environmental regulations in place.

In general, pyrometallurgical processes operating at temperatures up to 1300°C are used to process sulfide ores and discard the major impurities as a non-hazardous fused product, "slag". The primary environmental concern is the sulfur dioxide produced which must be fixed, sulfuric acid production being the most common route. Occasionally, byproducts such as sulfuric acid can improve the economics of a project. Hydrometallurgy leaches the copper or nickel at lower temperatures, thus leaving the sulfur and a number of other impurities in the waste residue. While hydrometallurgy eliminates the formation of sulfur dioxide, the technology can produce some hazardous residues and liquid effluents which must be treated prior to disposal. A wide range of commercially proven process technologies are available to meet the particular requirements of any given ore, environmental requirements or specific site conditions, and the details are described in the references listed. Secondary copper or nickel, that is, recycled scrap, is usually processed in primary smelters; however, in some areas sizeable secondary smelters are in operation using process technology which is very similar to that found in primary smelters. In these cases, however, the presence of volatile and heavy metals is a prime environmental concern. Sulfur is rarely present to any extent in recycled scrap.

The use of oxygen to enrich the combustion air in the smelting of sulfides has resulted in a trend towards higher sulfur dioxide (SO₂) process gas streams, ranging from 15 to 75% SO₂. Since very little if any auxiliary fuel is used in the smelting furnaces, the emission of NO_x is not a problem in the industry. However, volatile impurities such as arsenic, lead, mercury, fluorine, etc. are a concern and specialized processes are required to protect the environment. Similarly, furnace openings, launders, tanks, etc. are enclosed to prevent the escape of fugitive emissions to the workplace. The key is to provide a safe environment for the worker which will enable him to carry out his duties. Liquid wastes and effluents result from the bleed streams necessary to control impurity buildup, the removal of excess run-off and process water, neutralization of weak acids, etc. Frequently these streams can be treated to precipitate the heavy metals for impoundment or recycle, leaving an effluent which is safe to discharge to the watershed.

Hazardous wastes are those which endanger health or contaminate the environment, consequently they are, by definition, site-specific and dependent on a number of factors. Dusts bled from smelter hot gas cleaning systems will contain arsenic, lead, mercury and other hazardous elements of concern. These will be in the form of oxides, sulfates or similar compounds which can leach when exposed to the weather. The tonnages are usually small, but nevertheless they should be impounded, as are leach residues, in sealed ponds or processed in pyrometallurgical plants to produce an inert silicate slag.

The first priority for worker protection should be process selection and a plant design in which safety is a prime consideration. Various designs, systems for personal protection, and administrative controls are used. The objective is to control the level of potentially hazardous substances in the workplace to less than those legislated or the Threshold Limit Value recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). Allowance must be made for the startup or upset conditions which can and will occur periodically in any industrial operation. However, these situations can be minimized with good housekeeping, proper training, and a reasonable level of maintenance.

When selecting the technology best suited to protect the environment specific to a given smelter location, it is essential that a comprehensive waste management plan be developed which is workable and takes the local conditions into account. Various equipment are used to reduce airborne particulate emissions to acceptable levels. Gaseous contaminants are removed using any number of dedicated plant designs or one of various scrubbing systems which have been developed. Liquid effluents are adjusted for pH, usually 6.0+, and the heavy metals precipitated. Depending on the impurity balance, this precipitate may be returned to the smelter. The treated effluent may be used as make-up process water or discharged to the watershed, in which case it must meet local water quality specifications.

In any overview of environmental regulations, it soon becomes apparent that the discharge limits, methods of determination, etc. differ significantly from one jurisdiction to another. The majority do, however, specify ambient conditions at the point of impingement. For example, the overall sulfur dioxide emission limits for British Columbia, in Canada, are lower than the National Ambient Air Quality Standard in the U.S.A. due to the significant role the forests and salmon industry play in the Province. In Sweden, the limits are "site-specific" and are in effect a function of the production rate for that particular plant. Where liquid effluent limits are concerned, the Japanese limits target mercury due to the importance of the fishing industry in the Inland Sea and coastal waters. The majority of regulations require monitoring on a continuing basis of the various elements of concern as they progress through the process, groundwater levels and various impoundment areas.

1.1 PROPOSED DISCHARGE LIMITATIONS

Guidelines for pollutant discharge must be both technically and economically realistic and based on impact criteria which take into account the ecological and climatic features of the specific area. They must permit the development of a comprehensive waste management plan which reflects the particular features of the local environment. Finally, it is important that the final guidelines or regulations do not impede the recycle of hazardous materials which can be rendered harmless, or inert, in the high temperature operations of many smelters.

For those cases where there are no applicable environmental regulations, the following limits are proposed as a reasonable basis upon which to base a design which will provide a practical level of environmental protection.

Ambient Air Criteria:

Based on measurements taken at point of impingement at ambient conditions.

	<u>µg/m³</u>
Sulfur Dioxide: Annual Arithmetic Mean	80-100
Maximum 24-hour Mean	340-370
Dust Loading: Annual Geometric Mean of:	
- 24-hour Concentrations	75
- 24-hour Average (no more than once/year)	260

Effluent Concentration Limits:

	<u>mg/l</u>
Arsenic	1.0
Copper	1.0
Iron	5.0
Lead	0.5
Nickel	0.5
Selenium	1.0
Zinc	10.0

1.2 CONCLUSIONS

The efficient processing of copper and nickel feed materials requires the use of modern process technology designed to provide a high level of recycle or intermediate products, and the containment of gaseous and particulate emissions.

Hydrometallurgical processes eliminate the emission of sulfur dioxide but frequently produce hazardous wastes and effluents, whereas pyrometallurgical processes can produce large volumes of sulfur dioxide. They also produce a relatively inert slag which frequently renders hazardous elements inert and can facilitate the recycle of some hazardous wastes. Some hydrometallurgical processes can produce inert process residues, such as hematite (iron ore pellets).

Copper and nickel ores and concentrates can be processed safely to marketable products and still meet realistic environmental limits. Byproducts such as cobalt, zinc, sulfuric acid or precious metals will frequently be produced, which improve the economics.

2 INTRODUCTION

Copper is frequently found in association with nickel in sulfide mineral deposits. Mining methods and mineral processing equipment are the same for each ore with only certain operating parameters being adjusted to accommodate the specific mineral and produce a concentrate. In addition, the basic design of the equipment used in the smelting of sulfide concentrates is the same for each metal. Only as processing proceeds through to refined metal do the processes and technology diverge.

The scope, or purpose, of this document is to provide a very simple outline of the various technologies in commercial operation for the processing of copper or nickel ores, the major environmental problems which result, and some examples of the emission limits in force in some specific jurisdictions. To provide some guidance for cases where there are no up-to-date environmental regulations in place, guidelines are outlined which are attainable based on industry experience.

This document will summarize the more common smelting and refining processes for both copper and nickel, in particular where the processes differ. In the case of sulfide ores or concentrates, the emission of sulfur dioxide (SO₂) to the atmosphere and working environment is the major environmental concern. Oxide ores do not contain significant amounts of sulfur, but dust, soil erosion and associated hazards are a concern. Where mineral beneficiation and hydro-metallurgical processes are used in place of smelting or in conventional refining, the treatment of liquid effluents and the safe disposal of the various residues are the principal concerns.

3 MANUFACTURING PROCESSES

3.1 MINING AND MINERAL BENEFICIATION

For low grade deposits of either sulfide or oxide ores, the open pit method is the most practical and lower cost system for the mining of large tonnages of ore. Large track-mounted drills prepare the ore for blasting, and the broken ore is hauled to the crushing plant by truck or conveyor. Higher grade orebodies are normally mined by underground methods. Vertical shafts are sunk below the surface adjacent to the ore deposit and tunnels are extended to the ore. Pneumatic drills and mechanized equipment drill and blast the ore which is hoisted through the shaft to the crushing plant.

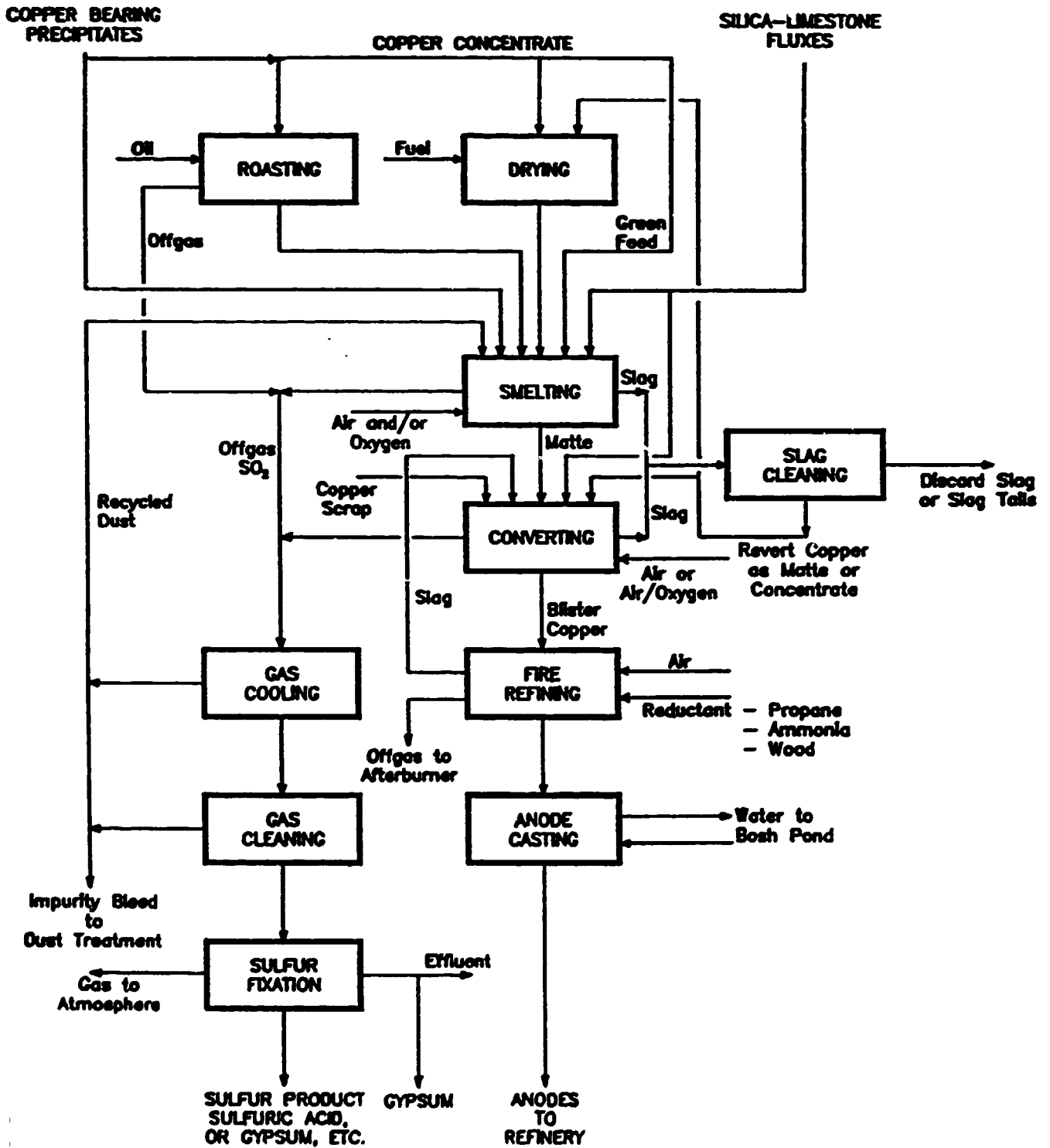
Mineral beneficiation (1) continues the crushing of ore received from the mine and ends with grinding to ensure that the copper or nickel minerals are liberated from the worthless materials. In cases where the next process step is leaching (most frequently in the case of oxide copper ores), the ore needs only to be ground to the extent required to expose the mineral surfaces to the leaching agent. For sulfide ores, selective flotation normally follows grinding.

In the flotation process, the finely ground ore is mixed with water and special reagents (some of which may be toxic), and agitated by mechanical and pneumatic devices. These produce air bubbles in the ore-water mixture which is known as "slurry". The reagents provide an attraction between the surface of specific minerals and the air bubbles. As the bubbles rise to the surface they carry these minerals with them, leaving unwanted components to be discarded as a waste, known as "tailings". Collection of the froth from the surface of the flotation cells yields a concentrate which is dewatered and filtered to produce a low moisture filter cake for further processing in an appropriate smelter. The final product from sulfide ores may be a bulk copper-nickel concentrate or individual copper or nickel concentrates, depending on the requirements of the downstream processes.

3.2 COPPER PROCESSES

Mineral beneficiation and/or feed preparation are the first stages of the manufacturing process. The second involves either smelting to remove additional impurities (in particular

Figure 1. Copper Smelter Process Flow Diagram



iron and sulfur) to further concentrate the values, or leaching to extract the desired metals. The third and final stage is refining, usually electrorefining, which removes the remaining impurities, minor elements such as precious metals, and produces a 99+ % pure copper.

The smelting of untreated or "green" concentrate is no longer acceptable from the point of view of energy efficiency or the environment, and is being phased out of industry practice.

Modern technology (2) utilizes roasting to remove and capture some of the sulfur and volatile impurities such as arsenic or mercury, or the concentrate will be dried to remove excess moisture. Fuel oil, natural gas, steam or preheated process air will supply heat to the dryer. As shown in Figure 1, the concentrate is then combined with copper-bearing residues, precipitates, etc., and a controlled amount of flux and fed to the smelting furnace.

The flash smelting process (1)(2) has now become the industry standard, although the electric furnace is still used in particular cases. In flash smelting, the dry furnace feed mix, containing less than 1% moisture, is fed to the furnace along with preheated air, oxygen-enriched air (30 to 40% O₂), or pure oxygen. The iron and sulfur are oxidized, and the heat generated by the exothermic reactions can be sufficient to smelt concentrate to produce a liquid matte (35 to 65% Cu) and a fluid slag. Normal smelting furnace temperatures are in the range of 1250°C to 1350°C. While flash smelting is the most common process, there are others which use lances in place of burners or reactors of various types, all designed to efficiently utilize the heats of reaction and prevent emissions to the atmosphere.

The furnace matte still contains iron and sulfur. These are oxidized in the converting step to sulfur dioxide and iron oxide by injecting air or oxygen-enriched air into the molten bath. With the addition of a flux, the iron and other oxides form a slag which floats and is skimmed from the surface, as is the case during smelting. Secondary copper (scrap) is frequently used as a coolant to control temperature. The converting process can be either batch or continuous, depending on the technology adopted. The product is normally a blister copper (98.5% Cu, 0.8% O₂).

In countries where there is no significant primary production, secondary copper smelters will operate using processes and equipment similar to those employed in the primary industry to process copper scrap and residues. The impurities, however, are usually different and many, such as lead, zinc and precious metals, are recovered in the gas cleaning system as byproducts. Organic components may be stripped prior to smelting or left in the feed to provide fuel. In either case, secondary smelters must meet the same environmental and safety regulations as primary smelters.

Due to the intense nature of modern smelting processes, certain auxiliaries are required to maximize the recovery of values and to protect the environment. Slags are cleaned prior to discard using slow cooling and flotation or, alternatively, an electric furnace to minimize losses and recover the copper values as a concentrate or electric furnace matte. Process gases are cooled using air-to-gas heat exchangers or waste heat boilers prior to the removal of particulates in an electrostatic precipitator or baghouse. The offgas then receives a final scrubbing in a wet gas cleaning circuit and the sulfur is converted to acid, liquid SO₂ or other sulfur product. The precipitator or baghouse dust frequently must be treated in a separate circuit to control impurity build-up in the smelter and hydrometallurgical processes have been developed for the purpose. Disposal of some of these bleed stream products can be a problem, particularly those containing antimony, arsenic or mercury. Collection and containment of the various vent gases is necessary in a modern smelter and in some cases, they must be scrubbed with lime or other alkali to remove SO₂.

The final smelting or first refining process is fire refining, where blister copper goes through an oxidation-reduction process to produce copper anodes (99.5% Cu) for electrolytic refining. Depending on the reductant used, afterburners may be required on the offgas system to ensure complete combustion.

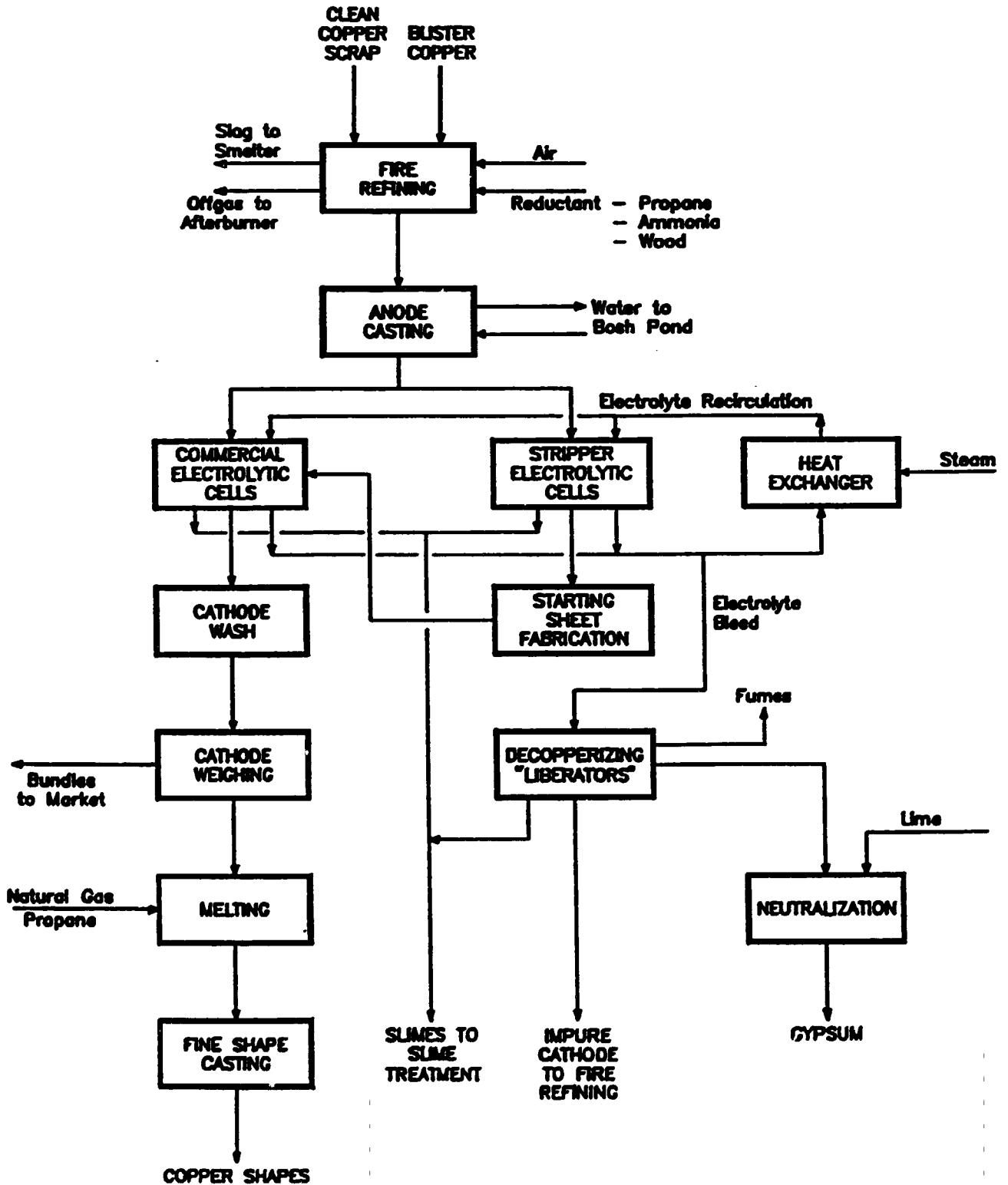
The most common hydrometallurgical processes leach the input with ammonia or sulfuric acid to extract the copper, particularly from oxide ores. These processes can operate at atmospheric pressure or as pressure leach circuits. Leaching of low grade deposits "in-situ" or as heaps of ore, is very efficient and becoming more common in the case of copper. The hydrometallurgical processes overcome the problem of sulfur dioxide emissions, but effluent treatment of solution bleed streams and disposal of the residues are environmental concerns.

Intermediate sulfur compounds can be formed and an oxy-hydrolysis circuit is required to protect the environment. In addition, the ability to recover byproduct precious metals is limited with hydrometallurgy, restricting its application to materials low in precious metals. Solvent extraction or ion exchange technologies have been improved to the point where most leach solutions can be upgraded to a level where the metal values can be recovered by electrowinning. In this process, copper is plated onto cathodes from a leach solution containing 20 to 50 grams Cu per liter (gpl) and 30-150 gpl free sulfuric acid in electrowinning cells equipped with inert anodes, usually lead.

Most copper is refined using the electrolytic process. Here, copper is plated from impure copper anodes onto pure copper starting sheets (cathodes), both immersed in a copper sulfate-sulfuric acid solution, when an electric current passes through the solution (Figure 2). Impurities such as selenium, precious metals, etc. settle to the bottom of the electrolytic cell and are removed periodically for further treatment. In the majority of cases, cathode copper of more than 99.9% Cu purity is produced in the electrolytic process; however, it requires more careful process control to achieve the same level of purity with the electrowinning process.

Residues, precipitates, etc. from a refinery are usually returned to a smelter for the recovery of values, consequently, the environmental concerns are limited in most cases to the emission of fumes and the relatively small volume of liquid effluents.

Figure 2. Copper Electrolytic Refining



3.3 NICKEL PROCESSES

Primary nickel is produced from two very distinct types of ore. Sulfide deposits are very similar to, and frequently found in conjunction with, copper ores. The second ore type is oxide, which is commonly referred to as a "laterite" ore and is normally found where the climate is tropical. This type of climate over time breaks the rocks down to soil or clay. The weathering process will extract nickel, when present, and deposit it in layers at varying depths below the surface; this process is known as "lateritic weathering". Unlike the hard sulfide ores, laterite nickel ores are soft clay-like as a result of the effects of weathering and form in strata near the surface of the earth. There are two main types of these oxide ores: the limonite type is found in the upper levels of the laterite deposit in which ferric oxide minerals are predominant. The second is garnierite, which is a silicate type of ore and forms in the lower layers during the laterization process.

Oxide, or "laterite" nickel ores cannot be concentrated as described previously for the sulfide ores. Mining consists of a large earth-moving operation using electric shovels, front-end loaders and off-road trucks - much the same equipment as in conventional open pit mining. Mineral processing is confined to screening out and discarding low grade boulders leaving the remainder of the ore as mined to be processed. Large tonnages of laterite nickel ores must therefore be processed to achieve reasonable nickel production rates (2). The choice of processes which can be considered for primary nickel production depends on which of the major ore types will be used as smelter feed. The major process steps are summarized in Figure 3.

3.3.1 Nickel Sulfide Processes

The smelting processes used for nickel sulfides are very similar to those described previously for copper. The older nickel smelting processes, such as the blast or reverberatory furnaces, are no longer acceptable from the point of view of energy efficiency or the environment, and are being phased out of industry practice. Modern technology (2) utilizes roasting to remove and capture some of the sulfur and volatile impurities such as arsenic or mercury, or the concentrate will be dried to remove excess moisture. Fuel oil, natural gas, steam or preheated process air will supply heat to the dryer. The concentrate is then combined with nickel-bearing residues, precipitates, etc., and a controlled amount of flux and fed to the smelting furnace.

The flash smelting process (2)(3) has now become the industry standard, although the electric furnace is used in particular cases or where higher smelting temperatures are required. For example, some nickel concentrates and nickel laterite ores can be high in magnesia and require high temperatures to maintain a fluid slag. In flash smelting, dry sulfides containing less than 1% moisture, are fed to the furnace along with pre-heated air, oxygen-enriched air (30 to 40% O₂), or pure oxygen. The iron and sulfur are oxidized, and the heat generated by the exothermic reactions can be sufficient to smelt concentrate to produce a liquid matte (up to 45% Ni) and a fluid slag. Normal smelting furnace temperatures are in the range of 1350°C to 1550°C. While flash smelting is the most common process for sulfide concentrates, the electric furnace is the common smelting unit for laterite nickel ores. Pressure leaching and other hydro-metallurgical processes are also used in the nickel industry, particularly in operations where there is no fuel value in the feed materials and the precious metals content is negligible.

Flash or electric furnace matte still contains iron and sulfur. These are oxidized in the converting step to sulfur dioxide and iron oxide by injecting air or oxygen-enriched air into the molten bath. With the addition of a flux, the iron and other oxides form a slag which floats and is skimmed from the surface, as is the case during smelting. Secondary nickel-bearing scrap is frequently used as a coolant to control temperature. The nickel converting process is a batch process. The product is a high grade nickel matte (75%).

Due to the intense nature of modern smelting processes, certain auxiliaries are required to maximize the recovery of values and protect the environment. Slags are cleaned prior to discard using an electric furnace to minimize losses and recover the nickel values as an electric furnace matte. In cases where there is a reasonable level of cobalt in the smelter feed, the slag cleaning circuit can be adjusted to maximize the recovery of cobalt as a separate byproduct. As with copper, process gases are cooled using air-to-gas heat exchangers or waste heat boilers prior to the removal of particulates in an electrostatic precipitator or baghouse. The offgas then receives a final scrubbing in a wet gas cleaning circuit and the sulfur dioxide is usually converted to acid. The precipitator or baghouse dust frequently must be treated in a separate circuit to control impurity build-up in the smelter and several hydrometallurgical processes have been developed for the purpose. Disposal of some bleed stream products can be a problem, particularly those containing antimony, arsenic or mercury. Collection and containment of various vent gases is necessary in a modern smelter and in some cases, they must be scrubbed with lime or other alkali to remove SO_2 .

3.3.2 Laterite Nickel Processes

Laterite nickel ores have a high percentage of free and combined moisture, and the first step in their processing is the removal of the free moisture. Next, the ore is fed to the reduction furnace to remove the chemically-bound water and reduce the nickel oxide, while controlling the amount of iron oxides reduced. As noted previously, these ores have no significant fuel value and electric furnace smelting is the standard for laterite ores since the reaction heats are not significant and high temperatures in the range of 1500°C are required to accommodate the high magnesia content.

Some laterite nickel smelters add sulfur to the smelting furnace charge and produce a furnace matte which is processed in the same manner as matte from sulfide ores. Others will reduce sufficient iron to produce ferronickel products, and this is the process adopted by most laterite nickel operators.

Hydrometallurgical processes based on ammonia or sulfuric acid leach are also used in laterite nickel operations. There can be limitations, however. For example, garnierite (silicate type) ores are usually high in acid soluble magnesia, eliminating sulfuric acid leach as an option. The ammonia leach is usually applied to the ore after the reduction roast step which adds to the cost.

OVERVIEW OF NICKEL ORE PROCESSING

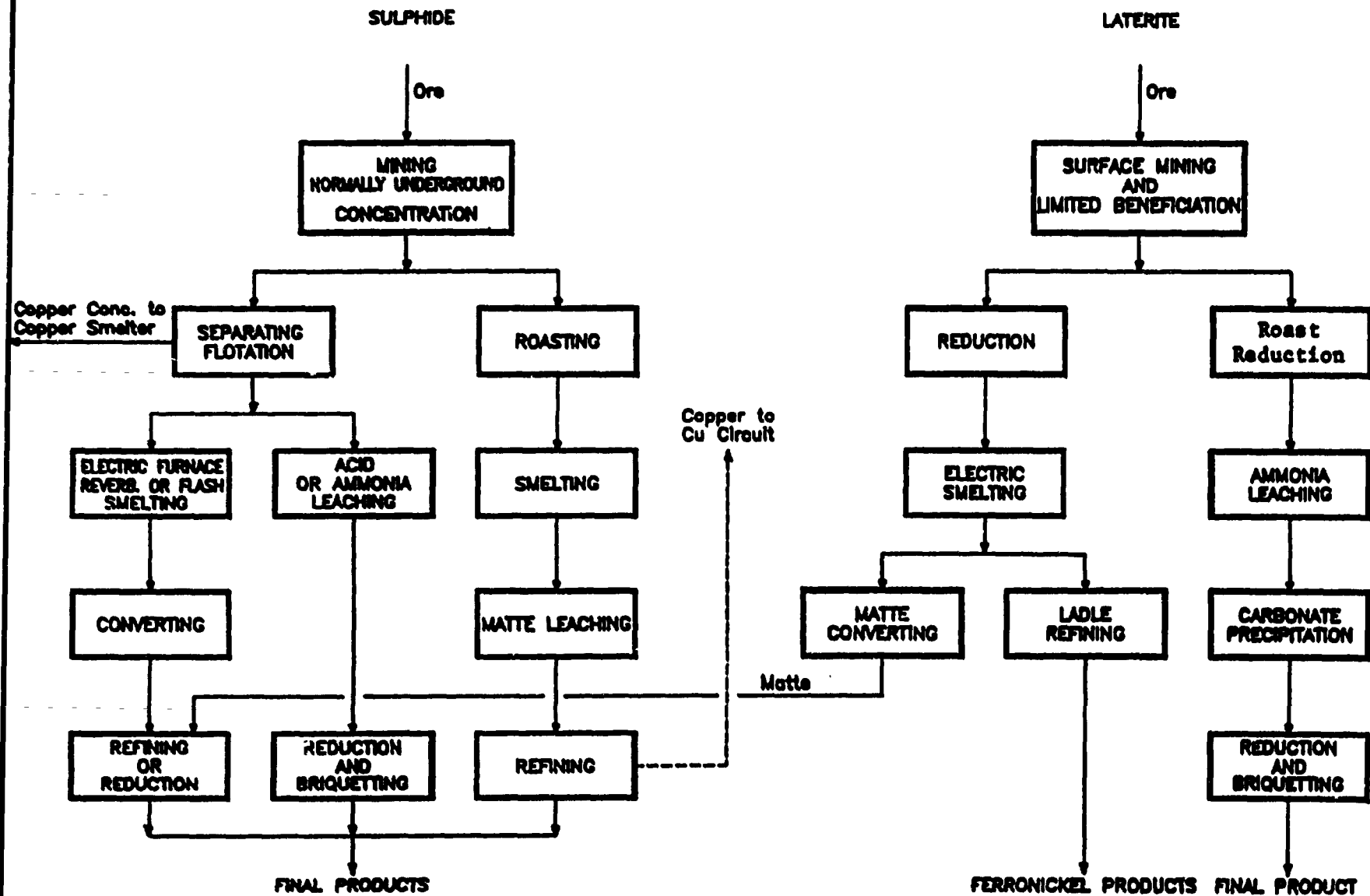


Figure 3. Overview of Nickel Ore Processing

3.3.3 Nickel Refining

Various processes are used to refine nickel matte (4) (6). Fluid bed roasting and a chlorine-hydrogen reduction will produce high grade nickel oxides (95+ % Ni). Vapour processes, such as the Carbonyl process, can be used to produce high purity nickel pellets, but nickel carbonyl is very toxic and requires complex systems to ensure safe operation. In this process, copper and precious metals remain as a pyrophoric residue requiring separate treatment. In electrorefining, the process is very similar to that for copper but the electrodes are separated by diaphragm compartments to prevent the passage of impurities from anode to cathode. The electrowinning process, that is, the removal of nickel from solution in cells equipped with inert anodes, is more common with nickel than with copper. In some processes a chloride electrolyte is used in the electrowinning cell; in others, sulfate electrolyte solutions result from leach or solvent extraction processes. In the production of ferronickel (the more common product from laterite operations), refining is a pyrometallurgical process and directed towards the removal of such impurities as sulfur, carbon and phosphorous.

3.4 PRIMARY RAW MATERIALS

The primary raw materials feeding a copper or nickel smelter are concentrates and fluxes as described in Table I.

Table I Typical Range of Analysis for Smelter Raw Materials

Percent	Sulfide Concentrates		Oxide Ores	Flux	
	Copper	Nickel	Nickel	Silica	Limestone
Copper	20-30	1-5	-	-	-
Nickel	-	3-12	1.6-2.9	-	-
Iron	22-32	25-43	13-21	0.5-2.0	0.5
Sulfur	30-34	19-31	-	-	-
Silica	-	-	-	85-95	-
Lime	-	-	-	0.5-1.0	50-55
Moisture	6-12	9-15	20-32	-	-
Mesh Size	80-90% -200	7-80% -200	-65mm		

Appropriate scrap metal, residues and recycle dusts, process scrap, etc. will be added along with the above materials. The amount and type of materials which can be processed will depend upon plant capacity, impurity levels and the smelting process. In general, smelting processes are more adaptable with respect to feed materials than leaching.

3.5 ECONOMIC AND ENVIRONMENTAL FACTORS IN PROCESS SELECTION

The mineralogy and composition of an orebody and the proposed smelter location all have a significant bearing on which processes can be considered. It should be noted that for any metallurgical plant, it is the impurities present in the feed materials which have the greatest impact on the ability of the plant to meet environmental regulations at an affordable cost. With respect to location, the following are key economic considerations:

- a) Energy supply and cost, particularly where electric furnace processes or high levels of oxygen enrichment (90%+) are being considered.
- b) Environmental regulations governing the disposal of residues and slag, and the containment of pollutants such as sulfur, arsenic, etc.
- c) Design capacity. The capital costs of some of the newer smelting processes are such that a smelting rate of at least 1000 MTPD concentrate is required to be economic.
- d) Byproduct recovery can improve project economics through the sale of aggregate, acid, precious metals and energy. In this respect, a tidewater site can offer significant advantages, particularly where byproduct acid is produced.

3.6 TYPICAL CONSUMPTION DATA

A reliable supply and sufficient capacity of electric power is essential for any metallurgical plant. For smelting processes, excluding the electric furnace process, typical power consumption would be in the range of 320 to 520 kWh/MT of copper or nickel concentrate, including oxygen and sulfuric acid plants. The electrolytic refining of copper will require between 250 and 300 kWh/MT cathode copper; electrowinning processes require considerably more power, in the range of 2200 kWh/MT cathode copper. By comparison, a leach-electrowinning process for copper would consume between 950 and 1100 kWh/MT concentrate.

Fuels of various types are required to make up for heat deficiencies in the feed materials, preheat ladles, maintain flow in launders, etc. When equipped with the appropriate environmental controls, modern smelting furnaces can utilize a range of "dirty" fuels such as high sulfur coal or oil, scrap plastics, etc. In these smelters, the offgases are cleaned and industry experience indicates that the temperature is sufficiently high to destroy any noxious combustion products which may result. Once the metal is refined, clean fuels such as propane, natural gas or light industrial fuel oil are used to avoid contamination in the melting, casting and other processes.

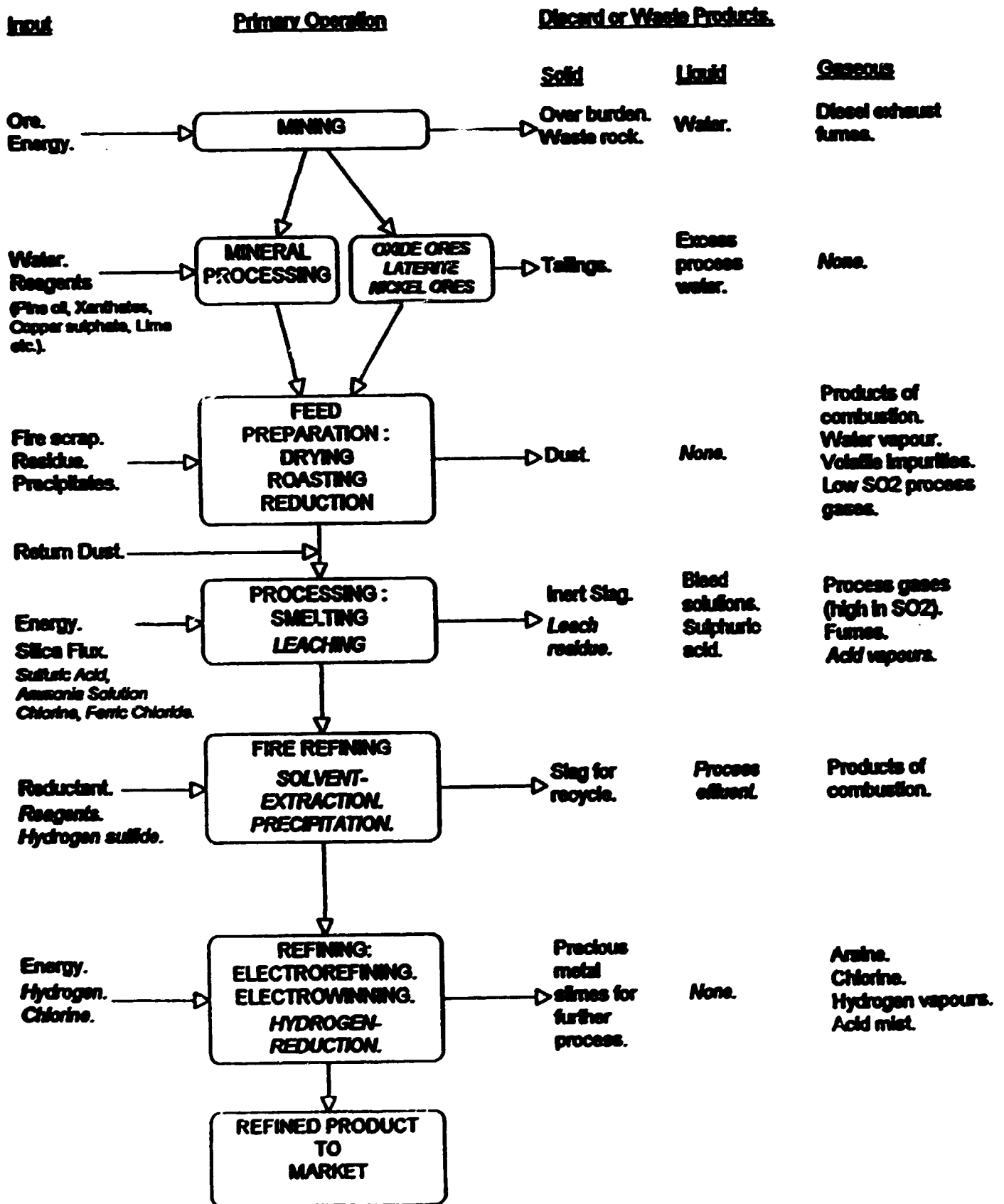
Water is required for refractory cooling, make-up for solutions bled from the circuit for impurity control, gas cooling and scrubbing, cathode washing, etc. Normally treated effluents, excess process water, etc. are collected in a large settling pond and can be recycled to the process. A typical smelter-refinery complex, with flotation slag cleaning and a sulfuric acid plant, would require approximately 6 to 9 m³ of water per MT of concentrate.

4 WASTE CHARACTERIZATION AND IMPACTS

4.1 WASTE QUANTITIES AND IMPACTS

The smelter input and discard or waste products are summarized in Figure 4 to provide an overview of the following sections.

Figure 4. Metallurgical Process Waste Sources



4.1.1 Atmospheric Emissions

These are of particular concern where sulfide ores are being treated pyrometallurgically. The sulfur dioxide (SO₂) concentration in the process gases will depend on the level of oxygen enrichment, and higher enrichment levels are being used to increase the sulfur dioxide strength, as indicated in Table II, and reduce the total volume of the process gas stream to reduce the equipment size and cost of gas cleaning.

Table II Typical SO₂ Levels in Process Gas Streams Before Sulfur Fixation

Smelting Furnace	% SO ₂ by Volume
Fluid Bed Roasters	6.0 to 12.0
Electric Furnaces	0.5 to 3.0
Flash Furnace - Outokumpu Design	15 to 30
- Inco Design	70 to 80
Noranda Reactor	6 to 10
Mitsubishi Continuous Process	15 to 25

Source: Reference 2

As an additional benefit, very little if any NO_x is produced by the newer processes. Offgases contain fine dust particles and may contain volatile impurities such as arsenic, fluorine and mercury, depending on the furnace feed. These are removed from the gas stream ahead of the sulfur fixation plant in wet gas cleaning or other specialized circuit (Fig. 1).

Fugitive emissions will occur at furnace openings, from launders, casting molds and ladles carrying molten materials, which allow sulfur dioxide and volatile elements to be emitted to the working environment. When fine ores or concentrates are being transported, there can be wind or material handling losses at each transfer point totalling as much as 0.5% of the weight of the material handled, depending on the plant design, level of maintenance and care in operation. Where the material contains free silica, this dust loss can be a health concern particularly in connection with silicosis. Proper enclosure of transfer points, launders, bins and tanks will contain these emissions which can then be ducted to gas cleaning equipment specifically designed for the purpose.

Some vapors are produced in hydrometallurgy and the various refining processes. Chlorine, hydrogen and acid mist can be emitted from electrorefining cells and, when present in solution, arsenic in the form of arsine can be emitted when the concentration of copper is reduced in electrolyte purification or effluent treatment circuits. Emissions of this type are contained with the use of vented hoods, blankets or other systems designed to protect the workplace from undesirable vapors as well as reduce solution and heat losses.

4.1.2 Liquid Wastes

Liquid wastes and effluents vary widely from plant to plant, and with the location of the plant. In flotation processes, large volumes of water will be used to convey the solid wastes to the tailings pond which will act as a reservoir for the storage and recycle of plant process water. Runoff from the plant site for the first half hour during periods of heavy rain is

frequently collected in a separate pond to recover the entrained solids and allow for water treatment prior to discharge of any excess to the water shed.

The build-up of impurities in various process solutions, granulation circuits, boiler and cooling water systems result in bleed streams to control the impurity levels within permissible limits. These are not large volume streams but must still be treated before discharge. In copper electrorefining, a proportion of the electrolyte (up to 0.5 m³ electrolyte per MT cathode) is bled continuously and circulated through the purification circuit to remove arsenic, antimony, selenium, etc. prior to its return to the main circuit. Usually, one element will be the major or controlling impurity determining the size of this stream and only a small portion would be bled off for treatment and discard. Solutions bled from certain leach processes may contain undesirable intermediate compounds which must be destroyed prior to discharge.

Wash water from the backwash of filters, final washing of products, including the excess from quench tanks, is usually circulated back directly to the individual operation. Where there is an excess, however, it will be discharged to the central pond as part of the plant process water supply.

4.1.3 Solid Wastes, Sludges and Byproducts

In the extractive metallurgy of sulfide ores, the largest tonnage of solid wastes is flotation tailings, usually discharged as a slurry from the flotation circuit, and discard slag from the smelter. The latter is a dense silicate and can be either in lump form, coarse granules, or as fine flotation tailings, depending on the method of slag cleaning. These solid wastes are the major sources of metal loss and consequently have a significant bearing on the recovery of values. Discard slags usually contain between 0.5 and 0.7% Cu, or 0.2 to 0.9% Ni (2), are normally non-hazardous and are frequently used as aggregate, clean fill, and for sandblasting. Tailings produced during the concentration of ores are not inert and in most cases must be impounded in lined ponds with appropriate systems to monitor potential leakage.

Residues resulting from leaching processes and sludges from effluent treatment systems in almost all cases have to be impounded in sealed ponds. The various treated water systems, such as boiler feed water, cooling water, etc. all have bleed streams to control impurity build-up which must be treated to adjust pH and precipitate heavy metals prior to discharge. Weak acid from the wet gas cleaning circuit and effluents from leaching and refining circuits are usually neutralized with lime, which results in a gypsum precipitate containing the copper, nickel and other heavy metals. Depending on the particular impurities present, this sludge can be recycled to a smelter; alternatively, disposal with tailings can be a benefit by stabilizing the tailings pond, etc.

Some leach processes fix sulfur as a gypsum sludge; these, along with chloride wastes, can be difficult to handle physically, and can be a disposal problem due to the substantial tonnages involved.

4.1.4 Hazardous Wastes

Hazardous wastes are determined by various tests or criteria, depending on the particular jurisdiction. In actual practice, a hazardous waste is one that endangers health or

contaminates the environment, consequently it can be site-specific and dependent on a number of factors.

Dusts bled from the smelter hot gas cleaning system to control impurity build-up may contain arsenic, lead, mercury, selenium and other hazardous elements. They will be in the form of oxides, sulfides, or similar compounds which will weather and leach when stockpiled outside. The tonnage is usually small, less than 0.2% of the smelter feed, and is frequently processed in a separate plant to recover any values present and produce an inert slag.

Due to their very nature, almost all sludges and leach residues are hazardous wastes and must be treated further or contained in sealed ponds equipped with groundwater monitoring systems to detect any leakage.

Based on current process technology for copper and nickel, slag or similar fused products are the most inert or non-hazardous wastes produced by the metallurgical industry. The ultimate solution to the disposal of some hazardous wastes is through a pyrometallurgical process which produces a silicate slag; however, their ability to absorb certain volatile impurities is limited.

4.2 UPSET AND EMERGENCY CONDITIONS

All metallurgical operations, particularly pyrometallurgical processes, benefit from continuous smooth operation, free of sudden changes, process upsets or emergencies. Power failures and the resulting crash shutdowns can damage equipment, which leads to spills of chemical solutions, molten materials and the uncontrolled emission of pollutants, and potentially hazardous conditions.

Since process upsets and emergency conditions can and will occur, most frequently during start-up and early operation, modern plant design calls for the provision of a standby diesel electric power system. This must be sufficient to energize emergency shut-off valves, allow cranes, furnaces, etc. to move to safe positions, power the ventilation system which removes noxious gases and fumes, and power the emergency light and alarm system.

The area under launders, furnaces and other equipment which contains molten materials, particularly matte, must be clear of all power cables and service lines and barricaded in such a manner that a molten spill cannot flow into water or contact structural steel components.

4.3 ENVIRONMENTAL IMPACT ON RECEPTORS

Dust collection and recycle is given a high priority in smelting and refining operations to protect the environment and is a key factor in the recovery of values, consequently the impact on the surrounding environment from particulates is relatively small. Once deposited on the ground or in the water system, impurities can accumulate and enter the food chain. Plant life, for example, will absorb heavy metals from the soil and has been analyzed by geologists in some cases as a means of determining the metal content of that soil. However, the actual impact of such impurities will depend on site-specific factors such as climate, soil alkalinity, porosity, depth to bedrock, etc. This point must be considered by regulators when setting ambient standards.

Arsenic, lead and similar contaminants contained in bleed dusts and stockpiled outside will, in most locations, be leached with time. Without proper containment measures to prevent dust losses and leaching action, these contaminants can enter the water table and create a health hazard. Efficient dust collection and containment and good worker hygiene, including the use of dust masks, will protect the employees from potentially hazardous dusts and fumes, including silica. Where these materials cannot be treated, they must be stored in sealed containers which prevent leakage to the environment.

Of the gaseous emissions, sulfur dioxide is the principal contaminant. Emissions generated in some processes, such as arsine, hydrogen sulfide, chlorine, etc. are usually intermittent and very low in volume but, even though toxic, can be safely vented to atmosphere at source. In the pyrometallurgical processing of sulfide ores, however, substantial tonnages of sulfur dioxide are produced which can amount to between 40 and 60% of the weight of concentrate smelted. Large volumes of high strength sulfur dioxide will damage vegetation, cause acidity in surface waters and promote the leaching of other contaminants from the environment. The high strength gases are normally processed to produce a market grade sulfuric acid. Weaker gas streams, usually less than 1% sulfur dioxide, are scrubbed and the sulfur removed as gypsum, sodium or ammonium sulfate.

Some processes produce intermediate sulfur compounds which are hazardous to the environment. Leach circuits can produce intermediate sulfur compounds such as thionates, sulfamates and thiosulfates which destroy vegetation and must be destroyed in an oxyhydrolysis circuit prior to discharge. Similarly, intermediate gaseous compounds must be incinerated prior to discharge to protect the environment.

4.3.1 Contaminants of Concern

The contaminants which cause concern in the processing of copper and nickel concentrates are dependent on the contaminants in the original ore. In general, sulfide ores contain a wider range of these contaminants than do oxide or laterite nickel ores. The following sections list contaminants of particular concern in the copper and nickel industry; however, there are other elements listed in subsequent sections which can be of concern in specific cases.

Arsenic

Arsenic will be volatilized early in the smelting process and collected as an oxide as the temperature is reduced in the gas cleaning circuit. With recycle of the dust to the smelting furnace, a circulating load builds up and some dust must be removed from the circuit to prevent downstream contamination of the product, and hazardous conditions such as emissions from molten streams, generation of arsine, etc. Arsenic compounds are toxic and can be ingested, inhaled or absorbed through the skin.

Lead

Lead is more frequently associated with copper ores than with nickel, and is distributed among the dust, slag and matte or blister copper during smelting. Lead will be emitted to atmosphere while molten matte and copper are being transferred, and the fume will be concentrated in sections of the gas cleaning circuit. Lead is toxic with extended ingestion; special protection must be used and blood levels monitored closely. In the discard of

wastes, lead sulfates, oxides, etc. are of concern and special impoundment measures required.

Mercury

Mercury is in the order of five times as toxic as lead and can accumulate in the food chain and cause medical problems. For example, at concentrations of 20 ppm in the brain, neurological problems can occur. In pyrometallurgical processes, mercury is driven off very early in the process and leaves in the process gas. Since sulfuric acid is a very efficient mercury collector, one of a number of mercury removal processes is required ahead of the acid plant to ensure that the product acid contains less than 1 ppm mercury (5).

Nickel

Although nickel is an essential metal in modern technology, nickel carbonyl is very toxic and respiratory cancers have been reported in processes where nickel matte from sulfide ores is roasted to produce nickel oxides. It should be noted that there is considerable ongoing work in connection with the toxicity of nickel and all its inorganic compounds (6). Various operating techniques and processes have been developed which overcome potential hazards, and these are taken into consideration with proper plant design.

Silica

The processing of ores or flux containing free silica can produce fine dust which, if not contained and collected, can be inhaled and with time cause silicosis. However, the use of proper ventilation, respirators and annual chest X-Rays will control the hazard. When the X-rays are positive, the workers are transferred to areas of the plant which are free of dust.

Sulfur

The main contaminant in sulfide ores is the sulfur removed as sulfur dioxide or intermediate sulfur compounds. In all cases, sulfur fixation processes are required and the effluents from hydrometallurgical processes must be treated.

5 POLLUTION PREVENTION AND CONTROL

5.1 MANAGEMENT CONSIDERATIONS

In the early stages of the smelting or hydrometallurgical processing of copper or nickel, large volumes of materials such as slags or leach residues are produced which are normally discarded. As extraction proceeds to the refining stage, the solutions, slags and residues are too high in values to be discarded and must be recycled or processed further to minimize metal losses.

5.1.1 Byproducts

In smelting and refining copper or nickel, opportunities to reduce wastes by changes in the range of products are limited. Primary and secondary products are normally determined by the process and equipment used. Wherever practical, a smelter and refinery will produce byproducts which can be used elsewhere simply to reduce or eliminate disposal and

impoundment costs. For example, in ammonia leach processes, where a market exists, there is the option of removing sulfur as an ammonium sulfate fertilizer rather than as gypsum.

In certain countries where natural resources are limited, gypsum from vent and weak gas scrubbers has been used for wallboard or cement production. In other cases, particularly when there are some values contained, gypsum has been returned to the smelting furnace feed where up to 5% CaO can improve slag characteristics.

While liquid sulfur dioxide can be produced from smelter process gases containing over 65% sulfur dioxide, sulfuric acid is the normal sulfur byproduct from smelters treating sulfide concentrates. Depending on smelter location, byproduct sulfuric acid can be a profitable item. Smelters located close to phosphate fertilizer plants or uranium mills are particularly well suited in this respect, as are those located on tidewater where acid can be shipped to offshore markets.

Silicate slag can be granulated, crushed or cast into lumps and thus provide a wide range of aggregate products for sandblasting, coarse fill, bedding for railroads, or spun into fibres for insulation.

5.1.2 Process Changes

The basic process is usually fixed to a large extent by the feed materials, primarily the concentrate, and the plant location. The opportunity to minimize waste products is therefore limited to the technology selected; even then, the opportunity to minimize wastes will depend primarily on the specific impurities in the plant feed. The higher the impurity levels, the more difficult and expensive will be the waste minimization.

Oxygen enrichment is being used to an increasing extent to raise the sulfur dioxide content of process gas streams in order to reduce their volume and permit efficient fixation of sulfur dioxide. This is considered preferable to the use of various absorption-desorption systems to increase the strength of the sulfur dioxide gas streams.

Hot air and certain process gases can be recycled to air preheaters or used as combustion air for dryers, etc., saving energy and providing an efficient removal of any entrained particulates. Similarly, condensate, rainwater and excess process water can be recycled to the circuit for washing, dust control, gas scrubbing and other process applications where water quality is not a particular concern.

Good housekeeping is the key to safe operation, minimum loss of values, reduced maintenance and a reduction in waste products. To control dusting and minimize handling losses, concentrate storage and blending are carried out in enclosed buildings; conveyors, transfer points, etc. are covered and vented to dust collection equipment. In hot, dry climates, the roadways are sprayed with water to control dusting. The plant yard around buildings and roadways is usually paved and the run-off water ducted to a central settling pond. In some plants, as much as 500 metric tons per year of metal-bearing material is collected from ponds of this type. At vehicle exits, wash stations clean the wheel wells and undercarriage of all vehicles leaving the plant.

As noted in the previous sections, on-site recycling has long been a standard procedure in smelting and refining as a means of maintaining an acceptable recovery of values.

5.2 TREATMENT TECHNOLOGIES

When selecting the technology best suited to protect the environment specific to the smelter location, it is essential that a comprehensive waste management plan (9) be developed taking local conditions into account. Similarly, ground conditions, susceptibility to earthquakes, soil erosion, etc., must all be considered and should govern the treatment technology selection.

5.2.1 Emissions to the Atmosphere

Airborne particulate emissions are reduced to acceptable levels with the use of cyclones, electrostatic precipitators or baghouses and scrubbers. Gaseous contaminants are removed from a gas stream using an acid plant when the concentration is high in sulfur dioxide or various alkali, and dual alkali scrubbers for the lower strength gases. Vapors such as mercury are removed using one of a number of dedicated scrubbing processes.

The U.S. Clean Air Act lists some technologies which the EPA believes can be considered to reduce airborne emissions. Changes in smelting technology which utilize oxygen enrichment, the production of sulfuric acid using double catalysis technology and certain gas scrubbing systems would be classed as Best Available Technology (BAT); however, they may not necessarily be economic.

All metallurgical acid plants incorporate a wet gas cleaning system to remove particulates, fume and sulfur trioxide from the gas stream. The single catalysis plant has a lower conversion efficiency than the standard double catalysis design, and will emit a tailgas containing 1500 to 2000 ppm SO₂. In some cases, the tailgas is fed to a weak gas scrubbing system and sulfur dioxide emission level reduced to less than 500 ppm SO₂ normal for the double catalysis design.

For the weaker gas streams containing less than 1% sulfur dioxide, various scrubbing systems have been developed. For metallurgical gas streams where the ratio of CO₂/SO₂ is usually low, limestone is not a particularly efficient scrubbing medium. Lime, sodium carbonate/hydroxide regenerated with slaked lime, magnesium oxide and several other reagents are used to fix the sulfur, usually as gypsum. The latter can be used in wallboard manufacture, the cement industry, or impoundment in tight ponds.

Under very special conditions, the higher strength gases, usually over 70% sulfur dioxide, can be used to produce liquid SO₂ or elemental sulfur. This sulfur will contain a number of impurities and require refining before it is marketable. Consequently, it is a very expensive alternative and can rarely compete with natural sulfur.

5.2.2 Liquid Effluents

Liquid effluents result from bleed streams required to control impurity build-up which have been adjusted for pH, usually 6.0+. Heavy metals are precipitated along with the sludge in the waste water treatment plant. Various systems are used, but most add lime for neutralization and produce a gypsum residue. Depending on the impurity balance in the smelter-refinery, the sludge can be returned to the smelter for recovery of values and to fix impurities in an inert slag.

The treated effluent may be stored in a pond to be used as make-up water or discharged to the watershed, in which case it must meet local water quality specifications. This can usually be achieved with a standard alkali neutralization, normally lime, settling and final pressure filtration now considered BAT.

In cases where yard dusting is prevalent, such as in laterite operations or hot dry climates, the treated effluent can be used to wet down roads and control dusting.

5.2.3 Solid Wastes

The main solid waste from copper or nickel smelters is discard slag. In almost all cases, this material is inert and non-hazardous and can be used for landfill, sandblasting, or aggregate.

The much smaller quantities of dusts, purification sludges and residues are recycled to the smelter where possible, and would be considered BAT. However, it is frequently necessary to bleed some impurities from the circuit to avoid building up a circulating load of undesirable elements. These bleed streams are rarely inert and usually classed as hazardous wastes (9). Normally these wastes are impounded in sealed containers or in sealed ponds which currently would be considered the Best Practical Technology (BPT). However, a number of processes are being developed to treat these materials and recover values while producing an inert slag.

Plasma technology is being adapted by a number of developers. For example, Tetronics has used plasma arc to produce a nickel-chromium ferroalloy containing 85% of the nickel and chromium in the bleed dust (10). Zinc, lead and cadmium are collected in a baghouse for further processing in a zinc plant, and the discard slag is non-hazardous.

Various cyclone reactors are being developed. The St. Joe Flame Reactor (11) and Lurgi's Flame Cyclone (12) are two designs which have been piloted. All these processes operate at high temperatures (up to 1800°C) with short retention times, while metal recoveries in the range of 90 to 99% are achievable.

5.3 HAZARDOUS MATERIAL HANDLING

Regulations have been developed for most industrially developed areas which govern spillage, on-site storage, transport and off-site disposal of process wastes. Solid hazardous wastes are classed as inert when the leachate produced under defined conditions contains less than the limits listed in Table III.

Table III Hazardous Waste Leach Test

Substance	Maximum concentration in leachate when using	
	Acetic Acid ^a (mg/l)	Hydrochloric ^b (mg/l)
Arsenic	5.0	1.5
Cadmium	1.0	0.3
Chromium	5.0	1.5
Lead	5.0	3.0
Mercury	-	0.005
Silver	5.0	-

^aU.S. EPA Register 261.22 to 261.24
^bJapanese EPA Ordinance 13
Source: Reference (6)(9)

In some cases the dusts, residues and precipitates fed to a copper or nickel smelter may be classed as hazardous and require special handling and storage procedures. However, as the table indicates, the definition of "hazardous" and how it should be measured is not standard throughout the world; various agencies adopt different standards and methodology.

The regulations in North America are quite complex but in brief, they require wastes classed as hazardous to be shipped and stored in approved containers properly marked as to contents and potential hazards. At present, residues and sludges classified as hazardous can be impounded in sealed ponds equipped with systems to measure groundwater quality; however, in the near future the use of ponds for final disposal may not be approved.

Noxious or toxic gases and fumes are normally scrubbed and collected as a sludge or residue prior to discharge of the gas stream. Where possible, this residue will be returned to the smelter or leach circuit for recovery of values, or it is sent to a hazardous waste facility. One of the advantages of pyrometallurgy is its ability to absorb some hazardous materials and produce inert, or non-hazardous, products.

Process gas streams containing over 5% sulfur dioxide are processed to sulfuric acid in plants of either the single catalysis or double catalysis design. From an environmental point of view, the double catalysis system is preferred since it can provide a 99.5% conversion efficiency and a tailgas containing about 500 ppm sulfur dioxide. This would result in between 96 and 98% of the sulfur in a typical smelter feed being fixed in some form so as not to be emitted to the atmosphere.

5.4 CAPITAL AND OPERATING COSTS

5.4.1 Capital Costs

The direct capital cost for a smelter-refinery complex will depend to a large extent on its location. For example, in warm climates, lower cost, open-sided buildings can be used. Within the total cost there can be a number of trade-offs; for instance, high levels of oxygen enrichment increase the size and cost of the oxygen plant itself, but the resulting lower

volume, high-strength furnace offgas reduces the size of the gas cooling and cleaning equipment. In most cases, one will offset the other, particularly where an acid plant is used.

In terms of capital costs, hydrometallurgical plants are usually lower cost than equivalent pyrometallurgical plants; however, the selection of the final process technology is invariably based on technical factors rather than cost. The requirement to produce inert, non-hazardous waste products to protect the environment frequently favors pyrometallurgy. The smelting furnace area itself usually accounts for less than 20% of total capital cost, so the savings resulting from one furnace design over another does not significantly affect project economics. Environmental controls, including the sulfur fixation plant, will be close to 35% of the total capital cost for a smelter-refinery complex. A primary advantage of many hydrometallurgical processes is their ability to eliminate the large volumes of sulfur dioxide offgases.

For a plant smelting 1100 MTPD of sulfide concentrate and producing 100,000 MTPY of refined copper or 30,000 MTPY of nickel, the total installed cost of major plant areas, in U.S. dollars at the April 1992 cost level, would be in the range of:

- a) Smelter, incl. feed preparation - \$85 to \$98 million
- b) Electrolytic refinery - \$55 to \$70 million
- c) Cryogenic oxygen plant - \$19 to \$22 million
- d) Sulfuric acid plant - \$45 to \$60 million
- e) Auxiliary facilities, incl.
environmental controls - \$46 to \$52 million

Laterite nickel plants must handle large tonnages of relatively low grade ores, consequently their capital costs will usually be higher, over twice those shown above for sulfide concentrates. Much of the increased cost results from infrastructure costs. However, normally they do not include oxygen or sulfuric acid plants nor an electrolytic refinery, which can be an appreciable saving.

Metallurgical type acid plants include a wet gas cleaning circuit consisting of scrubbers and mist precipitators to ensure that the feed gas is clean. The final cost of the sulfuric acid plant will depend on the process gas volume and sulfur dioxide concentration. For this reason, modern sulfide smelters utilize oxygen enrichment to increase the process gas strength and reduce the volume, thereby minimizing acid plant costs. Other environmental costs are covered under Auxiliary Facilities and include the collection and scrubbing of the low strength fugitive emissions from ladles, launders, tap holes, etc., and the effluent treatment plants.

5.4.2 Operating and Maintenance Costs

The main components in the cost of operating a metallurgical plant are labor and energy, primarily electrical energy. The cost of power and fuel are the major cost items in electrolytic refining and in the smelting of laterite nickel ores. Labor costs vary widely throughout the world, but so does productivity; in general, where labor costs are low more employees are required, and in the final analysis the total operating labor cost component may not represent a major cost saving. In laterite nickel operations, the cost of labor is small in comparison to the energy cost, consequently the operating costs for laterite nickel are generally higher than for sulfide nickel operations.

Significant differences in labor, power and fuel costs result in a wide spread in direct operating costs between plants. In general, the total direct operating cost for copper smelting will be in the range of 26.5-39.87¢/kg (12-18¢/lb.) of copper, of which some 30-35% will be for maintenance. For electrorefining, the cost would be in the range of 6.6-11.0¢/kg (3-5¢/lb.) of copper, with only about 17% required for maintenance.

Operating costs for nickel will vary considerably, depending on the type of ore, process used, and whether the final product is refined nickel, nickel oxide, or ferronickel. Unlike copper, there is very little cost information published for nickel; the production of primary nickel is very competitive. Nevertheless, based on estimates from various sources, the current direct operating cost of the metallurgical plant is in the range of \$2.10 to \$3.95 US/kg (\$0.95 to \$1.79 US per pound) of nickel in product. This includes maintenance of the smelter and refining facility, which could be in the range of 18 to 25%.

6 OCCUPATIONAL HEALTH AND SAFETY ISSUES

The first priority for worker protection should be process selection and plant design in which safety is a prime consideration. The measures used to protect workers from contaminants include such engineering designs as enclosure of control rooms and individual processes, ventilation and mechanical dust recovery. Other systems include personal protective equipment and administrative controls. Medical surveillance and monitoring serve to check the effectiveness of the various measures. Personal hygiene and separate work clothes are key features in avoiding ingestion of arsenic, mercury and toxic chemicals. A wide range of chemicals are used in the industry as reagents and some require very specific handling procedures.

Threshold Limit Values are expressed as time-weighted averages (TWA), which is the time-weighted average concentration of a contaminant for a normal 8-hour day/40-hour week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect. TWAs permit excursions above the limit, provided they are compensated for by equivalent excursions below the limit during a workday. The current TWA standard set by the American Conference of Government Industrial Hygienists (7) for a number of substances which can appear in copper and nickel smelters and refineries are given in Table IV. For substances which do not appear in Table IV, the reader should consult the latest complete document (7).

Table IV Threshold Limit Values for Substances Found in Copper-Nickel Plants

<u>Substance</u>	<u>ppm</u>	<u>mg/m³</u>
Ammonia	25	17
Antimony and Compounds, as Sb	-	0.5
Arsenic and Soluble Compounds, as As	-	0.2
Arsine	0.05	0.16
Cadmium, dusts and salts; as Cd	-	0.05
Cadmium oxide fume, as Cd	-	0.05
Carbon black	-	1.5
Carbon monoxide	50	57
Chlorine	0.5	1.5
Cobalt, dust and fume	-	0.05
Copper fume	-	0.2
dust and mist	-	1
Cyanides as CN	-	5
Hydrogen sulfide	10	14
Lead inorganic dusts and fumes; as Pb	-	0.15
Mercury, all forms except alkali	-	0.05
Nickel, metal and insoluble compounds	-	1
soluble compounds as Ni	-	0.1
Nickel carbonyl	0.05	0.12
Nitrogen Oxide	3	5.6
Particulates not otherwise classified	-	10
Sulfur dioxide	2	5.2
Sulfuric acid	-	1
Uranium soluble and insoluble compounds, as U	-	0.2

Source: Reference 7

It should be noted that the above data are continually reviewed and updated to incorporate new information. On the other hand, some authorities apply stricter limits; for example, the American Occupational Health and Safety Administration (OSHA) adopted a much lower standard for nickel carbonyl at 0.001 ppm, or 0.007 mg/m³ (6). Nickel carbonyl is very toxic when inhaled, but acute toxicity by ingestion of nickel in most other forms is rare.

Under start-up or upset conditions, the ingestion of fine fume, noxious gases and similar emissions which may result is controlled with the use of properly fitted respirators. This usually prohibits the wearing of full-face beards which prevent the respirator from making a tight fit to the face. Removal of gaseous or particulate emissions from the workplace is an important feature in any well-designed plant. A well-designed smelter will keep contaminants below occupational exposure limits. For example, the time-weighted average exposure to SO₂ over a normal 8-hour day, 40-hour week, should not exceed 2.0 ppm (6)(7).

In pyrometallurgical operations, radiant heat, hot surfaces and the splash or spill of molten materials, particularly sulfides, can be hazardous. When large quantities of molten matte suddenly contact water or a cold surface, the reaction can be violent. To protect against minor splash or spill, clothing of a protective material or natural fibre should be worn which covers all body areas. In hydrometallurgical plants, acid-resistant materials should be used

and emergency showers placed at strategic locations throughout the plant. Cool water and well ventilated rest areas away from the hot working areas should be provided to permit workers to rest as required and avoid heat exhaustion (7).

7 GLOBAL OVERVIEW OF DISCHARGE REQUIREMENTS

7.1 ATMOSPHERIC EMISSIONS

In North America, the State or Provincial environmental agencies have the final say on air quality standards, provided they are in line with the Federal Guide levels. Table V and VI give air quality standards applied in Canada and the United States.

Table V. Canadian Provincial Air Quality Regulation - Ontario 1984

<u>Substance</u>	<u>1/2 hour average^a</u> ($\mu\text{g}/\text{m}^3$)
Arsenic	75
Arsine	10
Cadmium	5.0
Carbon Monoxide	6,000
Copper	100
Dust fall	8,000 $\mu\text{g}/\text{m}^2$
Lead	10
Mercury	5.0
Nickel	5.0
Sulfur Dioxide	830
Sulfuric Acid	100
Zinc	100

^aAt point of impingement

Source: Reference (6)

The U.S. National Ambient Air Quality Standards (NAAQS) sets forth the limits for sulfur dioxide at the point of impingement shown in Table VI. The point of impingement is usually defined as anywhere outside the plant fence where dispersion models predict maximum pollutant levels.

Table VI. Canadian and US Air Quality Standards for Sulfur Dioxide

<u>Averaging Period</u>	<u>United States</u> <u>NAAQS</u> ($\mu\text{g}/\text{m}^3$)	<u>Canada</u> <u>British Columbia</u> ($\mu\text{g}/\text{m}^3$)
Annual Arithmetic Mean ^a	30	25-75
Concentration over - 24 hr. ^a	365 ^b	160-260
- 3 hr. ^a	1300 ^b	375-665
- 1 hr. ^a	-	450-900

^aAt point of impingement

^bPermissible once a year

The objectives shown for the British Columbia Ministry of the Environment take into account the needs of particular receiving environments. Overall, they are lower than the U.S. limits due to a large extent to the role of the forests and salmon spawning grounds in the Province.

The 1992 guidelines for Sweden are summarized in Table VII, based on a copper smelter production of 350,000 metric tons per year of primary product, which includes lead and zinc. It should be noted that in Sweden limits are "site-specific" and therefore can be expressed in terms of "per ton of primary product". This is not normally the case since most standards are expressed in terms of ground level concentration, usually at the plant fence line and are not a function of the production rate.

Table VII. Swedish Emission Limits to Atmosphere - 1992 to 1993

<u>Substance</u>	<u>Annual</u> (Metric Ton/Year)	<u>Specific</u> (g/Metric Ton Product (Cu, Pb, Zn))
Arsenic	8	20
Cadmium	0.8	2
Copper	10	30
Lead	30	85
Mercury	0.35	1
Dust	250	700
Sulfur Dioxide ^a	5,000	14,300
Zinc	40	110

^aSwedish Environmental Protection Agency recommended ground level concentrations of 100 $\mu\text{g}/\text{m}^3$ and 50 $\mu\text{g}/\text{m}^3$ during the winter half-year.

Source: Reference (8)

Studies are under way in Sweden directed towards the further reduction of arsenic, cadmium and mercury emissions.

7.2 LIQUID EFFLUENTS

Smelters and refineries are normally required to meet effluent criteria for the area or industrial complex within which they are located, which in some cases could be those applicable to mines and mills. The limits are not a function of the metallurgical process, but apply to any liquid discharge; consequently, the effluent from leach circuits would also have to comply with the criteria. Examples of permissible effluent levels are shown in Table VIII.

Table VIII. Permissible Liquid Effluent Levels

<u>Substance</u>	<u>Germany</u> <u>Smelter Effluent</u> <u>Random Tests</u> (mg/l)	<u>Canada</u> <u>Maximum Monthly</u> <u>Mean Concentration</u> (mg/l)	<u>Japan</u> <u>Maximum</u> <u>Concentration</u> (mg/l)
Arsenic	0.1	0.5	0.5
Cadmium	0.2	-	0.1
Copper	0.5	0.3	3.0
Lead	0.5	0.2	1.0
Nickel	0.5	0.5	-
Total Mercury	0.05	-	0.005
Zinc	2.0	-	5.0
Suspended Solids	-	25	150
pH	-	6.0	5.8-8.6

Source: Reference (6)

Both Canada and Japan have particularly sensitive aquatic environments and therefore emphasize the mercury and pH components.

As is the case with atmospheric emission guidelines, the Swedish liquid effluent discharge guidelines are expressed in annual and specific terms. For the copper smelter described previously, the 1992-1993 discharge limits are as shown in Table IX.

Table IX. Swedish Discharge Limits to Watershed

<u>Substance</u>	<u>Annual</u> (Metric Ton/Year)	<u>Specific</u> (g/MT Product (Cu, Pb, Zn))
Arsenic	20	10
Cadmium	0.4	0.05
Copper	2	0.1
Lead	2	0.1
Mercury	-	0.1
Zinc	8	2.0

Source: Reference (8)

7.3 NOISE LEVELS

In a mine, mill or smelter, there can be a considerable amount of noise. In Sweden, the noise from industrial activities is regulated not to exceed certain levels at the nearest domestic residence as shown in Table X.

Table X. Swedish Industrial Noise Limits - Existing Plants*

<u>Time Period-Hours</u>	<u>Maximum Noise Level - dBa</u>
0700 to 1800	55
1800 to 2200	50
2200 to 0700	45
Maximum Momentary Pulse	60

Source: Reference (8)

*For greenfield plants, the limits are 5 DBA lower.

In a mine or smelter it is the oxygen plant blower, air compressors and similar equipment which are the major contributors to the noise level in the surrounding area.

In the workplace there are several pieces of equipment and processes which contribute to the noise level. Table XI shows the Threshold Limit Values (TLVs) proposed by the American Conference of Industrial Hygienists.

Table XI. TLV - Noise Limits

<u>Duration per Day (Hours)</u>	<u>Sound Level (dBa)</u>
16	80
8	85
4	90
2	95
1	100

Source: Reference (7)

The guidelines stipulate that there should be no exposure of any duration of 140 decibels. In areas where the levels exceed the above TLVs, personal hearing protection is a job requirement.

8 TARGET PREFERRED GUIDELINES

Guidelines for pollutant discharge must be both technically and economically realistic and based on impact criteria which take into account the ecological and climatic features of the specific area. It is important when adopting emission limits and establishing environmental controls, that an overall waste management (9) plan has been developed and that the final result reflects the particular features of the local environment. For example, control and final limits for mercury and sulfur dioxide emissions will be more severe for plants located in heavily forested areas and where fish are sensitive, than would be the case in a desert location where the control of other process effluents, particularly acids, can be the governing factor. Finally, it is important to ensure that the final guidelines or regulations do not impede the recycle of hazardous materials to a smelter where high temperatures can render most of those materials inert.

With modern smelting technology, it should be possible to fix in products at least 96% of the sulfur contained in feed materials and design to meet the following ambient air criteria. The criteria are based on measurements taken outside the fence line at ambient conditions.

Table XII. Proposed Ambient Air Criteria

<u>Substance</u>	<u>Averaging Period</u>	<u>Level</u> ($\mu\text{g}/\text{m}^3$)
Sulfur Dioxide	Annual arithmetic mean	80-100
	Maximum 24-hour arithmetic mean	340-370
Dust Loading:	Annual geometric mean of 24-hour concentrations	75
	24-hour average not to be exceeded more than once per year	260

The figures given in Table XII are based on data in a UNEP report (6) and some recent U.S. National Ambient Air Quality standards. Where limits for individual elements are required, those given in Table V for Ontario are recommended.

The target levels for smelter-refinery effluents, including those from hydrometallurgical processes, should also be realistic and compatible with ambient water quality. In general, however, where specific regulations or base data are not available, the maximum limits shown in Table XIII would be reasonable and achievable.

Table XIII. Proposed Smelter-Refinery Effluent Limits

<u>Substance</u>	<u>Concentration Limits</u> (mg/l)
Arsenic	1.0
Copper	1.0
Iron	5.0
Lead	0.5
Nickel	0.5
Selenium	1.0
Zinc	10.0

9 MONITORING REQUIREMENTS

Monitoring of discharge requirements usually consists of accurate records being maintained and reported by the operator on a regular basis. The sampling, analysis and calculations will follow agreed procedures and be checked on a spot basis by independent consultants or agents representing the government regulatory agency.

Monitoring regulations will vary with each jurisdiction but, in general, they are similar to those outlined in the EPA Regulations 40 CFR Ch I (7-1-89 Edition), Sec. 60.165. In brief, they require the smelter operator to maintain a monthly record of the total input of

arsenic, antimony, lead and zinc, continuously monitor and record the opacity of dryer discharge gases and/or the concentration of sulfur dioxide emitted.

Effluent ponds are monitored by a system of deep wells surrounding the pond area. The water is analyzed on a regular basis for any leakage which might occur in the pond liner and seal system. Similarly, treated effluents are sampled prior to discharge to the water shed on a regular basis. In each case, records are kept.

Emission of sulfur dioxide to atmosphere is usually determined on the basis of a material balance, where all sulfur not fixed in products is considered to be emitted to atmosphere. In the working environment where emissions should be very low, monitoring of the actual emission point is frequently carried out.

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