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Environmental Aspects of Nickel Production Sulphide Pyrometallurgy and Nickel Refining

Report EPS 2/MM/2 November 1987

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ENVIRONMENTAL ASPECTS OF NICKEL PRODUCTION

Sulphide Pyrometallurgy and Nickel Refining

Environmental Protection Conservation & Protection Environment Canada





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Report EPS 2/MM/2 November 1987

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ABSTRACT

The production of nickel through the pyrometallurgy and refining processes of sulphide ore results in a release of pollutants to the environment. The most significant are the atmospheric emissions of sulphur dioxide and particulate matter containing heavy metals.

These emissions, unless contained, pose a potential hazard to human health and to the environment. The effects on the working environment and its protection are also addressed.

The high concentration of sulphur dioxide in emissions from modern smelting equipment favours the economics of their containment and conversion into either marketable by-products: sulphuric acid, liquid sulphur dioxide etc., or to environmentally inert substances. The technologies to contain atmospheric emissions are reviewed in detail with an indication of capital and operating costs.

Also reviewed are the practice and cost of their dispersion to the atmosphere.

RÉSUMÉ

La production de nickel par la pyrométallurgie et le raffinage des minerais sulphurés est une source de pollution de l'environnement. Les polluants les plus importants sont les émissions atmosphériques d'anhydride sulfureux et de particules contenant des métaux lourds.

Ces émissions, si elles ne sont pas contenues, présentent un danger potentiel pour la santé humaine et l'environnement. Ce rapport traite aussi de leurs effets sur l'environnement de travail et de mesures de protection disponibles.

La forte concentration d'anydride sulfureux dans les émissions des fonderies modernes joue en faveur de leur récupération et de leur conversion, soit en des produits à valeur commerciale- acide sulphurique, anydride sulfureux liquide ect. - ou soit en des substances sans danger pour l'environnement. Les technologies de mitigation des émissions atmosphériques sont examinées en détail dans ce rapport, avec un aperçu des coûts de capitaux et d'opérations.

On y passe aussi en revue la pratique et les coûts de la dispersion à l'atmosphère.

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1 INTRODUCTION

This technical review covers the most commonly used methods of extractive metallurgy and the equipment to produce nickel and nickel products.

It is concerned with the environmental aspects of these technologies and presents information either as found in technical literature or as made available by companies, governmental agencies, and individuals expert in the field.

Naturally, any particular plant may have its own peculiar installations and therefore somehow differs from the generalized descriptions that follow. The text, nevertheless aims to provide the reader with the essential elements on each topic and, whenever possible, with indications of costs from which extrapolations may be made. The text also provides references for further reading.

1.1 Two Types of Nickel Ore

The world's land-based nickel ores are of two generic types: sulphide and laterite. From both these ores, nickel is currently recovered. Sulphide ores account for about 55 percent of the world's mine production, and laterite ores for about 45 percent. Owing to the contrasting geological and mineralogical characteristics of these two types of ores, they are exploited by different methods of mining and extractive metallurgy.

The sulphide ores of nickel occur at numerous, widespread locations. The more important ones now being exploited are those in Canada, Australia, U.S.S.R., Republic of South Africa, Zimbabwe, and Botswana. In all these ores, nickel occurs as pentlandite usually associated with pyrrhotite, chalcopyrite, and traces of the metals of the platinum group, such as gold and silver. The ore composition, whether sulphide or laterite, varies from one area to another even within a single deposit.

The lateritic ores of nickel occur in many areas of the tropics and subtropics. Major deposits being exploited are located in Cuba, the Dominican Republic, Guatemala, Brazil, Australia, Philippines, Indonesia, New Caledonia, U.S.S.R., and Yugoslavia. Nickel is present as an oxide or complex silicate. The nickel laterites were formed through the weathering of nickel-bearing rock containing about 0.2 percent of nickel. The nickel in lateritic deposits is usually concentrated near the bottom of the zone of weathering, under a layer of iron-rich earth.

1

1.2 New Sources of Nickel

In 1950, only four countries produced nickel: Canada, New Caledonia, U.S.S.R., and South Africa. Canada, with 76 percent of the market share, was by far the major producer. Now 26 countries, many of them in the developing world, produce nickel. What contributed to the expansion of nickel production capacity in these countries were:

- the technological developments in the 1950s which enhanced the feasibility of laterite deposits;
- the decline in energy prices in real terms in the 1960s which benefitted the energyintensive laterite operations;
- the discovery of high-quality sulphide deposits in Australia and other countries; and
- the limited ability of traditional producers to expand production to meet the demand of a rapidly growing market.

Appendix A summarizes the principal world producers, processes used, products and capacity.

Figures 1 and 2 provide an indication of the quantity of material that can pass through each process and the number of plants processing it to produce nickel metal and other nickel products.

Some years ago, ocean nodules were considered a potential source of nickel and other metals. But extensive study by numerous groups over several years indicates that the logistical problems of ocean mining are overwhelming and the costs very high. Consequently, work on the recovery and treatment of ocean nodules has been discontinued.



Estimated quantities of material passing annually through each stage are given in thousands of tonnes contained nickel.

- FIGURE 1 FLOW DIAGRAM OF PRIMARY NICKEL PRODUCTION SHOWING THE NUMBER OF OPERATIONS AND TYPE OF PROCESS USED
- FIGURE 2 FLOW DIAGRAM OF PRIMARY NICKEL CAPACITY

2

BRIEF DESCRIPTION OF MAIN PROCESSES AND POLLUTANTS

This chapter contains a brief description of the main processes and equipment used in the pyrometallurgy of sulphide ores and in nickel refining. This brief description aims to identify the main sources of pollution and the pollutants generated and to quantify the pollutants.

2.1 Pyrometallurgy of Sulphide Ores

Nickel extraction from sulphide ores consists of a series of concentrating and refining steps. The process is designed to raise, step by step, the grade of nickel extracted in the course of decreasing its bulk.

The pyrometallurgical treatment of sulphide ores commonly includes three types of operations: roasting, smelting, and converting. By roasting the nickel concentrates, sulphur is driven off as sulphur dioxide, and iron is oxidized. In smelting, the roaster product is melted with a siliceous flux, which combines with the oxidized iron to form a liquid silicate and produce a solution of molten sulphides. In converting, more sulphur is driven off the sulphide melt, and the remaining iron is oxidized and fluxed for removal as a silicate.

The final product is a matte or nickel-rich sulphide ready for further processing. It may be cast directly into anodes for electrolytic refining; granulated by pouring the molten matte through water jets; or after solidification, it may simply be crushed for later sintering or reduction to metal. Copper-rich nickel sulphide matte may undergo matte separation into nickel sulphide, copper sulphide, and a nickel-copper alloy which contains most of the precious metals. These three phases may be separated further.

The pollutants of concern here are those associated with liquid and solid wastes and, above all, with the gaseous emissions.

Liquid effluents from pyrometallurgical processes are of minor importance because these processes are essentially dry. Liquid waste results from run-off from the smelter yard, bleed streams to control the build-up of contaminants in the boiler circuit, cooling water system, and when a sulphuric acid plant is attached to the smelter, weak acid from wet-gas cleaning systems. The bleed stream contains chromate, sulphates, and the various chemicals necessary to control pH, hardness, dissolved oxygen, etc., so that the boiler and cooling water specifications are met. Wet-gas cleaning systems, like those required to clean process gases for acid production, remove sulphur trioxide and produce a weak acid. They also collect arsenic, mercury, selenium, and fine dust particles containing other impurities.

In nickel smelting, a large tonnage of waste is solid, principally discarded slag. Depending upon the nickel content in the concentrate, the amount of slag can vary between 7 to 10 times the quantity of nickel produced. Where slag cleaning is necessary to reduce nickel and cobalt losses prior to slag discard, the normal method is by electric furnace. Subsequently, the slag can be transported in the molten state to the disposal area or pumped there after having been granulated. Nickel slags usually contain between 30 and 36 percent silica (see Table 1) and are considered inert under most environmental regulations.

	Type of Smelting Furnace				
Component	Reverberatory	Electric	Outokumpu Flash*		
nickel	0.2	0.17	0.1-0.2		
cobalt	0.1	0.06	0.3		
copper	0.08	0.01	0.3-0.4		
iron	38	_	40-45		
silica	36	35	30-32		
lime	2	-	1.0		

TABLE 1COMPOSITION OF TYPICAL NICKEL SLAG (%)

* After cleaning in electric furnace.

Other solids produced in a nickel smelter, such as ladle skulls, scrap, boiler and precipitator dust, are recycled to the smelting furnace and not discarded as wastes. The only solid wastes are the slag and sludges produced in the neutralization of plant effluents.

The major environmental problems in the pyrometallurgy of sulphide ores result from the release of sulphur dioxide and particulate emissions which can be categorized as either process or fugitive emissions.

2.1.1 Equipment Used in Ore Roasting. The sulphur dioxide and particulate emissions - the focus of this chapter - are discussed in the context of each type of equipment that, in the course of processing the nickel sulphide ores, generates them.

Multiple-hearth roasters. This type of roaster (Figure 3) consists of a series of superimposed circular hearths enclosed in a steel shell. The feed material is placed on the top hearth and worked downward by blades or rabbles attached to a central rotating shaft. As the feed progresses downward, it is heated by the rising hot gases produced by the exothermic reactions taking place in the lower part of the furnace. The intake and flow of air is regulated by doors on the lower hearths. The natural draft sucks in air to supply oxygen for oxidizing sulphur and iron.



FIGURE 3 MULTI-HEARTH ROASTER

In general, multiple-hearth roasters have air infiltration and low oxygen utilization, which results in a correspondingly low concentration of sulphur dioxide in the exhaust gas. While this type of roaster may produce exhaust gas at sulphur dioxide levels of 4 to 6 percent, much lower concentrations can normally be expected.

emissions Fugitive during should be charging of the roaster minimal not only because of the moisture in the feed but also because of the flow of material fed into the roaster. Gas may leak from holes in the shell or other openings around the shaft. Because of their high sulphur dioxide concentration, gas leaks are readily detected and corrected by repairs and adjustments to the furnace draft.

Specific data on particulate emissions are not available. A factor of 20 kg per tonne of concentrate feed has been suggested for uncontrolled emissions from copper roasters, other experts in the field, however, expect such losses to be in the range of 0.5 to 2.0 kg per tonne of concentrate feed. Particulate matter, containing nickel oxide, tends to be present inside the roaster building, particularly where the hot calcine discharge and transfer takes place.

For further reading, see references 2 and 3.

Fluid-bed roasters. The furnace consists of a cylindrical brick-lined shell with a grate at the bottom through which air is blown into the furnace at a rate sufficient to hold the feed in suspension. The mass has the characteristics of a fluid; therefore, the sulphide particles make excellent contact with the air. Roasting is rapid and efficient. The gas, carrying the lightest particles, goes through a cyclone, whereas heavier calcined particles are discharged through an overflow pipe at the side of the roaster. Heat is recovered from both the exhaust gases and the fluidized bed (Figure 4).



FIGURE 4 FLUID-BED ROASTER

This type of roaster is expected to produce exhaust gas with a sulphur dioxide content ranging from 10 to 15 percent.

Fugitive emissions and leaks should be minimal if the system, which operates under positive pressure, is air-tight, and properly maintained. Specific data on particulate matter emissions from fluid-bed roasters are not available; emissions would be a function of the gas-cleaning efficiency. They are expected to be 0.5 to 2.0 kg per tonne of concentrate feed.

2.1.2 Equipment Used in Ore Smelting

Reverberatory furnaces. The reverberatory furnace (Figure 5) was developed in response to the need of smelting material of fine particle size without excessive dust carryover into the exhaust gas. The temperature varies from about 1600°C at the firing end to 1200°C at the flue end. Exhaust gases carry a large amount of heat which is recovered in waste heat boilers or heat exhangers. Also, dust is recovered from these gases before they are finally released.



FIGURE 5 REVERBERATORY FURNACE

The reverberatory furnace is highly versatile; that is, it can accept wet or dry, lumpy or fine feed materials. It also has high energy requirements which can be lowered to some extent with the use of tonnage oxygen to enrich the air used for combustion.

A major disadvantage of this furnace is that it produces a weak SO_2 stream; it contains SO_2 in the 0.5- to 2.0-percent range.

Fugitive emissions can be associated with the charging of green or calcined feed, because rapid reactions with the bath result in rapid gas formation with pressure surges and the subsequent release of gas and particulate matter through feed pipes, thermal expansion spaces between bricks, and other openings. Emissions factors developed for this type of furnace, when it handles copper concentrates, indicate fugitive losses of the order of 0.5 kg of SO₂ and 1.2 kg of particulate matter per tonne of feed charged.

Specific data on uncontrolled emissions of particulate matter are not available. However, an emission factor of 10 kg per tonne of concentrate feed has been suggested for uncontrolled emissions from furnaces handling copper concentrates. Experts in the field suggest an emission range of 3.0 to 5.0 kg per tonne of concentrate feed. Although no specific data are available for reverberatory furnaces used in nickel smelting, the factors pertaining to copper can be assumed for estimating purposes.

For further reading, see references 3 and 4.

Electric furnaces. Electric furnaces (Figure 6) are similar to the reverberatory furnaces in that they offer a high degree of versatility: they can be charged with calcine, concentrate, or slag to recover entrained metal.



FIGURE 6 ELECTRIC FURNACE

The heat for smelting is generated by the passage of electric current through electrodes submerged in the slag layer. Because fuel is not burnt in the furnace, exhaust gas volumes are lower than those from other smelting furnaces, although a certain amount of dilution air enters the furnace because of draft.

The concentration of SO₂ in exhaust gases from electric furnaces smelting nickel concentrates reportedly varies between 0.5 and 2.0 percent, certainly much lower than the 5.0 to 6.0 percent reported for the smelting of copper concentrates. Potential leakage points are the expansion spaces, cracks, spaces around the seals where the electrodes enter the furnace, and charging points. Fugitive emissions can result from leakage whenever insufficient draft is maintained.

Typical particulate emissions from electric furnaces are expected to be in the 0.2 to 1.0 kg per tonne of concentrate feed. Where the gas flow is relatively small, the amount of entrained particulate is also small. Instances have been reported, however, where the gas temperature has risen to 800°C, and a stack effect in the charge pipes has resulted in serious fugitive gas and dust losses above the furnace in the building. Furthermore, where gas-cooling equipment is not provided downstream of the furnace, combustion may occur in the electrostatic precipitators if the gas temperature rises too high.

For further reading, see references 3 and 4.

Outokumpu flash smelting furnaces. Outokumpu flash furnaces are currently used to smelt copper, nickel, and copper-nickel concentrates. The furnace (Figure 7) consists of three distinct sections: a reaction shaft, a settler, and an uptake shaft.

The dried feed and air or oxygen-enriched air are fed into the concentrate burner at the top of the vertical shaft. The concentrate oxidizes rapidly in the reaction shaft and flows towards the horizontal settler. The heat generated by the exothermic oxidation reactions melts the solid particles. Molten material falls to the bottom of the settler, where it separates into matte or metal and slag layers.

Gas from the flash smelting furnace flows through the uptake shaft into the waste heat boiler, where it cools to about 350°C. Heat is recovered in the form of steam. From the boiler the gas passes through an electrostatic precipitator from where it can be fed to a sulphur recovery plant. Flue dust is recovered in the boiler and the electrostatic precipitator and is fed back into the flash smelting furnace.

The SO₂ content of the flash smelting off-gases can be in the 10.0- to 50.0-percent range or higher depending upon the amount of oxygen used. It can



FIGURE 7 OUTOKUMPU FLASH SMELTING FURNACE

subsequently be diluted to match the optimum operating requirements of the sulphur fixation process. Whenever off-gases must be cleaned before entering a sulphur fixation plant, the cost advantage lies with handling low volumes with a high SO₂ concentration, because the size and cost of the gas cleaning equipment decreases with volume of gas treated. Emissions of suspended matter depend upon the gas-cleaning equipment installed downstream of the furnace. Losses from the dryer upstream of the furnace are expected to be in the order of 0.4 kg/tonne of concentrate feed.

Fugitive emissions may be in the order of 0.1 percent of the total sulphur charged with the concentrate.

For further reading, see references 4, 6, and 7.

2.1.3 Equipment Used in Nickel-Matte Refining. In a nickel smelter the primary smelting furnace - reverberatory, electric, or flash - removes much of the iron, sulphur, and other impurities, leaving a nickel-rich matte which still contains iron, sulphur, and other impurities which must be removed before final refining can be carried out. This is normally done in a converter.

The Pierce-Smith converter. The principal function of the converter is to remove iron and to adjust the sulphur content in the final product to meet the requirements of the next step and minimize metal losses.

The Pierce-Smith converter (Figure 8) is a brick-lined horizontal steel cylinder with an opening at the top. The cylinder can rotate through a 120°C arc. Compressed air is delivered through a row of tuyeres into the interior. For charging, the converter is turned down to bring the opening to its forward position, the molten matte is poured in and siliceous material added. Then the air supply is turned on and the cylinder rotated to its normal (blow) position. While air bubbles through the molten charge, iron is oxidized and aggregated with the siliceous material to form slag, and sulphur is oxidized to SO₂. At predetermined cycles, the slag is skimmed off, and the matte removed by rotating the cylinder again so that its opening is in the lower (skimming) position.

The amount of SO₂ generated during the conversion of the nickel matte is basically the difference between its sulphur content at the beginning and at the end of the converting cycle. Gaseous and particulate emissions are generated during the entire converting cycle. Primary hoods have been designed to capture and discharge the emissions through the stack. Particulates are partially removed in the dust recovery system downstream. In practice, gaseous and particulate emissions escape from the hood during the converter cycle, when matte is being charged, when the tuyeres enter or leave the bath while the air is still on, and when the primary hood and off-gas system do not have sufficient capacity to handle the volume of gas generated. Older converter designs allowed for at least 200 percent air leakage into the primary hood and off-gas system to control the gas temperature.

Typical off-gas strength after cooling and cleaning can be expected to be in the 3.5- to 8.0-percent range depending upon the hood design.

Fugitive emissions are very difficult to measure, but some tests indicate that as much as 5 percent of the sulphur in the matte bypasses the primary hood and escapes to the converter aisle during the blowing step; an additional 2 percent escapes when the converter is rolled out from under the stack. Because of high fugitive SO₂ emissions to the work place, operators may have to wear masks when close to the converters and fresh air must be supplied to the crane cab.

With particulate matter in off-gases, an emission factor of 30.0 kg per tonne of feed has been suggested by some sources, while others expect such emissions to be much lower, but that would depend on the gas-cleaning effort.

For further reading, see references 2 and 5.



View of horizontal side-blown Pierce-Smith converter used in the copper and nickel industry



Steps in the converting cycle and position of the converter shell, relative to the hood, for each step.

FIGURE 8 CONVENTIONAL PIERCE-SMITH CONVERTER



FIGURE 9 TOP-BLOWN ROTARY CONVERTER

Top-blown rotary converters (TBRC). The converter (Figure 9) has a cylindrical shell with refractory lining, is closed at one end and open at the other. It can rotate along its longitudinal and lateral axes. It is rotated on its lateral axis when it needs to be tilted for charging flux additions and for skimming. Oxygen is supplied by a water-cooled lance blowing against the bath surface at an angle, while the open end of the converter is pointing upward.

The gases are carried off through a fume hood connected to a flue system which fits tightly over the open end of the converter. Rotation during the blow promotes the conversion reactions and removal of impurities.

The concentration of SO₂ in gases leaving the converter is reportedly up to 18 percent; it depends, though, on whether oxygen enrichment used. Once the SO₂ enters the hood where it may be diluted by in-leakage, the SO₂ concentration may drop considerably.

For further reading, see references 5 and 6.

2.1.4 Summary Considerations. What has been established so far is that off-gases that result from the roasting, smelting, and converting of sulphide concentrates contain a variety of gaseous and particulate matter. In addition to SO₂, these process and fugitive emissions contain heavy metals, usually arsenic, cadmium, cobalt, copper, mercury, and nickel. Their quantities in these emissions reflect the composition of the feed material.

Both a review of the few data available in literature on losses to the atmosphere and discussions with experts in the field reveal that actual numerical values fall within wide ranges, mostly because they are functions of such factors as the type of the equipment used, its maintenance, and the gas cleaning undertaken.

Typical SO₂ losses in off-gases are summarized in Table 2.

TABLE 2 TYPICAL SO₂ LEVELS IN OFF-GASES BEFORE SULPHUR FIXATION

Type of Equipment	% SO ₂ by Volume
Multiple-hearth roasters	2.0 - 5.0
Fluid-bed roasters	9.0 - 15.0
Reverberatory furnaces	0.5 - 2.0
Electric furnaces	0.5 - 2.0
Outokumpu flash furnace	10.0 - 15.0*
Pierce-Smith converters (open hood)	3.5 - 5.0
Pierce-Smith converters (tight hood)	5.0 - 8.0
Top-blown rotary converters TBRC	1.0 - 15.0

* Gas diluted with air after the cleaning process.

To optimize metal recovery, these off-gases are cleaned before discharge. Particulate losses to the atmosphere depend on the type of gas-cleaning equipment used and the care with which it is maintained. With conventional gas cleaning, estimated particulate losses to the atmosphere are in the ranges listed in Table 3.

Fugitive emissions depend upon the type of equipment used, its maintenance, and the ventilation system. The figures given in Table 4 are considered reasonable and typical, assuming ventilation hoods are in place and properly maintained.

Not only emissions into the work place are of concern, but also heat generated by the various pyrometallurgical operations. Splashes or spills of molten metals, particularly nickel-iron sulphide, are also a potential hazard.

Type of Equipment	Particulate Emissions (kg/tonne) of Concentrate Feed
Multiple hearth roasters	2.0 - 5.0
Fluid-bed roasters	0.5 - 2.0
Electric furnaces	0.2 - 1.0
Dryer upstream of Outokumpu flash furnace	0.4

TABLE 3TYPICAL PARTICULATE LEVELS IN OFF-GASES BEFORE
SULPHUR FIXATION

Pierce-smith converters (open hoods)

TABLE 4POTENTIAL SOURCES OF FUGITIVE EMISSIONS AND APPROXIMATE
LEVELS

1.0 - 2.0

	Fugitive E	Emissions (kg/min)	
Functions	so ₂	Particulates	
Roasters			
Charging, calcine discharge and transfer, leakage	very low	-	
Smelting furnaces			
Charging Leakage Matte tapping Slag tapping Converter slag return	very low 0.66 5.08 1.41	- 0.057 0.009 -	
Converters			
Charging Blowing Skimming and holding Leakage	1.80 0.10 1.10 0.10	- 0.095 -	
Miscellaneous			
Dust handling and transfer, ladles Slag dumping	1.50	-	

2.2 Nickel Refining

Refining is the final operation to decrease to an acceptable level those impurities that would have an adverse effect on metal or alloy performance and that are not readily eliminated during the preceeding extractive processes. The refining operation is generally considered separate from the extractive process, and in many cases the two plants are long distances apart so that the crude metal has to be shipped to the refinery for final treatment.

Unlike copper refining, where only one basic process is used, or lead and zinc refining where only a few basic processes are used for each metal, nickel refining is much more complicated. Nickel producers can choose from several processes. Some of these refining processes are used in different combinations. The type of refining that is used to purify the crude metal depends upon the impurities to be removed (whether or not the impurities are to be recovered as by-products), the desired purity of the refined metal product, and the source of energy most economically available.

This review is limited to the emissions produced and the effects on the working environment generated by those processes that are widely known.

It is difficult to combine the environmental problems associated with all nickel refining processes under a single heading since each refining process presents its own particular problems. In contrast, for all smelting processes the problems associated with sulphur dioxide gas, dust, and heat are similar and differ only in their severity and the ways to control them.

Schematic process descriptions are shown in Appendix B.

2.2.1 INCO Ltd. Nickel Sulphide Anode Refining Process

Working environment. Good ventilation and carefully enclosed equipment are required in several process areas for the following reasons:

- Sulphur dioxide is given off from surface oxidation of molten matte during handling and casting;
- Chlorine gas is used for cobalt removal; and
- Hydrogen sulphide is used for removal of copper and other impurities.

Emissions. The sulphur content of the matte is recovered in elemental form; consequently, there is no sulphur dioxide emission from the refining process itself. Off-gases from the cobalt and copper removal steps can be effectively scrubbed to avoid any discharge of excess chlorine or hydrogen sulphide.

2.2.2 Falconbridge Matte Chlorine Leach Process

Working environment.

- Chlorine is handled extensively throughout the process, requiring strict safety
 precautions. In particular, it is necessary to maintain a good working atmosphere in
 the nickel cell rooms by ventilation and by keeping the thousands of individual anode
 hoods tight to avoid escape of chlorine gas.
- Nickel and copper electrowinning must be conducted to keep electrolyte mist at low levels in the cell room atmosphere.
- The copper sulphide residue fed to the fluid-bed roasters still contains much nickel. Consequently, roaster dust contains fine nickel oxide particles. To avoid exposure to nickel oxide dust, the roasting operation is extensively automated; the dust is removed from the roaster area by a permanent sprinkling and collecting system.
- The process includes solvent extraction steps, requiring safety precautions against solvent fumes and fire hazards.

Emissions. The roasting operation produces a continuous flow of sulphur dioxide gas suitable for recovery as either liquid sulphur dioxide or sulphur acid.

2.2.3 Outokumpu Sulphate Leach Process

Working environment. This process is attractive because it does not require hazardous chemicals such as chlorine or hydrogen sulphide. Sulphate electrowinning, however, does produce acid mist, requiring good ventilation in the cell room.

Emissions. There are no emissions to the outside atmosphere.

2.2.4 Sulphuric Acid Pressure Leach Process

Working environment. Careful design and operation and maintenance of all pressure operations (leaching, nickel reduction, and cobalt precipitation) are required to ensure safety in these plant areas.

Great care is also required in the handling of ammonia used for neutralization and particularly of hydrogen used for reduction at high pressure. Ideally the hydrogen reduction autoclaves should be installed outdoors to prevent any leaked-out hydrogen from collecting under the roof to form there an explosive mixture with the air.

Hazardous hydrogen sulphide need not be used for cobalt precipitation, because other sulphide reagents are also effective.

Emissions. There are no significant emissions to the outside atmosphere because sulphur is removed in the form of ammonium sulphate.

2.2.5 INCO Ltd. Pressure Carbonyl Process

Working environment. This process involves such highly toxic gases as carbon monoxide and nickel carbonyl. Unusually strict precautions must therefore be taken to safeguard the work place. Such precautions include continuous monitoring of trace amounts of nickel carbonyl and automatic isolation of any plant area where a leak has been discovered. INCO Ltd. has demonstrated that the process can be safely operated, provided such precautions are designed into the plant and strictly adhered to.

To safeguard the employees requires the availability and use of impervious clothing, gloves, face shields, and other protective clothing to prevent any possibility of skin contact with liquid nickel carbonyl.

Emissions. Desulphurization in the top-blown rotary converter is a batch operation producing a discontinuous sulphur dioxide stream which is therefore less suitable than roaster gas for economic recovery of liquid sulphur dioxide or sulphur acid. At Copper Cliff, Ontario, the TBRC gas is discharged to atmosphere.

2.2.6 INCO Ltd. Matte Separation Process (Production of Nickel Oxide and Incomet)Working environment.

- The matte casting shop must be well ventilated to remove sulphur dioxide gas given off from surface oxidation of the molten matte.
- INCO's original sinter-roasting of nickel sulphide on a travelling grate sinter machine was a very dusty operation which created very dangerous conditions because of the carcinogenic effect of nickel oxide dust, which was, however, not known to INCO Ltd. at that time. The sinter machine also created poor working conditions because of sulphur dioxide gas leakage.

These problems have been largely solved by INCO's changeover to fluid-bed roasting in an enclosed system where the nickel oxide dust is removed from the gas stream by wet scrubbing.

Due to the toxicity of nickel oxide dust, it is desirable to keep a nickel oxide plant very clean by providing a system such as the one mentioned in connection with the Falconbridge matte chlorine leach process (2.2.2).

Chlorine gas handling precautions must be observed in the chlorination step.

Hydrogen gas handling precautions must be observed in the hydrogen reduction step, particularly because hydrogen is used there and recycled at an elevated temperature. This step should ideally take place outdoors. A nitrogen gas supply is needed to purge the system when required.

Emissions. Fluid-bed roaster gas has a sufficiently high sulphur dioxide content to be suitable for processing to sulphuric acid, but INCO Ltd. discharges it to atmosphere at Copper Cliff.

2.2.7 Sherritt Gordon Ammonia Leach Process

Working environment. Careful design, operation, and maintenance of all pressure operations (leaching, copper removal, oxydrolysis, nickel reduction, and cobalt precipitation) are required to ensure safety in these areas. In a suitable climate all the autoclaves should be installed ideally outdoors, which has been done at the Australian refinery of the Western Mining Corporation.

Great care is also required in the handling of ammonia, hydrogen sulphide, and particularly of hydrogen at high pressure.

In areas where a leach solution with excess free ammonia is filtered, adequate hooding of the equipment and sufficient ventilation in the building has to be provided to keep ammonia concentrations within the permissible limit in the work area.

Enclosed pressure filters are used for the separation of cooper and cobalt sulphide precipitates; this avoids emission of hydrogen sulphide into the work area. This area must nevertheless be well ventilated to remove any hydrogen sulphide from the discharged filter cakes.

Solid wastes and emissions. The solids of the leach residue consist mainly of very fine iron oxide, insoluble gangue, and residual sulphide minerals such as insoluble pyrite. The liquid of the residue contains free ammonia and soluble heavy metals (Ni, Cu, and Co) which are thoroughly removed and recycled to the main circuit. At one plant, the residue is repulped and rewashed three times before final discharge to a disposal pond.

At any potential site for this process, the sensitivity of the environment to ammonia and heavy metal ions must be carefully evaluated to determine not only the amount of washing required but also the design of the residue pond and the need for lining it.

3 THE WORKING ENVIRONMENT AND ITS PROTECTION

3.1 General

Nickel production consists of several sequential steps from mining, crushing, and milling to smelting and refining. During the later stages of nickel production, a worker may be exposed to various potential hazards associated with:

nickel and nickel compounds, sulphur dioxide, dust, carbon monoxide, hydrogen sulphide, arsenic and other heavy metals, polycyclic aromatic hydrocarbons (PAH), and physical stresses such as heat and noise.

Figure 10 below provides a simplified flowsheet of a smelting process and lists the sources of potential physical and chemical hazards.

3.2 Health Effects

The health effects from exposures to hazards listed in Figure 10 been widely investigated and it is beyond the scope of this work to make a comprehensive review of the findings. The substances may enter the human body through various processes: absorption through the skin, ingestion into gastrointestinal tract, and inhalation into the respiratory system.

The most commonly reported health effects from exposure to sulphur dioxide, nickel, nickel compounds, and dust are summarized in Tables 5 and 6.

With regard to the effects of a combination of contaminants present in the working environment besides nickel, sulphur dioxide and physical stresses, both data gaps and a lack of understanding of adverse health effects present a serious limit regarding interpretation. Notwithstanding that, it is important that workers be protected through regulations that employ adequate safety factors.

The review of all information on the epidemiology and environmental concentrations of nickel to determine the species of nickel and the amount associated with an increased risk of cancer is underway. The review is undertaken by a joint committee of the Commission of European Communities, the U.S. Environmental Protection Agency, the Ontario Ministry of Labour, Health and Welfare Canada, and the Nickel Producers' Environmental Research Association. The Committee is chaired by Sir R. Dell of Oxford University in England. Completion of the study is expected in 1987.


FIGURE 10 POTENTIAL SOURCES OF PHYSICAL AND CHEMICAL HAZARDS

3.3 Exposure Limits

Because the liberation of many toxic substances is inherent to industrial activities, including nickel production, extensive efforts have been made to determine permissible levels of human exposure, expressed for example as threshold limit values (TLV). Table 7 shows concentrations of contaminants determined by the American Conference of Governmental Industrial Hygienists (ACGIH). TLV is believed to represent

TABLE 5GENERAL HEALTH EFFECTS OF EXPOSURE TO SULPHUR DIOXIDE
(16)

SO ₂ Concentration (ppm)	Effects
3-5	Odour threshold.
8-12	Throat irritation, coughing, constriction in the chest, tearing and smarting or the eyes.
10-50	Exposure 5 to 15 minutes: increased irritation of the eyes, nose, throat, choking, coughing, and in some cases wheezing as a sign of narrowing of the airways (which increases the resistance of the air- flow).
150	Short-term endurance due to severe eye irritation and because of the effects on the membranes of the nose, throat, and lungs.
500	Highly dangerous after an exposure of 30 to 60 minutes.
1000-2000	May be fatal with continued exposure.

a level below which nearly all workers may be repeatedly exposed, day after day, without adverse effects. TLVs are continuously under review.

Another way of expressing threshold limit values is by 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 by equivalent excursions below the limit during a workday.

The current TWA standard by the American Occupational Health and Safety Administration (OSHA) for nickel and its compounds is:

Nickel carbonyl		$0.001 \text{ ppm} \text{ or } 0.007 \text{ mg/m}^3$
Nickel, metal and insoluble compounds	(as Ni)	1 mg/m ³
Nickel, metal and soluble compounds	(as Ni)	0.1 mg/m ³

Appendix C contains additional information on occupational exposure criteria.

3.4 Measures to Protect the Workers

Control measures used to protect the worker include such engineering controls as enclosure of processes, ventilation, and mechanical dust recovery equipment. Other

Material	Effects on Human Health
Metallic Nickel or Soluble Nickel	On inhalation of fumes: respiratory irritation, pneumonitis.
Compounds	On skin contact: allergic reaction resulting in a rash.
	Nickel and its compounds have been reported to cause cancer of the lungs and sinuses. This statement, however, is being disputed by those who contend that the available published data do not support the conclusion that nickel and all its inorganic compounds are carcinogenic.
Nickel Carbonyl	On inhalation or absorption: dizziness, shortness of breath, vomitting, increased potential of lung cancer, delirium, death.
Dust	Total suspended particles arise from several sources within a nickel smelter. The component of the particles determine the overall toxicity of the dust. If the individual components are not of a toxic nature, then the acceptable level of the dust in the working environment is related to the ability of the respiratory tract to clear the particles. Samples of particulates in a nickel smelter should be analysed for nickel, cobalt, chromium, arsenic, and other metals.

TABLE 6EFFECTS ON HUMAN HEALTH CAUSED BY MATERIALS ASSOCIATED
WITH NICKEL PRODUCTION

control measures include personal protective equipment and administrative controls. Medical surveillance and monitoring serve to check the effectiveness of control measures.

3.4.1 Engineering Control Methods. Enclosure of processes has helped control worker exposure. Fluidized bed roasters can replace multi-hearth equipment. Converters can be equipped with tighter hoods. Conveyor belts can be covered to reduce dust problems. Converters can be entirely enclosed.

Ventilation systems have been used both to capture contaminants at their emission source and to dilute the contaminants. They should be designed and maintained to keep the concentration of pollutants below occupational exposure limits, prevent any previously contaminated air from being recirculated, and remove contaminated air without passing it within the workers' breathing zone. For example, with regard to SO₂

	Selected C Dusts, Fur	Year	
Substance Carbon monoxide Chlorine Hydrogen sulphide Nickel carbonyl Sulphur dioxide Antimony and compounds (as Sb) Arsenic and compounds (as As) Cadmium, metal dust and soluble salts (as Cd) Cadmium oxide fume (as Cd) Cobalt, metal fume and dust Copper: dust and mist fume Fluoride fume (as F)	ppm	mg/m ³	when Measured
Carbon monoxide	35		1981
Chlorine		3	1975
Hydrogen sulphide		15	1975
Nickel carbonyl	0.05	0.35	1985
Sulphur dioxide	2		1981
Antimony and compounds (as Sb)		0.5	1975
Arsenic and compounds (as As)		0.5	1975
Cadmium, metal dust and soluble salts (as Cd)		0.2	1975
Cadmium oxide fume (as Cd)		0.05	1975
Cobalt, metal fume and dust		0.2	1975
Copper: dust and mist		1	1975
fume		0.2	1975
Fluoride fume (as F)		2.5	1975
Iron oxide fume (as Fe)		5	1975
Iron soluble salts (as Fe)		1	1975
Lead, inorganic fumes and dusts (as Pb)		0.15	1975
Mercury, all forms except alkyl (as Hg)		0.05	1975
Nickel, metal and insoluble compounds (as Ni)		1	1985
Nickel soluble compounds (as Ni)		0.1	1985
Sulphuric acid		l	1975

TABLE 7THRESHOLD LIMITS FOR SUBSTANCES WHICH MAY BE
ENCOUNTERED IN NICKEL PRODUCTION OPERATIONS

the ventilation system in a smelter should be designed to ensure a time-weighted average exposure, for a normal 8-hour day/40-hour week, not exceeding 2.0 ppm.

Mechanical dust recovery equipment (described in Chapter 5) is widely used.

3.4.2 Personal Protective Equipment. To protect employees, gaseous and particulate emission points must be hooded and vented to a central fugitive emissions control system (see Chapter 5). In addition to the safety glasses, hard hats, safety shoes, and hearing protection normally supplied, each employee must be provided with a respirator to filter out sulphur dioxide and fine particulates.

To avoid dermatitis, work clothes must be provided frequently enough for those employees working in the smelter itself, so that they can change them twice a week. The smelter must include change-house facilities.

In particularly hot areas where work is heavy, such as tapping or skimming a smelting furnace, fire-retardant clothing is recommended to protect the skin from splashes of molten metal. Only natural fibres, such as wool or cotton, should be used in areas where molten materials are present.

3.4.3 Administrative Measures. Administrative measures would include:

- pre-planned action upon detection of a gas leak, a molten metal spill, or other potentially serious situations;
- rotation of employees' tasks, thereby minimizing exposure to the hazard;
- pre-placement medical examinations to screen out persons who may be adversely
 affected by exposure to noxious substances not exceeding the occupational exposure
 limits within which other workers can work safely.

Where the work is particularly repetitive or very stressful, such as operating a hot-metal crane, workers are usually relieved every hour to allow them to rest away from the heat. Reasonably cold drinking water (10° to 15°C) must be available, and workers must be encouraged to increase their salt intake.

3.4.4 Monitoring and Air Sampling. Air monitoring systems should be set up in areas where potential hazards may be present. Measures to determine employee exposure are best taken so that the average 8-hour exposure is based on a single 8-hour sample or on two 4-hour samples. Air samples should be taken in the employees' breathing zone.

There are many methods available to monitor work environments. Sampling and analysis should only be performed by qualified persons.

3.4.5 Medical Surveillance. Medical surveillance is recommended and the following examinations should be made available to each employee who is exposed to nickel, nickel compounds, sulphur dioxide, dust, and other hazards.

- Initial medical examination, where a complete history and physical examination is carried out not only to detect pre-existing conditions that might place the exposed employee at increased risk but also to establish a baseline for future monitoring.
- The examination should be performed on an annual basis. A urinalysis should be performed on a monthly basis on workers exposed to nickel carbonyl.

3.4.6 Training and Supervision. Safety and accident prevention depends largely on the effectiveness of employee training. Employees should be trained and thoroughly instructed in all facets of their work, including:

- the hazards they may face;
- safe operating procedures;
- operating instructions for the appropriate personal protective equipment;
- procedures for reporting all leaks and equipment failures;
- procedures for reporting illnesses or adverse skin effects;
- proper first-aid and emergency procedures; and
- location and operation of safety showers and flushing stations.

Supervisors must ensure that approved personal protective equipment is worn, when required, to minimize the risk of over-exposure to potential hazards.

3.4.7 First Aid. Prevention is the best first aid, therefore the general precautions, safety procedures, and protective measures outlined earlier should be observed.

Personnel should know how to contact a poison control centre or hospital emergency department.

Finally, every smelter must be equipped with first-aid facilities capable of treating minor injuries such as burn, heat exhaustion, and other ailments requiring immediate attention. First-aid facilities should also be equipped with air packs for emergency rescue in the event of an accident.

For further reading, see references 15, 16, 17, 18, 19, 20, and 22.

4 ENVIRONMENTAL EFFECTS OF EMISSIONS INTO THE AIR

4.1 General

Besides nickel, sulphide ores contain other metals, among them lead: copper, arsenic, mercury, cadmium, and selenium. The ore is finely ground to separate a metal sulphide concentrate in preparation for smelting to produce nickel. The smelting process gives off gaseous emissions, which in addition to SO₂, may contain other pollutants such as particulate material and metal vapour. Some of the emissions escape from low level stacks or roof vents, or they are discharged during the ventilation of the buildings; others are discharged through stacks.

Some sulphur dioxide reacts with water vapour in the atmosphere to form sulphuric acid, and as such precipitates to earth. Some reacts with ammonia and other compounds in the air to produce sulphates that fall to earth as dry fallout or deposition. Pollutants may be carried hundreds or even thousands of kilometers by prevailing winds. This phenomenon is known as the long-range transport of airborne pollutants (LRTAP).

This section summarizes some of the extensive information available on the environmental effects of gaseous emissions on the receiving environment.

For further reading, see reference 13.

4.2 Effects on the Aquatic Environment

Areas susceptible to damage from acid precipitation are characterized by a low buffering capacity in soils and rocks. When soils and rocks cannot adequately buffer the acid, acid loading will eventually strip away the buffering capacity altogether, and surface runoff entering lakes and streams will directly reflect the acidity of the rainfall. Lakes and streams with low alkalinity are susceptible to acid precipitation because they are unable to neutralize the incoming acid for very long.

Acid precipitation leaches metals, such as aluminum, from the soils and sediments of watersheds, and discharges these metals into lakes and streams.

Suspended particles which may contain heavy metals from the smelting process may also find their way to lakes and streams thereby adding to the metal accumulation in the water column. High concentrations of heavy metals may then show up in sediments, plankton, and fish.

Detailed studies of watersheds have been carried out in sensitive regions of North America and Scandinavia with various sulphate deposition rates. Study results show that the number of species of plankton is lower in lakes of low pH than in lakes of higher pH.

Individual lakes may show several symptoms of acidification at the same time, among them high concentrations of aluminum and heavy metals. As the pH of the water drops, the most sensitive aquatic species begin to disappear. When the pH of the water drops to about 4.5, most fish will have ceased to exist, as well as many other desirable forms of life.

At this point the lake or stream is referred to as being acidified.

4.3 Effects on Soil

Soils vary widely with respect to their properties, support different types of vegetation, are subject to different cultural practices, are situated in different climatic zones, and may be exposed to a broad spectrum of acid loading.

The effects of acidic deposition may be minimal on soils from calcareous materials, except near a smelter (within 2 to 4 km). Heavy metals, however, are known to cause soil toxicity which can result in inhibition of seed germination, reduced seedling survival, and growth reduction.

4.4 Effects on Vegetation

High concentrations of heavy metals can be expected in vegetation around a smelter; for example, mercury in blueberries. In some cases, these concentrations could represent a hazard if affected plant species are eaten regularly.

Near smelters, the adverse effects on vegetation due to doses of high concentrations of sulphur dioxide over short periods of time and low concentrations over extended periods can be visible.

Acidic deposition has a direct effect on plants. The most common effect is injury to foliage which in turn causes atrophy of the plants. An important consideration for forests subjected to long-term acid precipitation is the cumulative effect of increased acidity of the soils and the inherent loss of useful nutrients.

4.5 Effects on Wildlife

Direct effects of acidic deposition or heavy metals emissions on terrestrial wildlife have not been widely reported, which suggests that they could be minor compared to effects on vegetation, soils, or aquatic environment. Nevertheless, in some instances, indirect effects have been suggested through contamination by heavy metals mobilized by acidity or through reduction of nutritional value of food sources.

4.6 Effects on Human Health

There seems to be a consensus that SO₂ and particulate matter may have adverse effects on human health when ambient air quality limits are exceeded. Human health problems related to exposure to heavy metals such as mercury, lead, and cadmium, which may be present as impurities in sulphide ores, have been reported world-wide. Lack of both data and understanding of all adverse effects present a serious limit on making in this review any specific statement with respect to the direct inhalation of pollutants emitted by nickel smelters to the environment outside of the plant. There is the potential for indirect health effects associated with the contamination of the food chain with metallic substances, such as mercury in fish when consumed by humans in large amounts.

Acidic deposition may liberate metals in some groundwaters and surface drinking water supply systems. Therefore, concern regarding recreational activities in acidified waters has been expressed.

4.7 Effects on Man-Made Structures

In Europe and North America, materials have suffered and are suffering under exposure to airborne pollutants, particularly SO₂. Materials at risk include structures of cultural value. Chemical degradation processes include deterioration of calcareous building materials by the removal of calcium carbonate through conversion to calcium sulphate and the removal of protective corrosion products on metals.

5 AIR POLLUTION CONTROL

5.1 General

The potential for both process and fugitive emissions from the main equipment used in nickel smelting has been reviewed in Chapter 2. The effects of these emissions on the environment inside and outside a smelter have been reviewed in Chapters 3 and 4. This chapter reviews the controls commonly applied to process and fugitive emissions. Reference is made, where appropriate and possible, to smelters where such controls have been installed and successfully operated.

Generally speaking, there are three main approaches to air pollution control:

- 1. process changes to prevent pollutant generation,
- 2. removal of pollutants after generation, and
- 3. dispersion of pollutants to reduce concentrations at ground level.

All these approaches should be examined at an early stage of formulating any air pollution control plan.

In this chapter, process changes are reviewed only in the context of the separation of high sulphide minerals before smelting; more emphasis is focussed on removal techniques. The dispersion approach is also briefly mentioned.

The control of gaseous emissions, particularly sulphur dioxide, is the main pollution problem facing the nickel-producing industry. Gaseous emissions result from combustion processes, transferring feed materials, handling and loading, melting metals, tapping and transferring, dust handling and transfer, fuel burning, leakages, etc. Sulphur is a major component in the concentrate feed to the smelting processes, and it is oxidized to SO₂ during the various operations.

Particulate material containing metals also constitutes a significant part of the potential air pollution problem, but it is usually removed as completely and efficiently as possible to increase the quantity of metal(s) produced. Particulate material in smelter emissions generally reflects the types of metal being recovered. When metals other than nickel are present in nickel sulphide ores, they may be partially removed in the milling stage and the remainder discarded with the slag, emitted to the atmosphere, or retained in the nickel matte and products as impurities or valuable materials.

Some emissions, such as mercury, with boiling points sufficiently low that they exist as vapour at discharge temperature, can be controlled chemically. Other emissions

can be controlled physically with electrostatic precipitators, scrubbers, cloth filters, or mechanical separators. The choice of physical control depends upon the chemical composition and physical size of the emissions, and the temperature of the process.

This chapter addresses pyrometallurgical processes only; some considerations regarding refineries have been incorporated in Chapter 2.

5.2 Containment of Sulphur Dioxide Emissions

Only a few proven approaches taken in non-ferrous metallurgical plants can be considered to reduce the emissions from a smelter. These are:

- ore treatment (rejection of high-sulphur minerals),
- recovery as sulphuric acid,
- recovery as liquid SO₂,
- recovery as elemental sulphur, and
- scrubbing of gases.

5.2.1 Rejection of High-Sulphur Minerals. In sulphide ores, nickel is present in the mineral pentlandite (NiFe)₉S₈, usually associated with pyrrhotite ($Fe_{n-1} S_n$, where n is usually equal to 8, but can vary from 8 to 16), chalcopyrite, and traces of the platinum group metals.

From the viewpoint of sulphur containment, the pyrrhotite content of nickel concentrates can be an important factor since it may contain 38 to 39 percent sulphur, thus greatly contributing to a potential sulphur problem in nickel smelting.

Processes are now used to separate the pyrrhotite fraction of the ore from the concentrate feed to the smelters. This separation has two main advantages:

- it concentrates a mineral high in nickel while decreasing the amount of material sent to the smelter, in effect substantially increasing the smelter production capacity; and
- it results in a decreased amount of sulphur converted to sulphur dioxide during the smelting processes.

Even though pyrrhotite has a tendency to float readily with pentlandite, it can be controlled in the flotation circuit. The rejected pyrrhotite then flows with the gangue material. It can then either be processed to sulphuric acid or disposed of in the tailings basin where it remains in stable condition, if properly submerged in water. Because of the separation and rejection of pyrrhotite, the smelter operating procedures and practices can be improved because less concentrate needs smelting. This can reduce the costs, particularly those for energy, which in turn can offset the costs associated with the increased losses of nickel contained in the rejected pyrrhotite. Pyrrhotite rejection is widely and successfully practised at the three Canadian nickel smelters, were more than 50 percent of the sulphur once present in the concentrate is now retained with the pyrrhotite.

Therefore, when planning sulphur dioxide containment at a nickel smelter that processes sulphide ores, pyrrhotite rejection should be the first option to be considered. It could be the most economical means of sulphur dioxide control. This statement is generally true for rejection of up to 50 to 60 percent of the pyrrhotite content of the ore. Above that, nickel losses may be too high to make this approach attractive. Its economics must therefore be calculated for each case.

5.2.2 Recovery as Sulphuric Acid. Burning sulphur or sulphur-bearing materials produces SO₂ which can be converted to sulphuric acid at an acid plant. Acid production from SO₂ generated during nickel ore roasting and smelting has become a well accepted method of controlling SO₂ emissions. Compared to sulphur-burning plants, however, the manufacture of sulphuric acid from smelter gases is more difficult and costly. Its main disadvantage is that the feed gas contains several impurities which, if not removed at the conversion stage upstream of the acid plant, plug or poison its catalyst, or result in contaminated acid. In addition, sulphuric acid is expensive to transport over long distances and to store. Furthermore, iron pick-up during transit or during storage can be a limiting factor.

This description highlights only the two basic steps relevant to the production of sulphuric acid from smelter gases: (1) gas purification and (2) conversion and absorption.

Gas purification. Gases need to be thoroughly cleaned before entering the acid plant, because the impurities they contain when leaving the smelting furnace, roaster, or converter can gradually render the catalyst inactive. And if the impurities ultimately find their way into the acid, they make it unsuitable for such applications as fertilizer manufacture. (Design limits for cleaned gas entering the production section of the sulphuric acid plant are given in Table 8.)

A schematic flowsheet of the gas-cleaning process for smelter gases containing a high level of impurities is shown in Figure 11. Incoming gases at 205° to 325°C are scrubbed in a tower with a recirculating liquor such as weak sulphuric acid. Partially cleaned and partially cooled, the dusty gas proceeds to a second tower where more particulate and fume is removed and the gas further cooled before a mist precipitator provides additional cleaning.

When mercury is present in the concentrate at levels in the order of 100 ppm or more, particular care should be taken to prevent the mercury from entering the sulphuric acid. Mercury is assumed to be present in the concentrate as mercury sulphide, of which approximately 95 percent is expected to be transformed into metallic mercury and mercury oxide vapours during the roasting stage. Part of this mercury condenses inside the scrubbing and cooling towers; the remainder, in quantity corresponding to its equilibrium, is contained in the gas fed to the acid plant.

It has been found, that with gas temperatures of 30 to 40°C at the inlet of the drying tower of an acid plant, mercury content could be in the order of 30 to 40 mg/m³, and mercury in the acid could be in the order of 100 ppm. To remove that mercury an additional gas-cleaning step may be introduced as shown in Figure 11. Mercury removal processes, such as the one developed by Boliden, may remove more than 99 percent of the mercury contained in the gas so that its concentration is below 0.25 mg/Mm^3 .



FIGURE 11 GAS CLEANING (FLOW DIAGRAM)

Impurity	Trace Element Concentrations - Dry Basis (mg/Nm ³)
Chloride, as Cl	1.2
Fluoride, As F	0.24
Arsenic, as As ₂ O ₃	1.2
Lead, as Pb	1.2
Mercury, as Hg	0.25
Selenium, as Se	50
Total Solids (Dust)	1.2
H ₂ SO4 Mist, as 100% H ₂ SO4	50

TABLE 8APPROXIMATE DESIGN LIMITS FOR SMELTER GAS USED TO
MANUFACTURE SULPHURIC ACID

The effects of impurities in smelter feed on the capital and operating cost of gas-cleaning equipment have been studied in Canada. A summary of the findings, based on three different levels of impurities, is shown in Table 9, where Case I represents clean, Case II moderately dirty, and Case III dirty concentrates. Additional details are shown in Appendix D.

For further reading, see references 2, 4, 9, and 21.

Conversion and absorption. The conventional sulphuric acid process for treating smelter gases has been in use for many years with little significant change.

In a typical conventional plant the cleaned gas is dried in a packed tower by contact with 93 percent sulphuric acid to remove residual water and then compressed with a blower. The blower, which drives the gas through the plant, is the main energy consumer in the system. Before contacting the catalyst, the gas is preheated through a system of heat exchangers utilizing the heat of reaction in which SO₂ is converted to SO₃. Then the converted gas is passed through an absorption tower.

Single-contact single-absorption acid plants have conversion efficiencies between 96 and 98 percent and require at least 4.0 percent SO_2 in the feed to be autothermal. When the feed gas contains less SO_2 , additional heat must be supplied by burning sulphur or some other fuel. Single-contact acid plants will produce tail gas containing 2000 ppm of SO_2 or more.

Sulphuric Acid Production (t/d)	Costs (\$x10 ³ Can., 1983)							
	Case I		Case II		Case III			
	Operating	Capital	Operating	Capital	Operating	Capital		
600	845	3 556	1 083	4 770	1 141	6 230		
1000	1 356	4 754	1 515	6 482	1 594	8 459		
1 <i>5</i> 00	1 708	5 989	2 052	8 243	2 184	11 539		

TABLE 9	APPROXIMATE CAPITAL AND ANNUAL OPERATING COSTS OF GAS
	PURIFICATION BEFORE CONVERSION TO SULPHURIC ACID

Double-contact double-absorption acid plants have conversion efficiencies of 99.7 to 99.8 percent. They require at least 4.5 percent SO₂ in the feed to be autothermal and produce a tail gas containing between 100 and 300 ppm of SO₂. A typical conventional sulphuric acid plant flow diagram is shown in Figure 12; expected volumetric and mass SO₂ emissions are shown in Figure 13.

The operating characteristics of nickel smelters lead to several important design considerations that take into account the variability in gas strength and flow rate. Gas strength also varies with the smelting process, thus the design of an acid plant is unique to the smelter whose gases are being treated.

A continuously flowing gas containing 5 to 8 percent SO_2 and 30 to 50 percent more oxygen than SO_2 is normal for a conventional acid plant. Higher concentrations of SO_2 are desirable to keep acid plant size and cost to a minimum. With metallurgical plants, however, intermittent flow or weak SO_2 content can be expected, and therefore extra heat from external sources is required. Furthermore, an acid plant must be designed for the maximum or peak flow rate; thus, intermittent gas flow requires a larger design capacity for a given daily acid production.

The best approach is to blend one stream rich in SO₂, such as off-gases from a modern smelting furnace or fluid-bed roasters, with off-gases from converters (whose SO₂ content varies) or reverberatory furnaces (which have a weak concentration of SO₂).

Acid plant design must therefore take into account smelter operations and, conversely, smelter operations may be constrained by the operating requirements of an acid plant. Design specifications fix many parameters within the acid plant which, once on line can affect operation. The design basis must therefore be realistic and allow



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SULPHUR CONVERSION EFFICIENCY, % of feedstock sulphur

SO₂ EMISSIONS, kg/Mg of 100% H₂ SO₄ produced

FIGURE 13 VOLUMETRIC AND MASS SO₂ EMISSIONS FROM CONTACT SULPHURIC ACID PLANTS (13)

normal operating variations of the smelter. If the gas strength is low, there could be difficulties in making acid of acceptable strength. Being conservative in establishing design concentrations and gas flow rates of SO₂ is prudent.

Table 10 shows how gas strength and flow rate can affect capital and operating costs. Figure 14 indicates how gas strength affects energy consumption in single- and double-contact acid plants.

When estimating the capital cost of containing SO_2 and recovering it as sulphuric acid, other items must be considered in addition to gas purification and conversion.

TABLE 10	COST (\$ Can., 1983) OF FIXING SULPHUR AS SULPHURIC ACID FROM
	SMELTER GASES USING SINGLE AND DOUBLE CATALYSIS ACID
	PLANTS

Gas Grade (% SO ₂)	H2SO4 (100%) Production (tonnes/day)	Capital Cost (in \$ x 106)	Operating Cost (\$/tonne H ₂ SO4)
12(c)	530	24.69	11.09
5 to 8(v)	530	40.00	15.82
12(c) and 5 to 8(v)	530	28.84	12.46
12(c) and 5 to 8(c)	1070	44.31	9.41
12(c)	540	27.43	11.61
5 to 8(v)	540	44.47	16.74
12(c) and 5 to 8(v)	540	32.04	13.09
12(c) and 5 to 8(v)	1100	49.23	9.97
	Gas Grade (% SO ₂) 12(c) 5 to 8(v) 12(c) and 5 to 8(v) 12(c) and 5 to 8(c) 12(c) 5 to 8(v) 12(c) and 5 to 8(v) 12(c) and 5 to 8(v)	Gas Grade (% SO2)H2SO4 (100%) Production (tonnes/day)12(c)5305 to 8(v)53012(c) and 5 to 8(v)53012(c) and 5 to 8(v)53012(c) and 5 to 8(c)107012(c)5405 to 8(v)54012(c) and 5 to 8(v)1100	Gas Grade ($\%$ SO2)H2SO4 (100%) Production (tonnes/day)Capital Cost (in $$ \times 10^6$)12(c)53024.695 to 8(v)53040.0012(c) and 5 to 8(v)53028.8412(c) and 5 to 8(v)53028.8412(c) and 5 to 8(c)107044.3112(c)54027.435 to 8(v)54044.4712(c) and 5 to 8(v)54032.0412(c) and 5 to 8(v)54032.0412(c) and 5 to 8(v)110049.23

(c) continuous flow

(v) variable flow

For additional details, see Appendix D.

The resulting capital cost estimate will be the sum of the following factors, as they apply:

gas cleaning mercury removal acid plant acid storage loading and unloading facilities trucks, railways cars effluents treatment monitoring of SO₂ emitted modifications to piping or other existing facilities land acquisition financing charges

700 600 ENERGY CONSUMPTION, kWh/TON H₂SO₄ 500 ١ 400 300 200 ACID PLAN ACID PLANT 100 TYPICAL CONCENTRATION OF TYPICAL CONCENTRATION OF **REVERBERATED GASES** ROASTER/CONVERTER GAS 0 00 10 20 30 40 50 70 60 SO2 CONTENT OF GAS STREAM (DRY BASIS) %

FIGURE 14 ENERGY CONSUMPTION OF ACID PLANTS (11)

contingency on design modifications, omissions etc. other expenses specific to the smelter situation.

Similarly, operating costs will be a function of operating labour, supervision, utilities,

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operating supplies, maintenance, indirect costs, depreciation,

and other costs relevant to the specific location.

Appendix D shows detailed capital and operating cost estimates to fix sulphur in smelter gases as sulphuric acid.

Containment of Pierce-Smith converter gases. The relatively low strength (3.5 to 5.0 percent) and varying volume of converter gases make their processing to sulphuric acid a special case and the only practical alternative. The main problems to be overcome in the acid plant are the variations in SO₂ content and the fluctuating volume while the converter is in stack and the interruption in flow when the converter is out of stack. An additional complication is the need to cool the converter off-gases, mainly through dilution with air, from about 1200°C to approximately 600°C.

The first approach to SO₂ containment should therefore be directed toward maintaining a higher SO₂ strength by controlling and minimizing air infiltrations by:

- tight hoods designed to fit as close as practical over the converter shell. (The effectiveness of this solution is limited by the splashing of hot metal which tends to accumulate around the opening of the converter and eventually weld the hood to it.)
- decreasing infiltration or in-leakage resulting from soot-blowing with air, leaks in expansion joints, ductwork, etc.; and
- blowing oxygen-enriched air through the tuyeres.

A well maintained, relatively tight flue system can increase the concentration of SO_2 to between 5 and 6.5 percent during slag blow and to between 7 and 8 percent during metal blow.

The second approach is to minimize the variations in gas volume and SO₂ concentrations. Where two or more converters are required in a smelter, their respective charging, slag blow, and metal blow can be scheduled so that the variation in gas feed to an acid plant is minimized. The Mines Gaspé copper smelter at Gaspé, Canada, has successfully operated an acid plant fed with off-gases from two converters. The details of equipment modifications and the coordination between operators at the smelter and the acid plant are described in detail in reference 10.

In the production of sulphuric acid from converter gas, the variable gas feed is less desirable than a continuous source; where possible converter gases are blended with continuous gas streams from the smelting process. During periods of low gas strength, temperatures in the acid plant can drop. To maintain conversion efficiency, auxiliary heat must be applied. This increases the operating cost of the acid plant.

Appendix D shows detailed capital and operating cost estimates to fix sulphur in converter gases.

Disposal of sulphuric acid. Sulphuric acid storage, transportation, and ultimate disposal can represent a major problem when examining the feasibility of an acid plant.

Sulphuric acid is expensive to transport because it is shipped in special cars which return empty to the source of supply; therefore storage facilities to handle rail shipments should be available. The transport of sulphuric acid in very cold climates presents more problems yet.

Another important factor is the quality of the acid, and its production may require additional gas cleaning and impurity removal to meet specifications. Typical analysis and specifications are shown in Appendix D.

The price obtainable for acid in any geographic location is that of the acid from the cheapest source. Because of the large quantities involved, metallurgical acid is usually sold through long-term contracts at a price lower than spot prices.

Acid neutralization. Where it is neither practical nor economic to market sulphuric acid because of remote location or market saturation, the excess acid or the total production could be neutralized with limestone. This solution requires the purchase of limestone, its transport to the smelter, grinding, neutralization of the acid and disposing of the resulting gypsum in a pond.

The quantity of limestone required is greater than the acid to be neutralized so that transportation of the limestone could be the largest cost factor of the operation. The quality of the limestone is important. It should, for example, have a low magnesium oxide content to avoid formation of soluble magnesium sulphate. Additional costs could be incurred from the need to line the pond with an impervious liner and to monitor ground water quality.

Estimates of capital and operating costs of neutralizing sulphuric acid from a double catalysis plant with limestone are shown in Appendix D.

5.2.3 Recovery as Liquid Sulphur Dioxide. Sulphur can be economically recovered as liquid sulphur dioxide, provided that the gas flow is continuous with minimal variation in strength and that the sulphur dioxide concentration is the highest possible. In addition, proper consideration should be given to the existence of markets nearby for large quantities of this product.

Physical recovery processes. The gas is first absorbed in water under pressure and then compressed and refrigerated (Figure 15). Because the gas has to be compressed, its sulphur dioxide content is a very important economic factor because of the high energy requirements and costs of compression. Fluid-bed roasters and flash furnace gases are suitable for economical processing by water pressure absorption. Outokumpu flash furnaces can produce off-gases with a sulphur dioxide concentration up to 50 percent and are therefore highly suitable for recovery as liquid sulphur dioxide by physical processes. Clean gases must be thoroughly dried before compression and refrigeration. The only practical and economical drying agent for this purpose is concentrated sulphuric acid. For this reason it is highly desirable to combine sulphur dioxide production by physical recovery processes with a sulphuric acid plant. In such combination the moisture in the smelter gas provides dilution water for the sulphuric acid plant, while the tail gas from the liquid sulphur dioxide plant is processed in the acid plant.

Chemical absorption processes. Sulphur dioxide is chemically absorbed at atmospheric pressure by one of several possible processes. The most commonly used chemical absorbents are ammonium bisulphite and dimethyl aniline (DMA).

The ammonium bisulphite process reportedly recovers about 90 percent of the sulphur dioxide from dilute flue gases, even at concentrations as low as 0.5 percent. Tail gases contain as little as 0.03 percent. A serious disadvantage of this process is that it requires large quantities of ammonia and produces large quantities of ammonium sulphate.

The DMA process is used for recovering sulphur dioxide from smelter gases containing 4 to 10 percent sulphur dioxide. It has been used in several places including the Falconbridge nickel refinery in Norway.

The basic steps of the process are shown in Figure 16. After the gas has been cleaned, sulphur dioxide is absorbed by DMA in a tower which contains an absorption section, a soda scrubber, and an acid scrubber. The loaded DMA solution is stripped in the stripper section of the stripping column. The hot gas leaving the stripper, containing sulphur dioxide and DMA, is cooled in the upper part of the column. DMA is recovered as



FIGURE 15 PHYSICAL RECOVERY PROCESS OF SULPHUR DIOXIDE

water-soluble dimethyl aniline sulphate, while sulphur dioxide leaves from the top of the column ready for liquefaction.

Chemical absorption processes are considerably more expensive in both capital and operating costs than physical recovery processes, but they have the advantage of being applicable to gases of low sulphur dioxide content. They can be expected to extract up to 98 percent of the sulphur dioxide in metallurgical off-gases. Estimates of capital and operating costs to produce liquid sulphur dioxide with both types of processes are shown in Table 11. To make the comparison valid, it is assumed that the gas to be treated has the same sulphur dioxide concentration in both cases. Additional details are given in Appendix D.

TABLE 11COST OF RECOVERING LIQUID SULPHUR DIOXIDE FROM SMELTER
GASES (in \$ Can., 1983)

Production basis: 160 000 tonnes of liquid SO₂ per year.

	Physical Process	Chemical Process		
Capital cost	10 435 000	11 739 000		
Operating cost (\$/tonne SO ₂)	36.78	52.07		



FIGURE 16 PRODUCTION OF LIQUID SULPHUR DIOXIDE BY DMA ABSORPTION

5.2.4 Recovery as Elemental Sulphur. The recovery of sulphur dioxide as elemental sulphur offers several advantages over other recovery methods:

- it is a commercial product that is easily stored;
- it can be transported over long distances with minimal environmental risk; and
- it has the potential for a positive return on the investment.

Several processes have been developed for the conversion of sulphur dioxide to elemental sulphur, the major difference lies in the type of reductant used, which can be natural hydrocarbons, carbon, or hydrogen sulphide.

Outokumpu Oy of Finland has devoted considerable effort in developing and operating a system of commercial scale applicable to copper and nickel flash smelter gases.

In the Outokumpu process, shown in Figure 17, a reductant is added in the flash furnace uptake where a mixture of hydrogen sulphide, carbonyl sulphide, and sulphur dioxide is formed. The mixture is cooled in a boiler, cleaned in an electrostatic precipitator, and then taken through a hot catalytic reactor at 420° to 440°C and a cold catalytic (Claus) reactor at 200° to 220°C. Sulphur condenses at each step. After the last sulphur condenser, the gas stream contains carbonyl sulphide, hydrogen sulphide, and carbon disulphide which are very objectionable air pollutants. They can be oxidized to sulphur dioxide in an incinerator before venting through a stack. Additional fuel is needed for this oxidation. The Outokumpu process is expected to capture 90 to 95 percent of the sulphur dioxide in the feed gas as elemental sulphur. This process has the advantage of being very flexible with respect to the reductant used. The large volumes of toxic gases (H₂S, COS, and CS₂) generated require safety precautions.

Estimates of capital and operating costs to produce elemental sulphur through the Outokumpu process are shown in Table 12. Additional details are given in Appendix D.

TABLE 12COST OF RECOVERING ELEMENTAL SULPHUR FROM SMELTER
GASES (in \$ Can., 1983)

Production basis: (89 000 tonnes of elemental sulphur per year)

Process: Outokumpu

Capital cost	50 500 000
Operating cost (\$/tonne S)	125.05

The first commercial plant based on this process was operated at Kokkola, Finland, in 1962. It was shut down in 1977 because it became unprofitable due to the increasing price of fuel. The process was applied commercially in four other locations.

In Botswana the BCL plant was using coal as reductant. The sulphur plant was operated for only a short period of time; that is, until it was allowed to exhaust the gas without sulphur recovery.

In the USA, the Phelps Dodge plant was designed for light naphta reduction, but it was never put in operation because a demand for sulphuric acid arose in the vicinity during a late stage of plant construction. Thus for economic reasons a sulphuric acid plant was erected and the elemental sulphur plant left idle.

In USSR, the Norilsk plants were commissioned in 1981. They were designed to use coal as reductant but, after one year of operation, cheaper natural gas was used



FIGURE 17 OUTOKUMPU ELEMENTAL SULPHUR PROCESS

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instead. Since 1985, they have been the only Outokumpu-type elemental sulphur plants in operation.

The Outokumpu process could also be used on roaster gases. However, energy would be required to raise the gas temperature to 1350°C for the reduction phase of the process. The gases would then need to be cooled and cleaned before entering the catalytic reactor.

Typical tail gas composition of an elemental sulphur recovery plant like the one operated at Kokkola is shown in Table 13.

TABLE 13	TYPICAL COMPOSITION OF TAIL GAS FROM ELEMENTAL SULPHUR RECOVERY PLANT						PHUR		
Gas	so ₂	S	H ₂ S	CO ₂	СО	COS	H ₂ O	N ₂	02
Vol.(%)	0.6	0.0	0.5	11.7	0.3	0.2	11.9	74.4	0.5
Temp.					1	30°C			

Outokumpu has developed a process alternative for locations where the volume of sulphur products in the tail gas is not environmentally acceptable. It consists of a combination of elemental sulphur and sulphuric acid production where the only tail gas comes out of an acid plant.

A variation of the Outokumpu process, the RESOX process, has been developed by the Foster Wheeler Energy Corporation. This process uses coal for the reduction of sulphur dioxide to sulphur in a steam atmosphere at 500 to 800°C. Indications are that efficiencies up to 75 percent can be achieved in one pass through the reactor and further recovery is possible with an additional Claus-type reactor. The relatively low operating temperatures and the possibility of reducing the off-gases directly, without preliminary cleaning, are advantages that warrant further investigation, if production of elemental sulphur is considered.

5.2.5 Scrubbing of Smelter Gases. One alternative to recovering sulphur dioxide as sulphuric acid, liquid sulphur dioxide, or elemental sulphur is scrubbing it with a slurry or absorbent solution. All gases produced by a smelter can be scrubbed.

A number of systems have been developed and are now operating commercially on off-gases from thermal power stations. These systems, however, are not necessarily directly applicable to non-ferrous smelter gases. Those in use in metallurgical operations are generally treating off-gases with sulphur dioxide concentrations of below 3 percent. Only two such processes are briefly described in this section.

Generally speaking there are two main classifications of scrubbing processes: regenerative and non-regenerative processes.

Regenerative processes. A regenerative process, based on the absorption of sulphur dioxide using an ammonia solution, has been operated by Cominco at Trail, Canada, for several years. It is reported to achieve high efficiencies of sulphur dioxide removal from off-gases over a wide range of sulphur dioxide concentrations, well within those encountered with reverberatory furnaces. Since the absorber is a solution rather than a slurry, neither scaling nor plugging poses problems in the process. The system produces a concentrated sulphur dioxide stream which can be used to produce sulphuric acid, elemental sulphur, or liquid sulphur dioxide. The plant at Trail produces an ammonium sulphate solution, which is used at a fertilizer plant, and a gas containing sulphur dioxide and water vapour goes to an acid plant. The off-gas to the stack reportedly contains 0.1 percent sulphur dioxide. Although the Cominco process has not been used for treating nickel smelter gases, indications are that it would be technically feasible. Capital and operating cost estimates are not available.

For more details, see references 2 and 4.

Non-regenerative processes (lime/limestone scrubbing). The relatively simple process of scrubbing off-gases directly with a lime or limestone slurry, as is done at a number of power plants, has not been widely used with metallurgical gases. A scrubbing system using a mixture of lime and limestone is used by the Onahama Smelting and Refining Company to treat reverberatory furnace gases containing 1.5 to 3.0 percent sulphur dioxide. The process is sufficiently well developed to be generally applicable to the neutralization of gases from reverberatory furnaces. The final product is gypsum. The treated gas, discharged to the atmosphere through a stack, contains 40 to 60 ppm sulphur dioxide. The scrubbing efficiency seems to decrease as the sulphur dioxide content of the gas to be scrubbed increases. In addition, wet limestone scrubbing has reportedly some operating problems and is very costly, particularly because of its high energy consumption. Fixation of up to 99 percent of the input sulphur has been claimed for this type of operation.

A main disadvantage of the limestone process, compared to regenerative processes, is the need for large disposal areas to receive large quantities of waste solids

when gypsum cannot be marketed. Furthermore, leaching from the gypsum impoundment can create environmental problems. No cost data are available.

5.3 Containment of Fugitive Emissions

Fugitive emissions (Table 4), mostly sulphur dioxide and particulate matter, must be contained, if the metallurgical operation is to meet high levels of environmental standards. Fugitive emissions of sulphur dioxide can reach concentrations of up to 200 to 300 ppm, whereas particulate matter may contain heavy metals whose concentration in the working environment is limited by regulations. Containment of fugitive emissions may be carried out with local or general ventilation techniques. Once captured, fugitive emissions may either be routed directly to a control device or combined with other process off-gases prior to treatment in a control device. In many cases they can simply be directed to a stack for dispersion without any further sulphur dioxide or particulate removal. Although the total emission of these pollutants to the atmosphere remains the same, their concentration at ground level near the smelter decreases and ambient air quality improves.

Local ventilation systems consist of hoods or enclosures designed to confine and capture fugitive emissions at the source. There are several considerations to keep in mind when designing a hood, because it must accommodate thermal drafts and other disturbances affecting the source.

General ventilation is normally required when it is not possible or practical to use local exhaust hoods. This may happen when a local hood may handicap the operation, maintenance, or surveillance of a process or equipment, in which case general ventilation would become the preferred method of controlling fugitive emissions. General ventilation has historically been carried out by natural air changes.

An extensive discussion on sources and control of fugitive emissions is contained in reference 3; although the work relates to copper smelting, it is in principle applicable to nickel smelting.

A significant advance in controlling fugitive emissions from converters is represented by the installation of secondary hoods designed to capture pollutants escaping the primary hoods. One system, which reportedly has proven very effective, is that developed by Mitsui Mining and Smelting Co. and used at their smelter at Tamano, Japan. (A schematic diagram of the converter housing system at the Tamano smelter is shown in Figure 18). The primary hood is water-cooled at the top, and the back and sides are radiation-cooled. The secondary hood is designed to contain and remove the emissions



FIGURE 18 CONVERTER HOUSING/AIR CURTAIN SYSTEM AT THE TAMANO SMELTER

that bypass the primary hood. The enclosure consists of swing doors at the front and a movable roof to accommodate the crane cables. When the roof is opened, it activates an air curtain. Emissions during blow, charging, and skimming are therefore contained and eventually vented to the fugitive gas cleaning system. This system captures about 95 percent of the converter gases.

5.4 Containment of Particulate Emissions

Emissions produced during the smelting or roasting of sulphide ores contain a variety of gases, fumes, and particulates. Several cleaning steps are required prior to conversion of sulphur dioxide to sulphuric acid to recover valuable products. These steps are carried out in settling chambers, cyclones, electrostatic precipitators, wet scrubbers, and bag filters, depending upon particle size distribution, total load, temperature, and need to recover and recycle the dust collected.

Figure 19 shows typical collection efficiency curves for several types of devices for particulate removal.



FIGURE 19 TYPICAL COLLECTION EFFICIENCY CURVES FOR SEVERAL TYPES OF PARTICULATE REMOVAL DEVICES (3)

In the nickel and copper industry, settling chambers (balloon flues) are commonly used after reverberatory furnaces and converters, where gas temperatures are high and dust particles comparatively large. Settling chambers may collect up to 50 percent of the total dust loading of the gas system.

Cyclones, like settling chambers, are usually the first set of equipment in a gas cleaning plant. They have higher efficiencies with particles larger than 10 to 15 microns. In smelters where fluidized-bed roasters are used, up to 80 percent of the product leaves the roaster and is collected in a bank of cyclones.

Fabric filters do not have extensive application in the nickel smelting industry, because they have severe limitations at the prevalent operating temperatures and dust loading. They are best suited to dust and fume collection from gas streams containing highly volatile impurities such as lead, zinc, arsenic, and bismuth.

5.5 Dispersion of Pollutants

Dispersion of pollutants, i.e., discharge from a tall stack, has been used to minimize their environmental impact on the immediate vicinity of a smelter. An important feature of the design of a stack is related to defining the necessary conditions for restricting maximum ground level concentrations (GLC) below those specified by control authorities.

Canadian nickel smelters such as those operated by INCO Limited and Falconbridge in Sudbury have developed methods of monitoring and predicting sulphur dioxide concentrations at ground level in the region around the plant. With this information, production levels can be regulated to ensure that the stipulated sulphur dioxide ground level concentration is not exceeded. INCO Ltd. also operates a tall (381 m) stack which increases the transport range and results in enhanced dilution of emissions compared to shorter stacks previously operated. This approach minimizes the impact of stack emissions on the local region because it combines the dilution effect of the tall stack with control of GLC of sulphur dioxide through production cutbacks.

5.6 Approaches to Determine GLC Values

Values of GLCs in the environment around the plants can be determined by two general approaches:

- i) Measurement of sulphur dioxide GLCs using either fixed or mobile monitoring stations with data returned continuously and immediately to the smelter control centre by such data transmission techniques as telemetry.
- ii) Prediction of sulphur dioxide GLCs using meteorological forecasting data, stack emission data, and a mathematical dispersion model.

5.6.1 Direct GLC Measurement Techniques. Sulphur dioxide GLCs can be measured in fixed or mobile monitoring units. The fixed units have the advantage of ease of setup, maintenance, and choice of data transmission (telephone line or radio). The number of fixed stations needed to monitor plume dispersions in all directions and various distances from the smelter could be very expensive. In practice a number of key sites are selected for fixed monitoring. To complement the data, mobile sulphur dioxide monitoring units can operate in the field and track the stack plume and points of impingement. Mobile units suffer problems generally associated with the operation of a monitoring vehicle: vibrational stress on equipment, data transmission from radio shadow zones, and time lost while following the plume. Also, winter conditions and snowy overcast skies make vehicular travel and plume siting difficult and unproductive.

Data from mobile monitors and fixed monitoring stations are used to set stack emission rates when measured sulphur dioxide concentrations approach or exceed the GLC limits. Reductions in smelting throughput are then instituted. Measured data can also be incorporated in a predictive model so that, when sulphur dioxide GLC forecasts exceed limits, plant operations are curtailed.

5.6.2 Prediction Procedure. An alternative to the direct monitoring method of measuring GLCs, is to predict GLCs without the aid of direct GLC measurements. In this case, predicted GLCs and allowable stack emission rates are calculated using measured and forecasted meteorological data, stack emission data, and a plume dispersion model.

Meteorological data collected consists of wind speed, wind direction, and temperature at different heights above ground. Data on upper air conditions are collected using minisondes and radio-tracked balloons which indicate vertical profiles of wind speed, direction, and temperature.

Stack information necessary for the dispersion model consists of gas flow rate, temperature, and sulphur dioxide concentration. With very tall stacks, continuous measurements are sometimes made by sampling at one or two positions that give average stack data based on detailed stack sampling.

Dispersion models are built on experience with a particular site and stack as well as basic plume dispersion mathematics. The dispersion model includes calculation of the following:

- effective stack height,
- stability factor for the local atmospheric condition,

- solar influences such as solar altitude and solar heat input,
- ground level concentrations, and
- time of cutback to comply with GLC limit

5.6.3 Example of Monitoring in the Sudbury Region. The Sudbury region presents a unique example of monitoring by two nickel smelting companies and the Ontario Ministry of the Environment (OME). Figure 20 shows a map of the area referencing the location of sulphur dioxide monitor stations. The operating companies maintain a total of five sulphur dioxide monitors, whereas OME operates about 20, covering an area of 1600 km². INCO Ltd. also operates two mobile sulphur dioxide monitoring vehicles.

Data from the OME stations are processed continuously and the results forwarded to the control centres in the smelters to assist in planning operations and production curtailments, if necessary.

Plume tracking by mobile units. A device called Plume Tracker can be installed in a vehicle for detection of an overhead plume. The unit measures sulphur dioxide in the atmosphere above the vehicle as an integrated column and provides a concentration expressed as ppm of SO_2/m^3 based on ultraviolet absorption. The position of the plume and its dispersion can be mapped out from the measurements. This information is used to position remote sulphur dioxide detection systems and aid in the development of plume modelling.

Remote sulphur dioxide detection and data processing stations. Remote measuring and data transmission technology has advanced to a "second generation" level. Devices are available which, at remote sites, measure sulphur dioxide in ambient air, automatically self-calibrate, adjust the readout for time-dependent changes in the characteristics of the instrument-exciting energy source used to make the measurements, and send data by telephone line or instrumentation cable or by radio telemetry. The instruments in use in the Sudbury region are fluorescent-type analyzers capable of detecting 1 ppb of sulphur dioxide.

Cost of smelter gas dispersal by stacks. The cost of dispersal by tall stacks includes the capital cost and maintenance cost of the stack itself (see Table 14), and any costs associated with monitoring sulphur dioxide levels and cutting back smelter production in adverse weather conditions.



FIGURE 20 SULPHUR DIOXIDE MONITORING STATIONS IN THE SUDBURY AREA

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	Stack Height (m)		
	180	275	365
Erected cost	\$5 300 000	\$9 500 000	\$14 800 000
Maintenance @ 2% per year	\$ 106 000	\$ 190 000	\$296 000

TABLE 14COST OF DISPERSAL BY TALL STACKS (in \$ Can., 1983)

The capital cost of a tall stack varies with location, but the following are current typical order-of-magnitude estimates (in \$ Can., 1983) for a 7.6-m diameter concrete stack with a steel flue.
6 WATER POLLUTION CONTROL

6.1 General

Pyrometallurgical processes are essentially dry, therefore effluents are of minor importance. Liquid waste results from runoff from the smelter yard, bleed streams to control the buildup of impurities in the boiler circuit, solid-liquid separation from gas cleaning equipment, sanitary waters, etc.

When sulphuric acid is produced, the impurities in the process gas are transferred to the liquid effluent produced in the gas cleaning section of the acid plant. The effluent slurry is an acidic solution bearing a variety of heavy metals and as such it requires treatment before disposal.

The level of contaminants in the effluent depends upon the impurities in the concentrate treated and can be in the range listed in Table 15.

6.2 Effluent Treatment

A typical wastewater treatment flowsheet is shown in Figure 21. The effluent is mixed with lime in a neutralization tank to keep the pH high (pH 10 to 11) so that most of the metals precipitate as hydroxides, forming a sludge. The overflow from the thickener is reused in the mill or discharged to the tailings pond, while the sludge is dewatered for ultimate disposal as required by local regulations.

The selection of the levels of pH at which the metal hydroxides are to be precipitated depends upon the composition of the particular wastewater. Wastewater containing aluminum and zinc, for example, would likely justify 2-stage precipitation. Various methods are used to improve solid-liquid separation and the dewatering of hydroxide precipitates. The optimum pH, flocculant type and dosage, and sludge recirculation are determined by bench- or pilot-plant studies.

The final effluent, after pH adjustment, can be expected to contain the concentrations of pollutants listed in Table 16.

The final effluent may be discharged to a tailings pond or to the receiving environment, depending upon its composition and local requirements. The sludge is a mixture of heavy metal hydroxides and gypsum, which is usually impounded in tailings ponds designed to contain them in a manner whereby leaching of heavy metals is prevented. Apparently, at some smelters, the sludge is sent to a refinery for recovery of valuable metallic impurities.

Pollutants	Acid Plant Scrubbers (mg/L)	Cooling Water (mg/L)	Blowdown Slag Granulation (mg/L)	Boiler Blowdown (mg/L)
Chromate	-	0 - 250	-	_
Sulphate	400 - 2 200	500 - 3 000	62 - 310	-
Sulphite	-	-	-	0 - 100
Chloride	-	35 - 160	-	-
Phosphate	-	10 - 50	-	5 - 50
Zinc	0.7 - 14	0 - 30	0.04 - 36	0 - 10
Silica	-	-	-	25 - 80
Arsenic	up to 19	-	up to 6	-
Nickel	up to 0.1	-	0.06 to 0.2	-
Copper	up to 7 600	-	0.05 to 0.1	-
Lead	1 - 9	-	up to 7	-
Alkalinity	-	-	-	50 - 700
Hardness	-	-	-	50 - 500
Total Dissolved				
Solids	0.1 - 15 500	500 - 10 000	30 - 3 800	500 - 3 500
Suspended Solids	1 - 70	0 - 50	7 - 150	-

TABLE 15	TYPICAL RANGE OF POLLUTANTS IN WASTEWATER FROM NICKEL
	SMELTER OPERATIONS

The approximate capital and operating costs of treating the effluents from the three gas cleaning systems mentioned in Chapter 5.2.2 has been estimated as shown in Table 17.

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FIGURE 21 TYPICAL WASTEWATER TREATMENT FOR A NICKEL SMELTER (FLOWSHEET)

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TABLE 16	TYPICAL CONCENTRATION OF POLLUTANTS IN FINAL EFFLUENT
	AFTER LIME NEUTRALIZATION AND SEPARATION OF SOLIDS

Pollutant		Concentration (mg/L)
Arsenic	3	< 1.0
Copper		< 0.5
Lead		< 0.5
Nickel		< 0.5
Zinc		< 1.0
Total Suspended Matter		<25.0

Note: The above concentrations can be lowered by selecting the optimum number of precipitation stages and corresponding levels of pH for the given effluent. Other heavy metals having similarly low solubility in alkaline conditions can also be expected at low concentrations in the final effluent.

TABLE 17APPROXIMATE CAPITAL AND OPERATING COSTS OF WASTEWATER
NEUTRALIZATION AND DISPOSAL (in \$ x 103 Can., 1983)

Sulphuric Acid	Case I		Case II		Case III		
(t/d)	Operatir	ng Capital	Operatir	ng Capital	Operating	Capital	
600	450	560	675	1475	680	1545	
1000	695	690	937	2030	940	2090	
1500	1000	885	1270	2550	1275	2675	

For further reading, see reference (21).

7 REGULATORY CONTROL

7.1 Atmospheric Emissions

Generally speaking, industrial growth has resulted in an increased release of pollutants to the atmosphere and is in need of some control to limit the effects of these pollutants on the workforce inside a plant, the population around it, the vegetation, the cattle, and the property in the surrounding areas. As a result, pollution control instruments have been developed in various countries for the purpose of limiting sitespecific effects.

Nickel smelters are normally covered by the legislation governing non-ferrous metallurgical plants, and therefore are designed to meet the same criteria as those plants producing primary copper, lead, and zinc. Emissions to the atmosphere; that is, outside of the working environment, are usually regulated on the basis of SO_X and particulate matter. Particularly hazardous elements, such as lead, are required to meet certain limits at a boundary point.

In Canada, in the Province of Ontario, where major sulphide smelters operate, they are subject to the limitations listed in Table 18.

A summary of air quality standards affecting sulphur dioxide and particulate matter emissions in the United States, Canada, and the European Community is in Appendix E.

For additional readings, see reference (4).

7.2 Liquid Effluents

No specific regulations apply to liquid effluents from nickel smelters. In each case the smelter has to comply with local requirements.

In Canada, sulphide nickel smelters are considered part of the mining complex and their liquid effluents are subject to the federal mining requirements in addition to any other site-specific requirements imposed by local authorities, particularly where water resources are sensitive to specific contaminants.

A summary of mining effluent regulations in effect in Canada and Japan is shown in Appendix F.

7.3 Solid Wastes

The largest portion of solid waste generated by a nickel smelter is slag, which is usually inert. The environmental protection agencies in the United States and Japan

Contaminant	Concentration (µg/m ³) at Point of Impingement (1/2-h Average)
Arsenic	75
Ammonia	3600
Cadmium	5.0
Carbon Monoxide	6000
Chlorine	300
Copper	100
Dustfall	8000*
Ferric Oxide	75
Fluorides	17.2
Hydrogen Chloride	100
Iron	10
Lead	10
Magnesium Oxide	100
Mercury	5.0
Nickel	5.0
Nickel Carbonyl	1.5
Silver	3.0
Sulphur Dioxide	830
Sulphuric Acid	100
Suspended Particles (<44 microns in size)	100

TABLE 18	AIR POLLUTION CONTROL: GENERAL REGULATION (1984) IN THE
	PROVINCE OF ONTARIO, CANADA

 * Allowed concentration of dustfall at point of impingement (half-hour average): 8000 µg/m².

define a solid waste as being inert when it produces a leachate of a quality as characterized in Table 19, after having undergone specified test procedures:

TABLE 19LEACHATE TESTS

	U.S. EPA Register 261.22 to 261.24	Japan EPA Ordinance 13		
Leach Acid	Acetic (mg/L)	Hydrochloric (mg/L)		
Arsenic Cadmium Chromium	5.0 1.0 5.0	1.5 0.3 1.5		
Lead Mercury Silver	5.0 - 5.0	3.0 0.005		

8 CONSIDERATIONS IN PLANNING NICKEL SMELTERS AND REFINERIES

8.1 Nickel Smelters

8.1.1 Economic Evaluation. In the planning and siting of a nickel smelter, certain economic and social factors can influence the process selected.

Availability of utilities. The smelter must be located on a site preferably near tidewater, serviced by low-cost transportation, and electric power. For example, the current commercial pyrometallurgical processes require between 420 and 520 kWh per dry tonne of concentrate smelted, including electric furnace slag cleaning. Fresh water must also be readily available.

Easy access to markets for sulphur and sulphuric acid. To meet environmental requirements, the smelter must be located within easy access to sulphur markets, primarily those consuming large quantities of sulphuric acid.

The smelter and auxiliary plants require an area in the order of 20 hectares; but additional land, probably another 80 hectares, is required to store solid waste, such as slag, and to impound waste sludge in impermeable ponds. The site should be reasonably flat with stable soil conditions capable of supporting heavy loads. It is important also that the treated effluents from the smelter be allowed to be discharged to some receiving watershed.

8.1.2 Environmental Evaluation. In addition to evaluating the economics of a nickel smelter project, an environmental impact study is necessary and should include:

- A description of the site's environment before the smelter is built, to provide a basis upon which the operations can be monitored once they are on line.
- An evaluation of the environmental impact that the smelter will have after the start-up period.

8.1.3 **Provision of Suitable Working Conditions.** The number of employees working at the smelter complex is a function of both its size and the process selected.

To protect employees, gaseous and particulate emission points must be hooded and vented to a central fugitive gas scrubbing system. Each employee must be provided with a respirator to filter out sulphur dioxide and fine particulates, in addition to the normal safety eye glasses, hard hat, safety shoes, hearing protection, etc. To avoid dermatitis, two changes of work clothes per week must be provided for employees working in the smelter itself. The smelter must include change-house facilities. In particularly hot areas where the work is heavy, such as tapping or skimming the smelting furnace, the workers directly involved in the tasks should be relieved every hour and allowed to rest away from the heat. Where the work is particularly repetitive or very stressful, such as operating a hot-metal crane, rotation of workers every 2 hours is advisable.

Finally, every smelter must be equipped with first-aid facilities capable of treating minor injuries such as burn, heat exhaustion, and similar ailments requiring immediate attention. It should also be equipped with air packs for emergency rescue in the event of an accident.

8.2 Nickel Refineries

8.2.1 Economic Evaluation. The amount of space required, whether 10 or preferably 20 hectares, depends on the extent of auxiliary facilities, such as cobalt and precious metal separation and refining, sulphuric acid recovery, oxygen plant, sodium or ammonium sulphate plant, possible caustic-chlorine plant (if the chloride process is chosen), and hydrogen and ammonia plants (if the Sheritt process chosen). The area required depends also on the storage requirements for raw materials and finished products, which in turn depend on the refinery location in relation to raw material sources and product markets.

There are several options open in planning and siting a nickel refinery: it can be integrated with the smelter, built at a separate location, or integrated with the mine.

Integration with smelter. The location of a refinery close to a smelter can be attractive for technical and economic reasons which include the following:

- A refining process where sulphur is removed from matte by roasting or TBRC converting, the sulphur dioxide gas can be combined with smelter gases, for example, for further processing in a common sulphuric acid plant.
- Refining processes producing revert materials suitable for recycling to the smelter, which is what INCO Ltd. does with sulphide anode scrap and Outokumpu with atmospheric leach residue. The leach residue is resmelted at Outokumpu's Harjavalta smelter before the final pressure leaching step is added.
- Sharing of a number of infrastructures or auxiliary facilities such as offices, laboratory, shops, and in some cases also an oxygen plant,
- Use of byproduct heat from the smelter, such as waste heat from the boiler steam, in the nickel refinery circuit.

Separate refinery location. Most nickel refineries have, however, been established in separate locations, often far from the corresponding smelters. Doing so may have been for one or several of the following reasons:

- Availability of skilled labour and staff. Sophisticated technology is used in nickel refining, requiring accurate control of complex processes.
- Close contact with nickel markets. This was an important consideration in choosing the Port Colborne and Kristiansand refinery sites.
- Sources of inexpensive energy. Nickel refining requires considerable amounts of energy, either as electric power for electrolytic processes, or as natural gas or fuel oil for hydrogen reduction and carbonyl processes. Availability of cheap electric power was also a major factor in choosing the Port Colborne and Kristiansand refinery sites, while availability of cheap natural gas was important in the choice of Fort Saskatchewan as a refinery site.
- Flexible access to raw materials sources. Refineries on tidewater, such as Niihama in Japan (Sumitomo) and Kristiansand in Norway (Falconbridge), refine mattes from various overseas locations, in addition to matte from their own smelter.
- Proximity of markets for bulky sulphur byproducts (ammonium sulphate, sodium sulphate, or sulphuric acid) is desirable for some refining processes, but often difficult to achieve.

Integration with mine. The only refining process that produces a large amount of residue is the Sherritt Gordon ammonia leach process which is applied directly to nickel concentrates. For this process, which for economic reasons is limited to nickel ores with a low precious metal content, it could be advantageous to locate the plant close to the mine:

- to avoid freight on an amount of concentrate which is typically five times that of the corresponding matte, and
- because the leach residue could be discharged to a mill tailings pond where the tailings would dilute pollutants and improve settling characteristics.

On the other hand, mine sites are usually remote from the markets for the large amount of byproduct (ammonium sulphate for fertilizer), which is typically ten times the amount of nickel produced.

The two existing Sherritt ammonia leach nickel refineries have not been located close to the supplying mines. Instead, locations have been chosen where ammonia

can be obtained or produced economically and then, after the refining processes, readily shipped to markets for ammonium sulphate. These locations also provide an established infrastructure and human resources from existing communities.

8.2.2 Environmental Evaluation. The Sherritt ammonia leach process for direct treatment of nickel concentrates produces a large amount of leach residue requiring tight ponding. To provide an adequate residue disposal area, such a plant requires a much-larger site, say, twice the area needed for a matter effinery of similar nickel production capacity.

Potential gaseous emissions to the working areas and outside atmosphere include - depending on the selected nickel refining process - sulphur dioxide, ammonia, hydrogen sulphide, chlorine, vapours from organic solvents, hydrogen, carbon monoxide, and nickel carbonyl. With adequate plant design, equipment selection, gas scrubbing, conscientious maintenance, and ventilation, these emissions can be controlled to acceptable limits.

Amounts of solid wastes from matte refining are very small, since practically all matte components are usually recovered (nickel, copper, cobalt, sulphur, selenium, precious metals, etc.). A little iron and arsenic, as well as very small amounts of lead and zinc, which may correspond to 1 to 3 percent of the produced nickel must, however, be removed and safely discharged to waste; unless they can be recycled to a nickel smelter as INCO Ltd. did at Port Colborne.

Most nickel refining processes require substantial amounts of alkali (NaOH or NH₃) and acid (H₂SO₄ or HCl) as reagents. To control buildup of the resulting soluble salts in the circulating solution, it is necessary to bleed the barren solution (i.e. a solution from which all nickel and other heavy metals have been completely removed) containing ammonium or sodium sulphate from a sulphate solution system, or sodium chloride from a chloride solution system. These salt solutions cannot always be discharged to nature or to the sewer system. Ammonium and sodium sulphates from the Sherritt and Outokumpu processes are therefore recovered and, if possible, marketed. The Falconbridge nickel refinery produces a sodium chloride solution, which at Kristiansand can be discharged to the sea. The use of a chloride refining process at an inland location could, however, present a disposal problem regarding the bleed solution.

All these factors must be properly evaluated when an environmental impact study of a nickel refinery is carried out to provide the design and operating basis for such a plant.

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8.2.3 Provision of Suitable Working Conditions. Any nickel refinery requires the usual first-aid facilities, must provide gas masks with filters for ammonia, chlorine, etc. as required for the particular refining process chosen. Suitable clothing, gloves and boots or shoes must, of course, be provided, especially where electric shock hazards exist in electrolytic refining areas.

Special safety precautions are also required in pressure operation areas, including autoclaves with auxiliary equipment. Precautions are especially required when handling those gases, such as hydrogen, that under pressure form explosive mixtures with air. Special safety systems are required for the carbonyl refining process because of the extreme toxicity of nickel carbonyl vapour and, to a lesser extent, that of carbon monoxide.

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9 RETROFITTING OF OLD SMELTERS

In principle, to achieve ideal containment, all sulphur in concentrates should either be recovered in the form of marketable sulphur products, or be fixed in inert products such as slag and gypsum.

In practice, there are many practical and economic limitations and the degree of sulphur containment which can actually be achieved may be less than the ideal. How much can or should be done depends on the circumstances which vary greatly from case to case.

Demand for sulphur containment has existed for a long time, particularly where crop damage was being caused by sulphur dioxide or where densely populated areas were situated downwind from smelters. Some non-ferrous smelters discharged sulphurous gases to the atmosphere through stacks, and atmospheric discharge was an accepted practice in remote and often arid locations with little or no vegetation of economic value.

Under these conditions there was little incentive for sulphur containment, and plants were designed to meet the accepted standard of the time. Older smelters are typically equipped with the technology of the time, such as multi-hearth roasters, reverberatory furnaces, and converters with hood design allowing in-leakage. All this equipment produces low-grade sulphur dioxide gases unsuitable for processing to sulphur products.

These older smelters can be modernized for improved sulphur containment. Fluid-bed roasters can replace multi-hearth, flash smelting furnaces can replace reverberatory furnaces, tighter hoods can be installed on old converters. Such extensive remodelling can be expensive because changes may be required to the smelter building and auxiliary facilities. All of these are in addition to the sulphur fixation plant, by-product handling, storage, shipping, and other operations appropriate to the specific case.

Even in cases of extensive remodelling of an old smelter, 20 to 30 percent of the sulphur in the concentrate ends up in the converters from where it will be released either as low-grade off-gases difficult to treat or as fugitive emissions difficult to capture.

In summary, whether an old smelter should be modernized depends upon the amount of sulphur to be contained, the type of remodelling required, its cost, the availability of a market for by-products, and other similar considerations specific to the smelter.

With new smelters, the requirement for sulphur containment alters the criteria for optimum smelter location, and the lack of markets for sulphur products within economic shipping distance can be a serious limitation. Concentrates are transported over great distances and do not require special railway tank cars or special ships which must return empty from each trip which is the case with sulphuric acid or liquid sulphur dioxide transport.

10 SUMMARY AND CONCLUSIONS

The production of nickel through the pyrometallurgy and refining processes of sulphide ores presents potential hazards to human health and to the environment.

10.1 Release of Pollutants

Liquid effluents from pyrometallurgical processes are of minor importance, because these processes are essentially dry. A large amount of waste, however, is solid, primarily discarded nickel slag, which is considered inert.

The most significant release of pollutants in the pyrometallurgy of sulphide ores is related to the atmospheric emissions of sulphur dioxide and particulates containing heavy metals. These can be categorized as either process or fugitive emissions. Sulphur dioxide is formed during the combustion process inside various types of equipment used to obtain a product increasingly richer in nickel.

Exhaust gases from older types of equipment, such as multiple hearth furnaces, reverberatory furnaces, and open-hood converters, contain sulphur dioxide in concentrations too low for practical recovery. Exhaust gases from newer types of equipment, such as fluid-bed rosters, flash furnaces, and tight-hood converters, however, contain sulphur dioxide in concentrations sufficiently high for practical recovery. The atmospheric release of particulate material occurs in conjunction with sulphur dioxide emissions and in the handling and transferring of feed materials.

Some sulphur dioxide reacts with water vapour in the atmosphere to form sulphuric acid and as such precipitates to earth. Some reacts with ammonia and other compounds in the air to produce sulphates that fall to earth as dry fallout or deposition. Atmospheric emissions from nickel smelting may be carried over long distances by wind, resulting in the phenomenon commonly known as long-range transport of airborne pollutants.

Nickel refining is an operation generally considered separate from the extractive process. Often the two plants are long distances apart. Nickel can be refined by several processes, and some of them are used in different combinations.

With some exception, such as the nickel carbonyl process, the release of fallouts and the environmental problems associated with nickel refining are common to other chemical processes handling chlorine, hydrogen sulphide, ammonia, hydrogen, and other hazardous materials.

10.2 Effects of Pollutants

Effects on soils, vegetation, wildlife, and man-made structures by acidic deposition have been documented.

The aquatic environment is susceptible to damage from acid precipitation and accumulation of heavy metals.

Workers in nickel smelters and refineries are exposed to sources of potential physical and chemical hazards.

Indirect health effects can arise from acidic deposition through the contamination of the food chain.

10.3 Measures of Pollution Abatement

Measures of pollution abatement call for the control of emissions during processing or their dispersion, and the treatment of wastewater.

10.3.1 Control of Sulphur Dioxide. Only a few practical and proven approaches can be considered to reduce the sulphur dioxide emissions from a smelter. These are

- separation of high-sulphur minerals in the ore,
- oxidation to sulphuric acid,
- recovery as liquid sulphur dioxide,
- reduction to elemental sulphur,
- scrubbing of exhaust gases, and
- recovery as a discard product.

The separation of pyrrhotite from the concentrate feed to the smelter could be the most economical means of sulphur dioxide control. It should be the first option considered. Pyrrhotite rejection is widely and successfully practised at Canadian smelters. Its economics should be carefully considered because it becomes less attractive with the increase in the percentage of pyrrhotite rejected.

The production of sulphuric acid from sulphur dioxide generated during the roasting and smelting of nickel ores has become a well accepted method of controlling atmospheric emissions from nickel smelters.

The main disadvantage of sulphuric acid production from smelter gases is that the feed gas contains several impurities which, if not removed upstream of the acid plant, plug or poison its catalyst.

The cost of producing sulphuric acid from smelter gases has been well researched and defined. The major factor in the economics of sulphuric acid production

from smelters gases is the existence of readily accessible markets for it. When the marketing of sulphuric acid is neither practical nor economical because of either distance to markets or market saturation, the excess acid or the total production could be neutralized. The estimated capital and operating expenses of this operation can be substantial.

When the sulphur dioxide in exhaust gases is highly concentrated, it can be liquified. This operation can be economically attractive, provided there are markets nearby for the amounts produced.

The reduction of sulphur dioxide to elemental sulphur is attractive because it produces a commodity which can be easily stored, transported over long distances with minimal environmental risk, and has the potential for a positive return on investment. Several processes were investigated over the years in pilot plants, but only a few commercial plants have been operated for some time. The most recent developments in this area are directed towards processes which operate at lower than usual temperatures.

All gases produced in a smelter can be scrubbed with an absorbent solution. Capital and operating costs of this solution for nickel smelter gases are not available.

10.3.2 Control of Particulates. Particulate emissions from roasting and smelting operations can be contained with traditional physical and chemical operations.

When producing sulphuric acid from smelter gases, more than 99 percent of the particulate matter in the gas feed to the acid plant is removed during the gas cleaning step.

10.3.3 Control of Fugitive Emissions. Fugitive emissions can be removed from the working environment with local or general ventilation techniques. Once captured, fugitive emissions can be routed directly to a control device, combined with other exhaust gases for treatment, or directed to a stack for dispersion.

10.3.4 Dispersion of Pollutants. Dispersion of pollutants from a tall stack has been used to minimize their environmental impact in the immediate vicinity of a smelter.

Methods have been developed to monitor and predict the concentration of sulphur dioxide at ground level in the region around a nickel smelter. With this approach production levels can be controlled to maintain the sulphur dioxide concentrations below a desired level.

10.3.5 Treatment of Wastewaters. In a nickel smelter, wastewaters result from surface run-off, bleed steams, sanitary waters, and where sulphuric acid is produced, from the gas cleaning section of the plant. The wastewaters may contain various heavy metals. The typical treatment uses neutralization and clarification processes.

Typical capital and operating costs to control the wastewater generated in a gas cleaning facility have been researched and estimated.

10.4 Measures to Protect the Working Environment

Methods to protect the workers are available. They range from engineering measures within the plant to the provision of personal protective equipment and administrative measures to minimize exposure. The monitoring of the work environment, medical surveillance, training, and supervision are important to check the effectiveness of control measures.

10.5 Planning and Siting of Nickel Smelters

Economic and social factors should influence the planning and siting of a nickel smelter. The accessibility of sulphur markets, primarily those consuming large quantities of sulphuric acid should be an important consideration to meet environmental requirements.

Before the smelter is built, an environmental impact study is also necessary to evaluate the environment of the site, and to provide a basis upon which the operations can be monitored once they are on line. Appropriate measures should be adopted to protect the employees from chemical and physical hazards.

There are several options open in the planning and siting of a nickel refinery: it can be integrated with the smelter, built at a separate location, or integrated with the mine.

10.6 Use of Modern Technology

Ideally, all sulphur in concentrates should be recovered as marketable sulphur products or fixed as inert slag or gypsum.

In practice, there are many limitations to the amount of sulphur that can be contained. A major limitation could be the technology currently in use at a smelter. Traditionally used equipment, such as multi-hearth roasters, reverberatory furnaces, and open-hood converters can be replaced with more modern equipment producing exhaust gases of a quality suitable for processing to sulphur products. The modernization of an older smelter depends upon several factors; the most important ones are:

- the degree of protection required for the employees, the vicinity of that smelter, and the environment (water, land, air, etc.) affected by its waste disposal practices;
- the cost of the containment practices chosen; and
- the availability of a market for the by-products generated.

The means of controlling human health and environmental hazards associated with nickel production and refining from sulphide ores are therefore highly dependent on factors specific to the location and will differ from place to place.

The optimum solution for any given smelter may be a combination of any of the technologies and practices described in the previous chapters.

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APPENDIX A

WORLD PRODUCERS OF NICKEL

WORLD PRODUCERS OF NICKEL

	Company			Capacity (Tonnes/Year of Nickel)				
Country		Type of Feed	f Process Used	Ni Metal	Ni Oxide	FeNi	Matte	Others
Type of feed S = Sulphide ore L = Laterite ore SM = Sulphide ma LM = Laterite ma NiO = Nickel oxid	tte tte e	Pro MS HN EM FS VM	ocess used = Matte sr 1 = Hydrom 1 = Electror = Ferrosme 1 = Vaporme	nelting etallurgy netallurgy elting etallurgy				
AFRICA								
Bophuthatswana	Impala Platinum Holdings Ltd.	S	MS, HM	10 000				(NiCo)S
Botswana	BCL Ltd.	S	MS				48 000	
South Africa	Impala Platinum Ltd. Matthey Rustenburg Refiners	SM	НМ	12 000			15.000	
	Ltd.	5	MS, EM	19 000			15 000	
<i></i>	Western Platinum Ltd.	5	MS	10.000			3 800	
Zimbabwe	BSR Ltd.	2	MS, EM	12 000				
	Empress Nickel Mining Co. Ltd.	5	MS, EM	5 000ª				
ASIA								
China	Jinchuan Non-Ferrous Metals Co.	S	MS, HM	20 000				
	Talent Metal Corp.	S	MS		7 000 ^b			
Indonesia	PT Aneka Tambang	L	FS			5 000)	
	PT INCO	L	MS				36 000	
Japan	Nippon Mining – Hitachi - Saganoseki	LM L	EM FS	3 300		16 000)	

	Company	Type of Feed	Process Used	Capacity (Tonnes/Year of Nickel)				
Country				Ni Metal	Ni Oxide	FeNi	Matte	Others
ASIA (Cont'd)								
	Nippon Nickel	LM	MS		7 000			
	Nippon Yakim Kogyo Co. Ltd. - Oeyama	L	FS			10 000		
	- Toyama	L	FS			5 000 ^C	:	
	Pacıfic Metals Co. Ltd.	L	FS			25 000		
	Shimura Kako Co. Ltd.	LM	FS			7 0000	I	
	Sumtomo Metal Mining Co. - Hyuga	L	FS			18 000 ^e	:	
	- Niihama	LM	ЕМ	23 000				Oxide, Sulphate, Chloride
	Tokyo Nickel	L	MS		12 000			
Philippines	Marinduque Mining Corp.	L	НМ	28 000				3 000 (NiCO)S
AUSTRALASIA								
Australia	Queensland Nickel Ply Ltd. Western Mining Corp.	L	НМ		21 000			2 500 (NiC)S
	- Kalgoorlie	S	MS				66 000	
	- Kwinana	SM	НМ	30 000				
New Caledonia	Société Métallurgique Le Nickel	L	FS			46 000		
			MS				16 000	

	Company				ear of Nicke	1)		
Country		Type of Feed	Process Used	Ni Metal	Ni Oxide	FeNi	Matte	Others
CENTRAL SOUTH	AMERICA	- 1		<u> </u>		- k A - k	· · · · · · · · · · · · · · · · · · ·	
Brazil	CIA Niquel Tolantins	L	MS, EM	7 000				
	Codemin	L	FS			7 000		
	Morro do Niquel	L	FS			3 000		
Colombia	Cerro Matoso, S.A.	L	FS			23 000		
Cuba	Cubaniquel - Nicaro	L	НМ		23 000			
	- Moa Bay	L	НМ					24 000 (NiCo)S
	- Punta Gorda	L	НМ		3 000 ^f			
Domican Republic	Falconbridge Dominia C por A	L	FS			3 000		
Guatemala	Exploraciones Y Explotaciones Mineras Izabal S.A. (Eximbal)	L	MS				13 0008	Ş
EUROPE								
Albania		L	MS					5 000, matte, Ni metal, salts
Austria	Treibacher Chemische Werke A.G.	?	?					4 000h
Czechoslavakia	Niklova Huta	L	НМ	4 000				Salts
East Germany	V.E.B. Nickelhutte Ave	L	HM	1 000				
	V.E.B. Nickelhutte St-Egidien	L	FS		Briquettes	3 000		
	V.E.B. Ferrolegierungswerk Lippendorf	L	FS			3 000		

	Company			Capacity (Tonnes/Year of Nickel)				
Country		Type of Feed	Process Used	Ni Metal	Ni Oxide	FeNi	Matte	Others
EUROPE (Cont'd)								
Finland	Outokumpo Oy	S	MS, EM	16 500				
France	Société Métallurgie Le Nickel	LM	НМ	16 000				Salts
Greece	Larco	L	FS			3 000		
Norway	Falconbridge Nikkelverk A/S	SM	Em	45 000				
Poland	Huta Miedzi (Glogow)							2000 Salts
United Kingdom	INCO Europe Ltd.	NiO	VM	54 000				Ni-Co Salts
USSR	Norilsk Combine - Nadezdha	S	MS				50 000	Cu-Ni-Co
	- Norilsk	S	MS, Em	100 000				
	Severopnickel - Monchegorsk	SM	ЕМ	25 000				
	- Pechenga	S	MS, EM					
	Youjouralnickel - Verkni	L	MS, Em	25 000				
	Ovfalei							
	- Orsk	L	MS, EM					
	- Rezk	L	MS, EM					
	- Pobuzh	L	FS			10 000		
Yugoslavia	Kavadarci	L	FS			28 000		
	Kosovo	L	FS			5 300		

Country	Company	Type of Feed	Process Used	Capacity (Tonnes/Year of Nickel)				
				Ni Metal	Ni Oxide	FeNi	Matte	Others
NORTH AMERIC	<u>CA</u>							
Canada	Falconbridge Ltd.	S	MS				45 000	
	INCO Ltd Sudbury	S	MS		65 000			
			MS, VM	57 000				Salts
	- Port Colborne	NiO	ЕМ	25 000				Cobalt
	- Thompson	S	MS, EM	55 000				
	Sherritt Gordon Mines Ltd.	S	НМ	21 000				Fertilizer
United States	Amax Nickel Division, Amax Inc.	SM	НМ	36 000				
	Hanna Nickel Smelting Co.	L	FS			10 000		
				649 800	165 000	2 843 000	2 928 000	

Nickel Products / Capacity

a Closed in 1984

- b In 1984
- c Closed in 1982
- d Closed in 1983
- e Capacity reduced to 9 000 tonnes with the closure of one furnace in 1983
- f In 1986
- g Closed in 1984
- h Primary and secondary smelting
- i About 1984
- j Closed in 1984
- k Final capacity of the project is 12 000 tonnes

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APPENDIX B

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DESCRIPTION OF NICKEL REFINING PROCESSES

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B.1 INCO Ltd. Nickel Sulphide Anode Refining Process

This process (Figure 22) is used in Canada by INCO Limited at its plant in Thompson, Manitoba, and until recently at its plant in Port Colborne, Ontario.



FIGURE 22 INCO LTD. NICKEL SULPHIDE ANODE REFINING PROCESS

Molten nickel matte with a controlled sulphur content is cast into anodes. At Thompson the molten matte comes directly from the smelter converters. The matte anodes are electro-refined to pure nickel cathodes in diaphragm cells.

The impure solution arising from anode dissolution is purified by removing copper, cobalt, and other impurities before recycling it as a pure nickel solution to the cathode compartments of electrolytic cells. The pure nickel cathodes are cut to suitable size and marketed.

Slimes, consisting mostly of elemental sulphur but also containing precious metals, residual nickel sulphide, and various impurities, are deposited from the sulphide anodes at the cell bottom. These slimes are collected and heated to melt the sulphur which is then separated from the precious-metal residue by hot filtration.

Application of this process is limited to nickel mattes with low copper content, such as those produced at Thompson. Otherwise, matte separation is required, which means the nickel sulphide must be remelted before casting it into anodes, as was done at Port Colborne.

B.2 Falconbridge Matte Chlorine Leach Process

This process (Figure 23) is used by Falconbridge at Kristiansand, Norway. A similar process is used by Société de Nickel in France for refining matte produced from lateritic nickel ore from New Caledonia.



FIGURE 23 FALCONBRIDGE MATTE CHLORINE LEACH PROCESS

Nickel-copper matte is leached in a chloride solution with chlorine gas; both solution and chlorine are recycled from the nickel electrowinning cells. The 2-stage chlorine leach produces an almost copper-free nickel chloride solution, leaving a copper sulphide residue.

The nickel chloride solution is purified by removing iron, arsenic, cobalt, and residual copper, before being fed to electrowinning cells equipped with insoluble titanium wire mesh anodes coated with a noble metal oxide. High-purity nickel cathodes are deposited, while chlorine gas is emitted at the anodes, which are hooded to collect the gas for recycling.

The copper sulphide residue is roasted, and the resulting calcine leached with sulphuric acid in the form of spent copper electrolyte. The roaster gas is processed to liquid SO_2 or sulphuric acid. Copper is recovered from the copper sulphate leach solution by electrowinning with lead anodes.

The residue from copper leaching contains the precious metals and a substantial amount of nickel which is removed before the enriched residue is processed in the precious metals refinery.

B.3 Outokumpu Sulphate Leach Process

This is a comparatively simple process (Figure 24) which has been applied successfully on a small scale. In addition to Outokumpu's own plant at Harjavalta in Finland, this process has been adopted for comparatively small nickel refineries in Zimbabwe and Brazil. In Brazil, this process is being applied to lateritic nickel ore.

Ground nickel matte is leached at atmospheric pressure in two or more stages with recycled, spent copper sulphate and nickel sulphate electrolytes. The first-stage leach produces an almost copper-free nickel sulphate solution which is purified before being fed to diaphragm cells where nickel cathodes of high purity are deposited. The electrowinning cells are equipped with insoluble lead anodes.

The copper-rich solution from the second or further stages is fed to electrowinning cells where copper is deposited as an impure copper powder requiring further processing at a copper smelter or refinery.

Residue from the last atmospheric leach stage contains precious metals and residual nickel and copper sulphides. The precious metals are further concentrated by dissolving the nickel through pressure leaching with air or oxygen, before shipment to a precious metals refinery.



FIGURE 24 OUTOKUMPU SULPHATE LEACH PROCESS

B.4 Sulphuric Acid Pressure Leaching

Sherritt Gordon developed acid pressure leaching (Figure 25) to avoid dissolution of platinum group metals such as those occurring when its ammonia leaching process is applied to matte. Acid pressure leach was adopted for refining of platinum-rich matte by Impala in South Africa.

Ground nickel-copper matte is pressure-leached with air or oxygen in two stages. The first stage yields an almost copper-free nickel solution which is neutralized with ammonia and purified for recovery of nickel by reduction with hydrogen at high temperature and pressure. The precipitated nickel powder is further processed for marketing as sintered briquettes. The spent solution from hydrogen reduction contains



FIGURE 25 SULPHURIC ACID PRESSURE LEACHING

cobalt and residual nickel, which are precipitated as a mixed sulphide for shipment to a cobalt refinery. Ammonium sulphate is then recovered from the metal-free solution by evaporation and crystallization and marketed as fertilizer.

First-stage leach residue with a high copper sulphide content is releached, yielding a copper sulphate solution from which cathode copper is recovered by electrowinning. The second-stage leach residue is sent to a precious-metal refinery.

The Rustenburg nickel-copper refinery in South Africa uses a similar leaching process but recovers refined nickel by electrowinning instead of hydrogen reduction. It therefore produces sodium sulphate as a by-product, instead of ammonium sulphate.
B.5 INCO Ltd. Pressure Carbonyl Process

INCO Limited uses the carbonyl process (Figure 26) for refining nickel at Copper Cliff in Canada and at Clydach in Wales. It is a unique and very selective vapometallurgical process based on the volatility of nickel carbonyl, a very toxic compound of nickel and carbon monoxide. The process requires very special equipment and operating conditions, as well as sophisticated safety control systems.



FIGURE 26 INCO LTD. PRESSURE CARBONYL PROCESS

Only in metallic form does nickel react with carbon monoxide. Nickel matte must therefore be extensively desulphurized prior to carbonylization. This is done with oxygen at high temperature in a top-blown rotary converter (TBRC). The metallized matte is granulated and treated with carbon monoxide gas in pressure reactors. The resulting crude nickel carbonyl gas is condensed and purified by fractional distillation. The purified nickel carbonyl vapour is then decomposed to yield nickel pellets or powder of high purity and carbon monoxide gas for recycling to carbonylization. The main volatilized impurity is iron, which is removed as an iron-nickel powder for which a market exists.

The carbonylization residue contains cobalt, copper, precious metals, and sulphur in the matte, and therefore requires further complicated processing to separate and recover these elements.

B.6 INCO Ltd. Matte Separation Process - Production of Nickel Oxide and Incomet

INCO Ltd. developed this pyrometallurgical approach as an alternative to nickel refining processes for the purpose of producing, at lower cost, nickel products of lower purity than refined nickel, but which still satisfy quality requirements for less exacting nickel markets.

B.6.1 Matte Separation. A sulphur-deficient nickel-copper matte is cast in large blocks that are slowly cooled under controlled conditions to obtain separable crystals of nickel sulphide, copper sulphide, and a metallic fraction in which the precious metals, in particular the platinum group metals, collect.

The cooled matte is crushed, finely ground, and separated by a combination of flotation and magnetic separation steps into the following fractions:

 A nickel sulphide concentrate which can be further processed to nickel oxide or Incomet, as INCO Ltd. does at Copper Cliff (Figure 27), or electrolytically refined as done in the Soviet Union.

There is a similar nickel oxide plant in Japan.

- b) A copper sulphide concentrate for further smelting and refining to electrolytic copper.
- c) A metallic nickel-precious metals concentrate for further processing by nickel refining followed by recovery and separation of the precious metals.

Matte separation plants are operated at Copper Cliff in Canada by INCO Ltd., and at three locations in the Soviet Union.

B.6.2 Nickel Oxide. Matte separation nickel sulphide is sinter-roasted to an impure nickel oxide product. Originally this was done on a travelling-grate sinter machine, but now nickel sulphide micropellets are roasted in fluid-bed roasters to a granular product. In part, this is sold as Nickel Oxide 75 for nickel applications with low-purity requirements; the remainder is further processed as described next.



FIGURE 27 INCO LTD. NICKEL-COPPER MATTE SEPARATION PROCESS

B.6.3 Purified and Metallized Products from Nickel Oxide. Copper and other impurities forming volatile chlorides are removed from the nickel oxide granules by chlorination at high temperature in a fluid-bed reactor.

To increase nickel content and density of the product, the purified nickel oxide granules are reduced with hydrogen. This step is also carried out in a fluid-bed reactor and yields a metallized product with 96 percent nickel or more, sold by INCO Ltd. as Incomet. This product is not as pure as refined nickel but nevertheless suitable for a significant proportion of the nickel market.

B.7 Sherritt Gordon Ammonia Leach Process

The Sherritt Gordon ammonia leach process (Figure 28) was developed to recover nickel, copper, and cobalt directly from sulphide concentrates by hydrometallurgical means, thereby bypassing the smelting operation and thus the environmental problems connected with smelting, particularly SO₂ emissions.





Application of the Sherritt process is, however, limited to nickel concentrates with a low content of precious metals, since these are left highly diluted in a large mass of leach residue from which they are not economically recoverable. The nickel concentrates should also have a fairly low copper content, since copper is recovered as an impure sulphide product which must be returned to a copper smelter. Most nickel sulphide concentrates do, however, contain economically significant levels of precious metals and copper.

Application of the Sherritt process to this type of feed material is currently limited to two plants, Sherritt Gordon Mines Ltd.'s refinery in Fort Saskatchewan in Canada, and Western Mining Corporation's Kwinana refinery in Australia - both important nickel producers.

The nickel sulphide concentrate is pressure-leached in two countercurrent stages with air and ammonia. The leach residue is separated from the resulting slurry by settling and filtration, washed and disposed of to a tailing pond.

The solution, containing nickel, copper, and cobalt as complex ammine sulphate compounds, is purified in several steps. First, copper is precipitated as an impure copper sulphide by removing excess ammonia and, if necessary, adding hydrogen sulphide or another sulphidizing agent.

The copper-free solution still contains unsaturated sulphur compounds (thionates and thiosulphate) and ammonium sulphamate. Unsaturated sulphur compounds cause sulphur contamination of the nickel product, whereas sulphamate is a plant poison (herbicide) which must be avoided in ammonium sulphate fertilizer. These compounds are removed by oxidation to sulphate with air at high temperature and pressure.

Nickel is recovered from the purified solution by reduction with hydrogen at high temperature and pressure. The precipitated nickel powder is further processed for marketing as sintered briquettes. The spent solution from hydrogen reduction contains cobalt and residual nickel, which are precipitated with hydrogen sulphide as a mixed sulphide for shipment to a cobalt refinery.

Ammonium sulphate is then recovered from the metal-free solution by evaporation and crystallization and marketed as fertilizer.

APPENDIX C

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OCCUPATIONAL EXPOSURE CRITERIA FOR SULPHUR DIOXIDE AND NICKEL

	TWA*		STEL**		
	(ppm)	(mg/m ³)	(ppm)	(mg/m ³)	
Australia	5	13			
Belgium	5	13			
Bulgaria		10			
Canada, Ontario	2	5	(5)	(10)	
Finland	5	13			
Germany (East)	5	13			
Germany (West)		10		30	
Italy	7	10			
Japan	5	13			
Norway					
Netherlands	5	13			
Poland		10			
Romania	10			15 (max.)	
Sweden	2	5			
Switzerland	5	13			
USSR		10			
USA (NIOSH/OSHA)	5	13			
ACGIH	2	5	(5)	(10)	
Yugoslavia	4	10			

TABLE 20	OCCUPATIONAL EXPOSURE CRITERIA FOR SULPHUR DIOXIDE (International Labour Office, 1980)

* TWA = Time-weighted average exposure limits.
** STEL = Short-term exposure limit.

TABLE 21 OCCUPATIONAL EXPOSURE CRITERIA FOR NICKEL AND NICKEL COMPOUNDS (International Labour Office, 1980)

1. Airborne Exposure Limits

		Nickel Met and Insolub Compounds	al le 5 (as Nı)	Nickel Solu Compounds (as Ni)	ıble s	Nickel Carbonyl as Ni					
		TWA* (mg/m ³)	STEL** (mg/m ³)	TWA* (mg/m ³)	STEL** (mg/m ³)	TWA* (ppm)	(mg/m ³)	STEL** (ppm)	(mg/m ³)	Guideline or Regulation	Date of Issue
Australı	a			0.1		0.05	0.35			G	1978
Belgium				0.1		0.5	0.35			G	1978
Bulgaria		0.5								R	1971
Canada	- Ontario	1.0		0.1	0.3		0.1			G	1981
	- Alberta	1.0	2.0 3.0 (NIS)	0.1	0.3	0.05	0.34	0.15	1.0	R	1982
Finland	1.0					0.001	0.007			G	1975
Germany	(East)	0.5	1.0							R	1977
Germany	/ (West					0.1C	0.7			G	1979
Italy		1.0		0.1		0.001C	0.007			G	1978
Japan		1.0				0.001	0.007			G	1978
Norway		0.1C		0.1C			0.007C			G	1982
Netherla	ands	1.0		0.1		0.05	0.35			G	1978
Poland							0.007			R	1976
Romania	1			0.5	1.5	0.002			0.005	R	1975
Sweden		0.5 ^C (0.01 ^{Cl})		0.1		0.001 ^C				G	1978
Switzerl	and	1.0				0.5	0.35			R	1978
USSR		0.5		0.005			0.0005			R	1977
U.S.A.	NIOSH	0.015		0.015		0.001	0.007			G	1977
	OSHA	1.0		1.0		0.001	0.007			R	1972/1978 Ni (CO) (1985 same)
	ACGIH	1.0Cl		0.1	0.3	0.05	0.35			G	1985
			3.0 (NiS)								
Yugoslav	/ia			0.5		0.001	0.007			R	1971

Time-weighted average exposure limit
 Short-term exposure limit
 C = Classed as carcinogen; Cl = NiS classed as carcinogen

APPENDIX D

COST ANALYSES

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APPENDIX D

D.1 Gas Cleaning

In a study sponsored by Environment Canada (9), the generic performance of smelter gas scrubbing operations, effluent treatment, capital and operating costs were reviewed.

Three concentrates Cases I, II, and III, containing a range of quantities of contaminants where assumed to be processed in a flash furnace/Pierce-Smith converter operation.

				Other Elem	ients in Sa	mple		
	A	Assay Wt. (%)				Assay (ppr	n)	
	Zn	Pb	As	Hg	Se	Cd	Cl	F
Case I	0.17	0.05	0.001	0.05	40.0	-	200.0	80.0
Case II	4.0	1.7	0.09	1.0	700.0	-	200.0	100.0
Case III	4.0	6.0	0.1	100.0	1000.0	100.0	200.0	200.0

The following quantities of contaminants were assumed:

The assumptions where based on a hypothetical chalcopyrite-pyrrhotite and arsenopyrite feed at the rate of 1000 tonnes/day. The results of the study are considered generally applicable to nickel production.

Tables 22, 23, and 24 represent the material balance of the impurities, calculated for the three cases, after cleaning and conditioning shown in Figure 11 (4,5,6,9).

					A	oight		
	Totai Weight	<u></u>			Assay w	eignt		
Material	(kg/d)	Pb	Zn	As	Hg	Se	Cl	F
					kg/d			
Scrubber Inlet	430	20.0	27.0	8.4	0.049	18.8	63.0	58.0
Scrubber/ Mist. Prec. Catch	425	19.92	26.96	8.36	0.032	18.4	61.9	57.0
Catalyst Fouling	4.0	0.08	0.11	0.03	0.009	0.32	0.99	0.8
Acid Fouling	0.75	0.015	0.02	0.007	0.006	0.06	0.17	0.15
Stack Exhaust	0.25*	0.005	0.01	.003	0.002	0.02	0.06	0.05
				r	ng/Nm ³			
Scrubber Inlet Gas		6.31	8.51	2.65	0.015	5.93	19.8	18.2
Scr. Syst. Outlet Gas		0.03	0.042	0.012	0.005	0.12	0.34	0.3

TABLE 22	CLEAN CONCENTRATE:	CASE 1 - ACID	PLANT MATERIALS
	BALANCE		

* estimate only

	Total				Assay We	eight		
Material	Weight (kg/d)	Pb	Zn	As	Hg	Se	Cl	F
					kg/d			
Scrubber Inlet	1959	260	309	600	0.99	128	63	72
Scrubber/ Mist. Prec. Catch	1935	259	307.5	597	0.64	125.4	61.9	70.8
Catalyst Fouling	19.2	0.8	1.2	2.4	0.17	2.05	0.91	0.96
Acid Fouling	3.6	0.15	0.23	0.45	0.13	0.38	0.17	0.18
Stack Exhaust	1.2	0.05	0.08	1.15	0.05	0.13	0.06	0.06
TOTAL	1959	260	309	600	0.99	128	63	72
		mg/Nm ³						
Scrubber Inlet Gas	-	82.1	98	249*	0.31	40.1	20	23
Scr. Syst. Outlet Gas		0.32	0.49	1.25*	0.096	0.85	34	0.36

TABLE 23MODERATELY DIRTY CONCENTRATE: CASE II - ACID PLANT
MATERIALS BALANCE

* as AS₂O₃

	Total		Assay Weight								
Material	Weight (kg/d)	Pb	Zn	As	Hg	Se	Cd	Cl	F		
			<u> </u>		k	g/d					
Scrubber Feed	2944	960	300	660	99.0	185	1.4	63.0	144		
Scrub & Mist. Ppt Catch	2888	957	298.5	656.7	64.4	180.4	1.39	61.9	141.5		
Hg Scrubber	43.0	1.2	0.6	1.32	33.9	1.84	0.04	0.45	1.0		
Catalyst Fouling	8.9	1.2	0.6	1.32	0.4	1.84	0.04	0.45	1.0		
Acid Fouling	3.31	0.45	0.23	0.49	0.3	0.69	0.02	0.17	0.37		
Stack Exhaust	1.11	0.15	0.08	0.17	0.1	0.23		0.06	0.13		
TOTAL	2944	960	300	660	99.0	185	1.4	63.0	144		
			mg/Nm ³						. <u></u>		
Scrubber Inlet Gas	-	303	95.0	208	31.2	58.0	0.004	20.0	46.0		
Scrubber System Outlet Gas	-	0.95	0.48	1.05	0.22	1.5	0.03	0.34	0.74		

TABLE 24DIRTY CONCENTRATE: CASE III - ACID PLANT MATERIALS
BALANCE

D.2 Capital and Operating Cost Estimates

The estimates shown in Tables 25 through 28 are based on in-house data(2) escalated to 1983 cost level. In each case, capital costs cover the actual sulphur fixation plant only, with an allowance for such services as site preparation, water supply, maintenance shop, warehouse, main electrical substation, and administration buildings. They do not include the cost for ducts, flues, and gas cleaning equipment because these vary with each particular case. The cost are order of magnitude only; they vary with location and depend on whether the sulphur recovery plant is built within an existing smelter complex, or included as part of a new installation. Soil conditions, local requirements, and remoteness of the plant also have a bearing on the capital costs. Excluded are such items as site acquisition, any modification to the existing metallurgical complex, interests during construction, working capital in the form of start-up materials, spare parts, and eventual duties.

The operating cost estimates assume the gas feed is delivered free of charge to the acid plant and exclude costs for sale and distribution to the markets. The following unit costs have been used in estimating operating costs (in 1983 Canadian dollars):

Labour	16.75	per hour
Natural gas	0.137	per m ³
Heavy fuel oil	0.30	per litre
Light fuel oil	0.35	per litre
Steam	25.70	per tonne
Water	0.19	per m ³
Electric power	0.25	per kWh
Limestone	21.0	per tonne

	Continuous Gas Only	Variable Gas Only	Continuous Gas Base Load with Variable Gases		
Basis for Estimate				- <u></u>	
Production: TPD 100% H ₂ SO ₄	530	530	530	1 070	
Gases:					
 Continuous smelter gas, i.e. from roaster, flash furnace (% SO₂) 	12	-	12	12	
 Variable gas, i.e. from converters (% SO₂) 	-	5-8	5-8	5-8	
Capital Cost (in 1983 Canadian o	dollars)	<u></u>	<u></u>		
Single catalysis sulphuric acid plant ¹ Contingency @ 25% Auxiliary equipment and services	17 950 000 4 490 000 2 250 000	29 100 000 7 280 000 3 620 000	20 970 000 5 240 000 2 630 000	32 220 000 8 060 000 4 030 000	
TOTAL CAPITAL COST	24 690 000	40 000 000	28 840 000	44 310 000	
Production Cost (in dollars/tonn	e H ₂ SO ₄)				
Operating Cost:					
Supervision Operating labour Utilities ² Operating supplies ³ Maintenance ⁴ Indirect costs ⁵	0.83 1.57 2.10 0.35 4.37 0.86	0.83 1.57 3.69 0.35 7.08 0.86	0.83 1.57 2.62 0.35 5.10 0.86	0.42 0.88 2.53 0.35 3.92 0.45	
Subtotal Contingency @ 10%	10.08	14.38 <u>1.44</u>	11.33 <u>1.13</u>	8.55 0.86	
TOTAL OPERATING COST	11.09	15.82	12.46	9.41	
Capital Charges:					
Amortization & interest @ 15 years and 10% p.a.	17.38	28.18	20.31	15.60	
TOTAL PRODUCTION COST	28.47	44.00	32.77	25.01	

TABLE 25 COST OF FIXING SULPHUR AS SULPHURIC ACID FROM SMELTER GASES, USING A SINGLE-CATALYSIS ACID PLANT (2)

1 Includes engineering and construction overhead costs Includes natural gas, water and electric power

2

3 Includes limestone for weak acid neutralization and other operating supplies

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4 @ 3.3% p.a. of total capital cost

5 Includes property taxes, insurance, legal and technical counsel, etc.

	Continuous Gas Only	Variable Gas Only	Continuous Gas Base Load with Variable Gases		
Basis for Estimate					
Production: TPD 100% H ₂ SO ₄	540	540	540	1 100	
Gases:					
 Continuous smelter gas, i.e. from roaster, flash furnace (% SO₂) 	12	-	12	12	
 Variable gas, i.e. from converters (% SO₂) 	-	5-8	5-8	5-8	
Capital Cost (in 1983 Canadian o	dollars)				
Single catalysis sulphuric acid plant ¹ Contingency @ 25%	19 950 000 4 990 000	32 340 000 8 090 000	23 300 000 5 830 000	35 800 000 8 950 000	
services TOTAL CAPITAL COST	<u>2 490 000</u> 27 430 000	<u>4 040 000</u> 44 470 000	2 910 000 32 040 000	<u>4 480 000</u> 49 230 000	
Production Cost (in dollars/tonne	e H ₂ SO4)				
Operating Cost:	2				
Supervision Operating labour Utilities ² Operating supplies ³ Maintenance ⁴ Indirect costs ⁵	0.82 1.54 2.25 0.36 4.75 0.83	0.82 1.54 3.97 0.36 7.70 0.83	0.82 1.54 2.80 0.36 5.55 0.83	0.41 0.86 2.73 0.35 4.26 0.45	
Subtotal Contingency @ 10%	10.55	15.22 <u>1.52</u>	11.90 <u>1.19</u>	9.06 0.91	
TOTAL OPERATING COST	11.61	16.74	13.09	9.97	
Capital Charges:					
Amortization & interest @ 15 years and 10% p.a.	18.93	30.69	22.11	16.99	
TOTAL PRODUCTION COST	30.54	47.43	35.20	26.96	

COST OF FIXING SULPHUR AS SULPHURIC ACID FROM SMELTER TABLE 26 GASES USING DOUBLE CATALYSIS ACID PLANT (2)

1

2

Includes engineering and construction overhead costs Includes natural gas, water and electric power Includes limestone for weak acid neutralization and other operating supplies 3

4 @ 3.3% p.a. of total capital cost

5 Includes property taxes, insurance, legal and technical counsel, etc.





- 1 Capital costs do not include cost of capital, land costs, preliminary costs for permits, or environmental reviews.
- 2 Annual costs do not include taxes, insurance, depreciation, interest on capital, or credit for product acid.)
- 3 Based on 340 operating day per year

COST OF RECOVERING LIQUID SO₂ FROM SMELTER GASES (2) TABLE 27

	C (, F	Chemical Absorption Process Asarco's Dimethylaniline Process)	Physical Recovery Process (Compression & Refrigeration)
Basis for Estima	tes		
Production:	160 TPD liqui 350 operating	id SO2, corresponding to 56 0 g days)	00 tonnes annually (assuming
Gas processed:	Smelter gases scrubber syst	s with 12% SO2, cleaned in ho em	ot electrostatic precipitator or
<u>Capital Cost</u> (in	1983 Canadian	dollars)	
Liquid sulphur dioxide plant1 Contingency @ 2	25 %	9 391 000 2 348 000	8 348 000 2 087 000
TOTAL CAPIT	AL COST	11 739 000	10 435 000
Production Cost		\$/tonne SO ₂	\$/tonnes SO2
Operating Cost			
Supervision Operating labou Utilities ² Operating suppl Maintenance ⁴ Indirect costs ⁵ Royalties ⁶	r ies ³	2.78 5.24 21.12 5.05 9.64 2.75 0.76	2.78 5.24 11.04 1.38 10.15 2.75
Subtotal Contingency @ 1	0 %	47.34 <u>4.73</u> 52.07	33.44 <u>3.34</u> 36.78
Capital Charges		92.07	20.78
Amortization & @ 15 years & 1	interest 0 % p.a.	27.56	24.50
TOTAL PRODU	JCTION COST	79.63	61.28

Includes engineering and construction overhead costs Includes steam, water and electric power Includes chemicals and other operating supplies 1

2 3 4 5

(d 4.6 and 5.5% p.a. respectively Includes property taxes, insurance, legal and technical counsel, etc. Royalties payable for proprietary process

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TABLE 28 COST OF RECOVERING SULPHUR FROM SMELTER GASES (2)

Production:	270 TPD elemental sulphur, corresponding to 89 000 tonnes annually (assuming 330 operating days).		
Gas processed:	Natural gas reduced flash furnace gas, cleaned in hot electrostatic precipitator, and containing 8.4 $\%$ sulphurous gases (mixture of S vapour, SO ₂ , H ₂ S, and COS).		
Tail gas:	Estimate includes incineration of process plant tail gas, using natural gas as fuel, to burn excess H_2S and COS to SO_2 .		
Process:	Estimate is based on the Outokumpu sulphur recovery process, using the Orkla method for catalytic conversion of reduced smelting furnace gases.		

Capital Cost (in 1983 Canadiar	n dollars)	Production Cost (\$/tonne of Recovered S)		
Elemental sulphur plant ¹ Additional smelter auxiliary	26 100 000	Production Cost		
Subtotal ³ Contingency @ 25 % Sulphur plant tail gas stack ⁴	<u>36 010 000</u> <u>9 003 000</u> 45 013 000 4 115 000	Operating Cost Supervision Operating labour Utilities ⁵	2.04 8.87 76.24	
Contingency @ 25 %	<u>1 372 000</u> 5 487 000	Operating supplies ⁶ Maintenance ⁷ Indirect costs ⁸	4.37 18.62 <u>3.54</u>	
SULPHUR RECOVERY	50 500 000	Subtotal Contingency @ 10 % TOTAL OPERATING COST	113.68 <u>11.37</u> 125.05	
		<u>Capital Charges</u> Amortization & interest @ 15 years and 10 % p.a.	74.60	
		TOTAL PRODUCTION COST	199.65	

1 Based on 91% sulphur recovery from flash furnace gas, corresponding to about 50% fixation of sulphur contained in copper or nickel concentrates.

2 The sulphur plant requires substantial additions to smelter auxiliary facilities such as electric power, steam and water systems, maintenance shops, laboratory, etc.

- 3 Includes engineering and construction overhead costs.
- 4 Stack for discharge of incinerated sulphur plant tail gas.

5 Includes natural gas, steam, water and electric power.

- 6 Includes chemicals, catalyst replacement and other operating supplies. 7
- At following annual percentages of total capital cost:

3.5 % p.a. for sulphur plant and additional smelter auxiliary facilities 1.5 % p.a. for tail gas stack.

Includes property taxes, insurance, legal and technical counsel, etc.

8

Note: Items excluded from these costs are listed under Section 3.3.

APPENDIX E

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SUMMARY OF AIR QUALITY STANDARDS AFFECTING SMELTERS

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TABLE 29 SUMMARY OF AIR QUALITY STANDARDS AFFECTING SMELTERS

Country and Standard Basis of Determining Compliance		Basis of Determining Compliance	Sulphur Dioxide		Particulates	
		ppm	μg/m ³	μg/m ³		
UNI	TED STATES					
Fed	eral Ambient Air:					
(a) Prımary	Primary Standard	Annual arithmetic mean Annual geometric mean of 24-hour concentrations Maximum 24-hour concentration, permissible once per year	0.03	80	75	
			0.14	365	260	
(b)	Secondary Standard	Annual arithmetic mean Annual geometric mean of 24-hour concentrations Maximum 24-hour concentration of 24-hour concentrations	0.02	60	60	
			0.09	260	150	
		Maximum 3-hour concentration, permissible once per year	0.50	1300		
<u>CAN</u>	NADA					
Clean An (a) Ma:	an Air Act-Objectives: Maximum Desirable	Annual arithmetic mean Annual geometric mean	0.01	30	60	
		Average 24-hour concentration	0.06	150	00	
		Average 1-hour concentration	0.34	450		
(Ь)	Maximum Acceptable	Annual arithmetic mean Annual geometric mean	0.02	60	70	
		Average 24-hour concentration Average 1-hour concentration	0.11 0.34	300 900	120	
(c)	Maximum Tolerable	Average 24-hour concentration	0.28	800	400	
EUR	OPEAN ECONOMIC CON	AMUNITY				
Standard for Urban Areas	ndard for Urban Areas	Annual median of daily means	0.03-0.04	85-110	80	
		Annual median of daily values Annual median of daily means (winter, Oct-Mar) Annual median of daily values (winter, Oct-Mar) Maximum arithmetic mean over 24-hours Exceptional conditions (up to 3 days), maximum average 24-hour arithmetic mean	0.05-0.06		30	
			0.09-0.12	250-340	250	
			0.12-0.18	340-510	300	
FIN	LAND					
Air	Quality Objectives					
Maxımum Desırable		Annual arithmetic mean Average 24-hour concentration Average I-hour concentration		40 200 500	60 1 <i>5</i> 0	

APPENDIX F

SUMMARY OF EXISTING MINING EFFLUENT REGULATIONS IN CANADA, AND JAPAN

Contaminant	<u>Canada</u> Maximum Monthly Mean Concentration (mg/L)	<u>Japan</u> Maximum Concentration (mg/L)
Arsenic	0.5	0.5
Cadmium	-	0.1
Copper	0.3	-
Hexavalent Chromium	-	0-5
Lead	0.2	1.0
Nickel	0.5	-
Total Mercury Suspended Solids pH	25 6.0+	0.005 - -

TABLE 30SUMMARY OF EXISTING MINING EFFLUENT REGULATIONS IN
CANADA, AND JAPAN

Note: The reader should refer to the full text of these regulations.