

AIR POLLUTION CONTROL SYSTEMS ON INTERNATIONAL
COPPER AND NICKEL SMELTERS

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ABSTRACT

This report briefly examines the major sources of sulphur dioxide (SO_2) and its effects on the environment. Because of the harmful effects of SO_2 , many countries have formulated air pollution control regulations to limit emissions and provide for certain ambient air quality standards. These are given in outline for several countries.

Various smelting technologies used in the copper and nickel industries are discussed in terms of the matte grade produced and its implications on the strength, volume and continuity of the major gas streams in the smelter.

The various methods of removing particulate material from the gas streams prior to SO_2 capture and fixation are described. Sulphur dioxide emission control technology, either under development or in various stages of commercialization, is described, both for concentrated process gas streams and for the weak gas streams which emanate from fugitive emissions, acid plant tail gas and dilute process gas streams such as from the reverberatory furnace.

The by-products produced from fixation of sulphur may be used at the smelter site for conversion into other products, sold directly into various markets, or disposed of as stable waste materials after neutralization. The various alternatives are briefly reviewed.

The disadvantages in the traditional primary smelting processes are discussed in terms of their inability to utilize efficiently the inherent energy contained in the concentrate and the production of low gas strengths involving relatively high treatment costs.

The development of more energy-efficient processes, combined with the use of tonnage oxygen, coincidentally led to the production of gas strengths more suitable for capture and fixation of SO_2 . The imposition of more stringent emission controls and their impact on smelters is discussed in relation to process changes, engineering requirements and associated costs.

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CONCLUSIONS

The harmful effects of sulphur dioxide (SO_2) on the environment, i.e. on health, vegetation and property, has and will continue to lead to the imposition of more stringent air pollution control regulations on the copper and nickel smelting industries, particularly in the developed countries and in the developing countries when international financing is required for smelter projects. This will continue to have a profound effect on the industry, especially in the older smelters using the traditional, outdated technology (multi-hearth roasters and reverberatory furnaces) which is neither energy efficient nor suitable for recovering more than about 70% of the sulphur in the feed to the smelter. Future emission standards are likely to require that at least 90% of the sulphur is captured, although this may be more than is required to meet proposed ambient air quality standards. (Some areas in Japan already require a 99% sulphur recovery from copper smelters.)

Modern smelting technology is based on the concept of utilizing part of the inherent energy of the concentrate to produce a higher than 'natural' grade of matte in the primary smelting furnace. In "flash" smelting, which includes the Outokumpu and Inco basic variants, sulphide mineral particles are simultaneously roasted (oxidized) and smelted in the furnace reaction shaft to produce an upgraded matte, although in the Inco case this is limited. In the Noranda process, upgrading of the 'natural' matte grade is brought about by oxidation of the matte by blowing with oxygen-enriched air through submerged tuyeres. In the Mitsubishi continuous smelting process, upgrading of the 'natural' matte is achieved by top-blowing with oxygen-enriched air. In all cases the matte grade produced is a function of the oxygen : concentrate ratio and concentrate grade. The remainder of the inherent energy contained in concentrates is utilized in oxidation of the matte in converters. The use of oxygen-enriched reaction air in these processes results in economic and technical benefits in that by replacing part or all of the inert nitrogen, the gas volume is reduced, its SO_2 strength is increased and fuel requirements are decreased. The use of tonnage oxygen in the industry will therefore continue to increase.

There is now a tendency in the copper industry to produce as high a matte grade as is technically feasible (i.e. generally depending on impurity

content) to maximize the production of a continuous, constant volume and strength of gas from the primary smelting furnace, thereby minimizing the intermittent and variable gas stream from the converters. In nickel smelting, however, the inherent energy in the concentrate cannot be fully utilized in the primary smelting furnace because production of a high grade matte would result in unacceptably high nickel losses to the slag. Gas streams from all these modern processes are high in SO_2 , and when combined with converter gases, permit recovery of sulphur as sulphuric acid, the accepted control approach in the industry, and achieve better than 90% sulphur recovery. The use of a double absorption acid plant, scrubbing of acid plant tail gas, and collection and scrubbing of fugitive emissions (which contain 1-2% of the sulphur input to a smelter) permit better than 99% sulphur recovery, as evidenced at several modern copper smelters, particularly those in Japan.

Production of sulphuric acid is likely to remain the accepted control approach in the industry. Production of liquid SO_2 is feasible from highly concentrated off-gases such as from an Inco oxygen flash furnace. Reduction of SO_2 to elemental sulphur is technically feasible but is unlikely to be an economic proposition because of the high cost of reductants. However, the production of elemental sulphur has advantages in that it is a stable product which can be easily and safely stockpiled and transported for use at a later date.

Technology for the control of weak gas streams, such as those from reverberatory furnaces, is not so advanced. Whilst these processes are likely to find increasing application in the control of fossil fuel-fired power plant off-gases, a more attractive proposition in the smelting industry is likely to be the replacement of outdated technology by new, more energy-efficient processes which produce concentrated gas streams amenable to production of sulphuric acid.

In order to meet more stringent environmental legislation in the older smelters, it will be necessary to replace the outdated primary smelting processes by one of the more modern processes previously mentioned, or make modifications such as sprinkle smelting and installing oxy-fuel burners, and at the same time install new or additional pollution control equipment such as an acid plant. The costs of these modifications and additions are

likely to be prohibitive, and may place the economic viability of the smelter in jeopardy for the reason that there is frequently no financial return on such an investment unless it is accompanied by an increase in metal production. However, in countries where environmental legislation does not exist, the installation of pollution control equipment will not be necessary. Oxygen enrichment may be used to increase throughput and reduce fuel requirements, rather than to increase the SO_2 content of the gas streams for pollution control reasons. Credit, if any, from the sale of sulphur-containing by-products may not be sufficient to cover the incremental smelter operating costs attributed to their production as well as amortization of the investment. The key factor in determining the viability of process changes and installation of air pollution control equipment is likely to be the availability of markets for the by-products of sulphur containment. Because each smelter is unique in terms of the technology it employs and its location relative to by-product markets, each case has to be evaluated, both technically and economically, on its own merits, taking all factors into consideration. The increased production of acid which is expected to accompany sulphur containment programmes will be one of the major problems facing the smelting industry. In many cases, smelters that are not near major markets for acid will have to neutralize the acid and discard waste product gypsum, an expensive proposition. In certain extreme cases it may be more attractive to build a new smelter employing modern technology in a different location with ready access to markets for sulphur by-products, than it is to make extensive modifications and additions to an existing smelter.

INTRODUCTION

Because of the potentially harmful effects of sulphur dioxide (SO_2) on all aspects of the environment, i.e. health, vegetation and property, many countries, particularly the industrialized ones, have formulated legislation to limit the amount of SO_2 that may be emitted to the atmosphere. Whilst the major source of SO_2 pollution is from fossil fuel-fired power plants internationally, the total amount of SO_2 emitted from copper and nickel smelters is also significant and in certain countries (eg. Canada, Chile) may be the major source. On an individual plant basis, because of the large amount of sulphur in the feed to a smelter (from 25 - 35%), the effect of uncontrolled SO_2 emissions on the neighbouring environment can be a substantial problem.

In many countries, air pollution control regulations have been developed covering ambient air quality standards (to protect public health and welfare) and emission standards (which limit the absolute quantity of pollutant which may be emitted to the atmosphere).

Many of the older copper and nickel smelters are based on outdated technology (multiple hearth roasting and reverberatory smelting followed by converting) where there are frequently no facilities for capture and fixation of SO_2 , all gases being vented to atmosphere. These plants are often located in remote, arid regions where damage to the environment is perhaps less severe and more acceptable. The smelters were designed to meet the standards of the time when it was accepted practice to disperse gases into the atmosphere via a stack. There was therefore little incentive for sulphur containment. In cases where roaster and/or converter gases were converted to sulphuric acid, sulphur recovery varied from around 50 to 70%.

Over the last 30 years more energy-efficient smelting processes have been developed which utilize the inherent fuel value contained in the sulphide content of concentrates. Coincidentally, these developments have enabled concentrated gas streams to be produced where the SO_2 content can range from about 10% SO_2 up to 80% SO_2 in the case where technical oxygen as opposed to oxygen-enriched air is used. The use of tonnage oxygen has played an important part in developing new smelting technology to the extent of decreasing the requirement for hydrocarbon fuels to provide the thermal energy for smelting, and in producing concentrated gas streams suitable for the capture and fixation of SO_2 .

Production of sulphuric acid is the accepted control approach in the industry. Other possibilities are the production of liquid SO_2 , which is feasible from highly concentrated (80% SO_2) gas streams as in the case of the Inco oxygen flash smelting process, and the production of elemental sulphur. The latter is technically more complicated and because of the expense of the reductant required, is in any event, not presently an economic proposition. While the production of sulphuric acid from smelter gases is well established and technically proven, the economics of so doing are dependent on the location of the smelter relative to markets for the acid, which determines freight costs, and also the price which can be obtained for the acid, which is determined by alternative sources of supply to the consumer.

Control of weak gas streams (containing less than about 2% SO_2) which arise from the collection of fugitive emissions, acid plant tail gas, or reverberatory furnace gases, is less well established. However, several processes have been developed to various degrees of commercialization and reliability, either to concentrate the gas streams to a level sufficiently high that they can be fed to an existing acid plant, or alternatively to neutralize the gases by scrubbing to produce discardable or salable by-products. In certain cases it may be feasible to blend weak gas streams with concentrated streams for processing in an acid plant.

By combining modern smelting technology (generally flash smelting) with production of sulphuric acid, many copper smelters are achieving well in excess of 90% sulphur recovery. Several Japanese smelters, by using double absorption acid plants and scrubbing of weak gas streams, are achieving better than 99% sulphur capture (1). Compared with many other smelters in the world, the Japanese copper smelters are fortunate in that they are frequently located in a seaport industrial complex which offers advantages in ready accessibility to supplies and markets. Liquid and gaseous fuels and chemicals may be available from an adjoining petrochemical plant, that in turn, is a user of sulphuric acid. Adjacent fertilizer and pigment plants also may be ready customers for acid, and nearby wallboard and cement plants may be customers for by-product gypsum and smelter slag. However, a constraint on such a location is that the smelter will be required to capture at least 90% of the input sulphur but this

is not a problem when modern technology is employed. The necessity to install pollution control facilities will increase both the capital and operating costs of the smelter compared with others that have no such requirement imposed upon them. Japanese copper smelters, being custom smelters, frequently adopt a purchasing policy whereby they buy concentrates substantially free from deleterious impurities and high in inherent energy content, i.e. high in iron and sulphur. This allows treatment of smaller quantities of more heavily contaminated material if advantageous penalty rates can be negotiated.

The imposition of air pollution control regulations on smelters which do not have sulphur capture and fixation facilities already installed will adversely affect their economics, even to the extent of their viability being in doubt. However, the uniqueness of each smelter in terms of its location, smelting technology employed, and available markets for sulphur containing by-products, means that the impact of the costs of modifying or replacing processes by new technology and installing pollution control facilities can only be assessed on an individual basis. In certain cases, when taking all factors into consideration, it may be as financially attractive to build a new smelter, perhaps in a different location, as it is to make extensive modifications to an existing plant.

2 SULPHUR OXIDE EMISSIONS

2.1 General

The control of gaseous emissions, particularly sulphur dioxide (SO_2), is one of many pollution-related problems facing industry in general. Gaseous effluents most frequently result from combustion processes, including the oxidation of mineral sulphides in smelting processes, as well as fuels. The principal impurities in combustion flue gases generally include sulphur dioxide (SO_2), nitrogen oxides (NO_x), carbon dioxide (CO_2), and particulate material.

Although control of solid and liquid effluents are important, the most serious problem facing the copper and nickel smelting industries is the control of gaseous SO_2 emissions. Sulphur is a major component in the concentrate feed to the smelting processes, varying in the general range of 25-35% S. In relation to the metal content in concentrates, the mass ratio of sulphur to copper varies between 0.8 - 1.6 in copper concentrates, and 2.2 - 4.8 in the case of nickel concentrates (2). During the various unit operations sulphur is oxidized to SO_2 , although small amounts of sulphur trioxide (SO_3) may be formed under certain conditions of temperature and oxygen partial pressure.

In many countries, particularly the industrialized ones, it is no longer admissible to discharge gaseous emissions from the smelting process directly to the atmosphere via a stack without some measure of SO_2 capture and fixation because of the harmful effects of SO_2 on the environment.

2.2 Sources of SO_x Emissions

Some 90 - 95% of pollution-related sulphur oxide emissions are in the form of SO_2 (3). Man-made emissions of SO_2 discharging to the environment originate from a variety of sources, the distribution of which varies from one country to another depending on its degree of industrialization and, in particular, the size of its non-ferrous smelting industry. These differences are illustrated for the U.S. and Canada in Table 1 which gives the current nationwide distribution of SO_x emission sources in those countries (4). NO_x emissions

are also shown in the table and it is worth noting that they are not a problem in non-ferrous smelters. The reason is that compared with the quantity of SO_2 emitted from smelting sulphide concentrates, the quantity of SO_x and NO_x emitted from burning fuel in the furnaces is very small.

TABLE 1 CURRENT NATIONWIDE EMISSIONS OF SO_x AND NO_x IN THE U.S. AND CANADA
(10^6 stpa) (4)

	U.S.A. (1980 Estimated)		Canada 1979*		Total	
	NO_x	SO_x	NO_x	SO_x	NO_x	SO_x
Utilities	6.2	19.5	0.3	0.8	6.5	20.3
Industrial Boilers/ Process Heaters/ Residential/ Commercial	7.1	7.3	0.6	1.1	7.7	8.4
Non-ferrous Smelters	0.0	2.0	0.0	2.2	0.0	4.2
Transportation	9.0	0.9	1.1	0.1	10.1	1.0
Iron Ore Processing	-	-	-	0.2	-	0.2
Other	-	-	0.2	0.9	0.2	0.9
TOTAL	22.3	29.7	2.2	5.3	24.5	35.0

* Inco, Sudbury at 1980 emission rate.

In the U.S., utilities (the majority of which use coal and oils as fuel) are responsible for 66% of total SO_x emissions, while in Canada this source accounts for only 15% of the total. The concentration of populations into large metropolitan areas, with the resulting energy needs and industrial activity, results in many small emission sources accumulating in these areas which in themselves then become large sources of SO_x (and NO_x) emissions.

Table 1 indicates that this source (comprising industrial boilers, process heaters, residential and commercial properties) accounts for 25% and 21% of total SO_x emissions in the U.S. and Canada, respectively. The non-ferrous smelting industry in the U.S. accounts for nearly 7% of total SO_x emissions in that country, while in Canada the contribution is 42%. Except for transportation sources (which includes motor vehicles, vessels and railroads), over 97% of the man-made sources are stationary.

The problem in smelting is that virtually all the sulphur input to the smelter leaves in the gas phase, with relatively minor amounts contained in the solid phase products or discarded materials. In addition, because of the high sulphur content in the feed material, a copper or nickel smelter is a point source of high SO_2 emissions and therefore at a given location the smelter will likely be the major contributor to air pollution.

In order to protect the environment, it is therefore necessary to capture and fix the SO_2 as some marketable product, or one which can be safely stored, to an extent determined by environmental legislation and/or economic factors.

2.3 Effects of SO_2 Emissions

Sulphur dioxide is one of several forms in which sulphur circulates globally. The sulphur cycle also includes hydrogen sulphide gas, sulphuric acid aerosol, and several sulphate salts in aerosol form (3). An aerosol can be considered as a suspension of liquid droplets or solid particles in a gas.

Sulphur, in a free or combined state, occurs in practically all fossil fuels as well as in copper and nickel sulphide concentrates which are smelted and refined to produce the pure metal. Sulphur compounds released to atmosphere ultimately give rise to sulphurous or sulphuric acid or ammonium sulphate, depending on the reactions. Acids formed in the atmosphere fall with rain and affect crops and plants.

Sulphur dioxide may also oxidize in the atmosphere to form sulphates, a particulate form of sulphur compounds. These compounds may have adverse effects on human health and property, depending upon particle size, the particular form of sulphate present, dispersion as affected by weather conditions, and the presence of other pollutants which may magnify the effects.

Sulphur dioxide emissions, through the formation of acids and other compounds in the atmosphere can cause damage to human health, vegetation and property. Some of these effects are outlined below.

2.3.1 Health

High levels of sulphate concentrations are said to aggravate asthma, lung and heart disease (3). Sulphur dioxide in the presence of photochemical oxidants and by-products such as sulphuric acid and hydrogen sulphide has been shown to affect the respiratory tract. It is also widely believed that long term exposure to sulphates may increase the likelihood of respiratory illnesses such as bronchitis, emphysema and asthma. This effect is more probable when high concentrations of particulates are present.

2.3.2 Vegetation

Sensitive vegetation can be severely damaged even by low levels of sulphur dioxide (3). These levels are lower than those said to cause distress to pulmonary disease patients. Such effects result from the synergistic action of sulphur dioxide with low levels of ozone or nitrogen oxide which may be present. Wheat, barley, oats, white pine, cotton, alfalfa, buckwheat, sugar beets, and other crop plants have been reported damaged by relatively low levels of sulphur dioxide fallout. Studies made in the U.S.S.R. during the past decade showed that pine trees growing in an atmosphere having SO_2 concentrations of $500 \mu\text{g}/\text{m}^3$ had a growth loss of 48 percent in comparison with pine trees growing in an atmosphere free of SO_2 .

Figure 1 shows the harmful effects of SO_2 -bearing gases on vegetation which increase with increasing SO_2 concentration and exposure time (5). Since lichens, for example, store acid in their roots and then die, they are sometimes used as indicators of SO_2 fallout. In certain areas (eg. western Canada and U.S.A.) soils are deficient in sulphur, in which case the effects of SO_2 in the soil may have a beneficial effect on plant life.

2.3.3 Property

Sulphur oxides and their acid by-products will attack many exposed metal surfaces (3). Reactions will also occur on other substances such as marble, brick, stonework and granite. Plastics, rubber, paper, and many other similar materials will become discoloured and brittle when exposed. Buildings, bridges, steel girders, automobiles and highways are all affected by excessive SO_2 emissions.

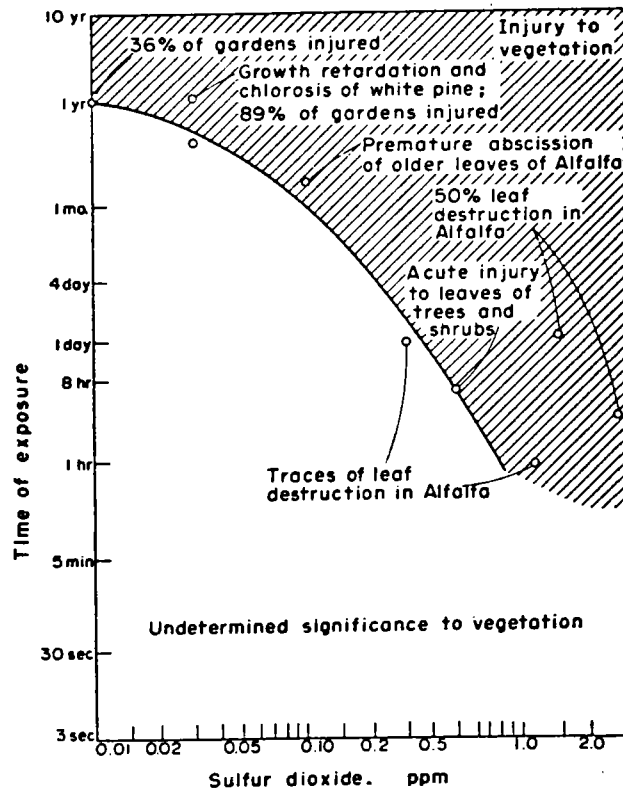


FIGURE 1 THE EFFECTS OF SO_2 -BEARING GASES ON VEGETATION (5)

3 AIR POLLUTION CONTROL REGULATIONS

3.1 General

Growth in industrial activity has increased air pollution considerably with coal and oil-fired power plants being the major contributors. This has led to a general demand for some degree of control over air pollution. Emissions caused by smelters are only a small part of the overall problem but in certain areas they are the major source of SO₂ emissions which have caused considerable damage to vegetation and property.

Although air pollution problems created by the smelting of copper and nickel sulphide ores and concentrates are not new, it is only during the last 20 years that air pollution control regulations have been formulated and become legislation in certain countries. In the past, legal actions instituted by individuals against smelter operators generally sought claims for damage to property. These were often settled by purchase of affected land or by cash payments to the claimants. Prevention was sought by building high stacks that dispersed the SO₂ fumes and particulates in a manner that obviated any gross damage to far-lying property.

3.2 Definitions

Air pollution control regulations and legislation have been developed principally in the industrial countries. Specific terminology is used and the following definitions (6,7), largely of U.S. derivation, will serve to give the reader a better understanding when interpreting the various regulations.

(i) Ambient Air

Ambient air means that portion of the atmosphere, external to buildings, to which the general public has access.

(ii) Ambient Air Requirements

Ambient air requirements refer to pollution in the air at the property boundary of the smelter operation, generally at ground level. They are usually designated as maximum SO₂ concentrations for various time intervals.

(iii) Emission Standards

Emission standards limit the amount of sulphur that can be discharged to the atmosphere, and are expressed as a percentage of the total sulphur charged to the smelter or as a mass of sulphur that can be emitted over a given time period.

(iv) Air Pollution Control Equipment

Air pollution control equipment means equipment used to eliminate, reduce, or control the discharge of air contaminants into the ambient air.

(v) Units of Measurement

The unit in most common use to express the concentrations of SO₂ in the air is in terms of weight per unit volume of air, i.e. micrograms of SO₂ per cubic metre of air ($\mu\text{g}/\text{m}^3$). Where analytical results are given in parts per million (ppm) of SO₂, the data can be converted by using:

$$1 \text{ ppm SO}_2 = 2850 \mu\text{g}/\text{m}^3 \text{ (at N.T.P.)}$$

This conversion factor applies to SO₂ only, and will not apply to any other substance having a different molecular weight.

(vi) Opacity

Opacity means the degree, expressed in percent, to which emissions reduce the transmission of light and obscure the view of an object in the background.

(vii) Fugitive Emissions

Fugitive emissions means emissions which escape from various points in a process due to leakage, materials charging and handling, transfer and storage, or other causes.

(viii) Pollution

Pollution may be defined as the addition, from either natural or man-made sources, of any foreign substances to the air, water or land media in such quantities as to render such medium unsuitable for specific or established uses.

(ix) Capture System

A capture system means the equipment (including ducts, hoods, fans, dampers, etc.) used to capture or transport particulate matter or gases generated by a process source to the air pollution control device.

(x) Continuous Monitoring System

A continuous monitoring system means the total equipment, required under the emission monitoring regulations, used to sample and condition (if applicable), to analyze, and to provide a permanent record of emission or process parameters.

(xi) Dust

Dust means finely divided solid particulate matter occurring naturally or created by mechanical processing, handling or storage of materials in the solid state.

(xii) Effluent

Effluent means any air contaminant which is emitted and subsequently escapes into the atmosphere.

(xiii) Emission

Emission means the act of passing into the atmosphere an air contaminant, visible or invisible.

(xiv) Episode Stage

A prescribed level of air contaminants or meteorological conditions where certain control actions are required to prevent ambient pollutant concentrations from reaching levels which could cause significant harm to the health of persons. (In Canada this is called the Air Pollution Index).

3.3 Gaseous Emissions

Many countries, particularly the industrialized ones, in which copper and nickel smelters are located, have strict air pollution standards for SO₂, both for ambient air quality and for allowable emissions. Legislation is aimed at reducing air pollution to defined levels, although as will be seen later, sulphur containment policies impose at times, severe economic and practical constraints on existing smelters, to the extent that their economic viability may be questionable.

Emission standards apply to allowable concentrations at the source, such as stacks, ventilating systems and other discharge points. Measurement of the amount of pollutant emitted is necessary for identification of specific pollution sources and design of remedial works (3).

3.3.1 U.S.A.

Primary copper smelters are located in the states of Arizona, Utah, Michigan, Montana, Nevada, New Mexico, Tennessee, Texas and Washington. There are no sulphide nickel smelters in the U.S.A. The Clean Air Act of 1970 established the principle that the Federal Government promulgate ambient air quality standards and the States bear the responsibility for the development of plans for implementation (7). In all cases, however, State regulations must at a minimum, provide for the attainment and maintenance of the Federal ambient air quality standards. In the same year, the Environmental Protection Agency (EPA) was given authority to deal with national air pollution problems. This led to the establishment of the following Federal primary and secondary ambient air quality standards:

3.3.1.1 SO₂ Ambient Air Quality Standards (3,6,8)

Federal Standards (NAAQS)

1. Primary Standards

Primary standards, which protect the public health, define how clean the ambient air must be so that it will not be harmful to human health.

- (a) 80 $\mu\text{g}/\text{m}^3$ (0.03 ppm), annual arithmetic mean.
- (b) 365 $\mu\text{g}/\text{m}^3$ (0.14 ppm), maximum 24-hr concentration, not to be exceeded more than once per year.

2. Secondary Standards

Secondary standards, which protect the public welfare, define how clean the air must be in order to protect against the known or anticipated effects of air pollution on property, materials, climate, economic values, and personal comfort.

- (a) 60 $\mu\text{g}/\text{m}^3$ (0.02 ppm), annual arithmetic mean.
- (b) 260 $\mu\text{g}/\text{m}^3$ (0.09 ppm), maximum 24-hr concentration, not to be exceeded more than once per year.
- (c) 1300 $\mu\text{g}/\text{m}^3$ (0.5 ppm), maximum 3-hr concentration, not to be exceeded more than once per year.

State Standards

In general, the various States have adopted the same ambient air quality standard as the national (federal) standard. However, four States have adopted more stringent standards as shown in Table 2 (6,8).

3.3.1.2 Emission Standards - as sulphur

Federal Standards

There are currently no Federal Standards applying to existing smelters. However, the New Source Performance Standard (NSPS) for sulphur oxide emissions from new primary copper zinc and lead smelters is 650 ppm (6,8).

TABLE 2 U.S. AMBIENT SO₂ STANDARDS (ppm) (8)

	National primary	National secondary	Arizona	Missouri	Montana	Washington
Annual arithmetic mean	0.03	0.02	0.02		0.02	0.02
Maximum 24-hour average (annual)	0.14		0.10			0.10
Maximum 24-hour average (90 days)		0.09		0.07		
Maximum 24-hour average (1% of 3-month period)					0.10	
Maximum 3-hour average		0.5				
Maximum 1-hour average (annual)						0.4
Maximum 1-hour average (twice in 7 days)						0.25
Maximum 1-hour average (4- days)				0.25	0.25	

State Standards

Some States have regulations on existing smelters, while others have set general standards covering all facilities producing sulphur oxide process emissions. In some cases, States have set standards on new facilities in addition to the Federal NSPS. Table 3 presents the SO₂ emission standards in the various States (8). Depending on the jurisdiction, control is based on regulating the total amount of sulphur released, or on concentration of sulphur in the stack gas, or on percent removal from the sulphur originally present in the feed. The strictest standards require 90% sulphur removal.

The ambient air quality and emission standards are frequently under review and the latest supplements of the Environment Reporter, State Air Laws, published by The Bureau of National Affairs, Inc., Washington, D.C., should be consulted for the latest revisions to the regulations. Several U.S. copper smelters are under litigation at the moment. As an example of the changes that are being made, Table 4 gives sulphur emission limits for Arizona copper smelters as published on May 14, 1979 (6). However, because compliance with the ultimate emission limits in all but two of the smelters* (refer to Table 4) has been shown to be currently either economically unreasonable or technologically unsound, considering the pollution control equipment already installed, interim limits have been established as shown in the table. The ultimate sulphur emission limits have been set such that compliance can only be maintained by the continuous operation of each smelter's sulphur removal equipment at its maximum feasible efficiency. Compliance with the interim limits is conditional upon all presently installed sulphur removal equipment being operated at its maximum feasible efficiency, and upon a supplementary control system being operated such that the state ambient air quality standards are maintained.

3.3.2 Japan

3.3.2.1 National Ambient Air Quality Standards

These standards prescribe that the 24-hour average of hourly SO₂ concentrations must be 0.04 ppm or less and that the maximum hourly concentration permitted is 0.1 ppm (1,8). The Japanese standards are therefore somewhat more restrictive than those in the U.S.A., including the four States which have adopted more stringent standards than the NAAQS.

TABLE 3 U.S. SO₂ EMISSION STANDARDS (8)

State	Type of facility	Standard
1. Arizona	Copper smelter (existing)	Meet the ambient state SO ₂ standard (0.02 ppm)
	Copper smelter (new)	Release of no more than 10% of sulfur in feed; or an emission limit of 6500 lb/hr; or reduction to meet the ambient standard; whichever is most restrictive
2. Idaho	Lead/zinc smelter	Maximum 1-hour average of 1900 lbs. SO ₂ by 7-31-77 and maximum of 1200 tons SO ₂ for any consecutive 7-day period
3. Illinois	Any source ^a	200 ppm SO ₂
4. Michigan	Any source ^a (existing)	No SO ₂ regulation except power plants
5. Missouri	Any source ^a (new)	2000 ppm
6. Montana	Nonferrous smelters	500 ppm
7. Nebraska	Any source ^a	<p> Total Feed of Sulfur, lbs/hr Cu. Zn. Allowable Sulfur Emission, lb/hr 1,000 100 100 5,000 500 348 10,000 1,000 304 20,000 2,000 264 40,000 4,000 1,270 60,000 6,000 1,000 80,000 8,000 1,000 100,000 10,000 1,000 >100,000 10,000 5,000 </p> <p>During any consecutive 12 months, less than emissions during 1971 calendar year; and during any 24-hour period, less than maximum emitted during any consecutive 24-hour period in 1971</p>
8. Nevada	Copper smelter (existing)	Release of no more than 40% of sulfur in feed
	Nonferrous smelters (new)	<p> Copper: $Y = 0.1 X$ 0.77 Lead : $Y = 0.49 X$ Zinc : $Y = 0.282 X$ 0.85 </p> <p>where X = total sulfur in feed and Y = SO₂ emissions</p>

TABLE 3 (Continued) U.S. SO₂ EMISSION STANDARDS (8)

State	Type of facility	Standard
9. New Mexico	Nonferrous smelters (existing)	Release of no more than 40% of sulfur in feed
	Nonferrous smelters (built after 12-31-74)	Release of no more than 10% of sulfur in feed
10. Ohio	Nonferrous smelters	Copper: $Y = 0.2 X$ 0.77 Lead: $Y = 0.98 X$ 0.85 Zinc: $Y = 0.564 X$ where X = total sulfur in feed and Y = SO ₂ emissions
11. Oklahoma	Nonferrous smelters	Same as Ohio
12. Pennsylvania	Zinc smelter	Roasting: 500 ppm (2-hour moving average) Sintering: $Y = 0.054 X$, where X = calcine feed rate to the sinter plant and Y = SO ₂ emissions
13. Tennessee	Any source ^a	500 ppm
14. Texas	Nonferrous smelters	Copper: Reverberatory furnace - 6000 ppm; all other operations 650 ppm (both 6-hour average) Lead: Sinter machine - 2500 ppm; all other operation 650 ppm (both 2-hour averages)
15. Utah	Any source ^a	Zinc: 1000 ppm (2-hour average)
16. Washington	Any source ^a	Meet the ambient SO ₂ standards 1000 ppm, unless it can be shown that the ambient standard is not exceeded

^a "Any source" refers to sources releasing process SO₂ emissions.

TABLE 4 ARIZONA SULPHUR EMISSION LIMITS (1979) (6)

COMPANY	SMELTER	Average stpd S in any calendar month	
		Ultimate	Interim
Magma	San Manuel	148	448
ASARCO	Hayden	82	301
Phelps Dodge	Douglas	120	561
Phelps Dodge	Morenci	145	407
Phelps Dodge	New Cornelia	32	89
Kennecott*	Hayden	68	N/A
Inspiration*	Inspiration	85	N/A

Japanese prefectural and local governments may have even more stringent SO_2 standards than the national standards.

The Japanese government issues an emergency warning advising a 30% reduction in SO_x emissions if any of the following ground level SO_x concentrations are met: 0.2 ppm (3 hours), 0.3 ppm (2 hours), 0.5 ppm (1 hour), 0.15 ppm (48 hours). A 60% reduction in emissions is advised if the SO_x concentration reaches 0.5 ppm (2 hours). A special emergency is issued ordering an 80% reduction in SO_x emissions if the ground level concentration reaches 0.5 ppm (3 hours) or 0.7 ppm (2 hours) (8).

3.3.2.2 Emission Standards

The Japanese national SO_2 emission standard for each SO_2 -emitting facility is determined by applying the formula (7, 8):

$$q = K \cdot 10^{-3} \cdot H_e^2$$

where q = volumetric gas flow rate (Nm^3/h of SO_x)

H_e = smoke ascent height (i.e. height of stack + plume rise above stack) in metres.

K = a constant, established by Government order for each of the air control regions in Japan.

Instead of a single standard, the standard to be applied at any given smelter is a function of the region in which it is located (the K -value) and its effective stack height. The K -value inversely determines the degree of regulation, with more heavily industrialized and polluted regions being assigned a lower K -value. The value of K ranges from 17.5 in outlying areas to 3.0 in major industrial centres. Special standards applicable to new construction in heavily industrialized areas have K -values ranging from 2.34 to 1.17. The K -values for the various areas in Japan are shown in Table 5 (9).

As in the case with ambient air quality standards, the emission standards in Japan are more stringent than those in the U.S.A. All major smelters in Japan are required to capture at least 90% of the sulphur in the smelter feed and several are required to capture 99% of the sulphur (1). These high rates of SO_2 control are obtained by utilizing generally flash smelting tech-

TABLE 5 REGULATION ON SULPHUR OXIDES EMISSION (K-VALUE) IN JAPAN (9)

a) General Standards		
	Area	K value
1	6 areas: Central Tokyo, Yokohama-Kawasaki, Nagoya, Yokkaichi, Osaka-Sakai, Kobe-Amagasaki	3.0
2	21 areas: Chiba, Fuji, Kyoto, Himeji, Mizushima, Kita-Kyushu and others	3.5
3	1 area: Sapporo	4.0
4	4 areas: Hitachi, Kashima and others	4.5
5	3 areas: Toyama, Kure, Tohyo	5.0
6	9 areas: Annaka, Niigata, Okayama, Shimonoseki and others	6.0
7	3 areas: Tomakomai, Hachioji, Kasaoka	6.42
8	6 areas: Sendai, Fukui, Hiroshima and others	7.0
9	8 areas: Asahikawa, Utsunomiya, Mihara, Tokushima and others	8.0
10	8 areas: Akita, Kanazawa, Ohtsu, Fukuoka, Nagasaki and others	8.76
11	6 areas: Takasaki, Urawa, Narita, Naha and others	9.0
12	4 areas: Shizuoka, Sasebo and others	10.0
13	15 areas: Hakodate, Gifu, Takamatsu, Minamata and others	11.5
14	6 areas: Mishima, Kurume and others	13.0
15	20 areas: Aomori, Morioka, Yamagata, Nagano, Kagoshima and others	14.5
16	Other areas	17.5
b) Special Standards		
6 areas:	Central Tokyo, Osaka-Sakai, Yokohama-Kawasaki, Kobe-Amagasaki, Yokkaichi, Nagoya	K = 1.17
8 areas:	Chiba, Fuji, Himeji, Mizushima, Kitakyushu and others	K = 1.75
14 areas:	Kashima, Toyama, Kyoto, Fukuyama, Ohmuta, Ohita and others	K = 2.34

Note: Special standards are applied to newly constructed facilities only.

nology in conjunction with sulphuric acid manufacture for most of the SO_2 , with acid plant tail gas scrubbing to yield salable gypsum and sodium salt by-products. Final tail gas SO_2 concentrations of 50 ppm or less are reported at some plants (8). In addition, special hooding is installed on converters, tapping and other transfer points to capture fugitive emissions, which are then scrubbed at some smelters achieving the highest level of SO_2 control. Table 6 gives data on smelting and emission control practice at eight major Japanese copper smelters (10).

In addition to meeting an emission standard, all sources must also pay a penalty for any sulphur oxide emissions, even if they are in compliance with the appropriate emission standards (8). The assessment rates are calculated each year on the basis of the costs of compensation benefits to respiratory victims and the nationwide emission volume. The assessment rates thus match the pollution conditions found in certain regions. However, to encourage pollution control, the government provides various financial incentives including construction loans and subsidies, accelerated depreciation, and tax reductions for nonpolluting equipment (8).

In Japan, emission control is based on regulating the total amount of sulphur released.

3.3.3 European Economic Community (E.E.C.)

On March 19, 1976, the E.E.C. proposed a directive on health protection standards for SO_2 concentrations associated with suspended particulates for urban atmospheres in Europe. The regulations cover health protection standards and exceptional concentrations and are shown in Tables 7 and 8 (9).

3.3.4 Republic of South Africa

The Palabora copper smelter is located in the Republic of South Africa, as are the Rustenburg, Impala and Marikana nickel-copper smelters.

Emission standards at the Palabora smelter require that 70% of the sulphur fed to the reverberatory smelter is recovered. Palabora fixes a total of 72% of the total sulphur fed to the smelter by treating converter

TABLE 6 COPPER-SMELTING TECHNOLOGY AND SO₂ EMISSION CONTROL PRACTICE IN JAPAN (10)

SME LTER	Copper capacity, 1,000 metric tons per year	Smelting process	Offgas SO ₂ , pct	Furnace gas treatment	Acid plant tail gas scrubber	Sulfur capture, pct
Ashio: Furukawa Mining Co. Hitachi: Nippon Smelting Co.	40 150	Flash furnace P-S converters Flash furnace, O ₂ enriched, P-S converters	- (1) 10-12 4- 6	St acid plant - DT acid plant ST acid plant	- - None do	91 97
Kosaka: Dowa Mining Co.	60	Flash furnace P-S converters	8-10 4- 6	do do	CaO slurry do	99
Naoshima: Mitsubishi Smelter Co. (2 systems).	150 50	Fluid-bed roaster Reverberatory furnace P-S converters 3-furnace continuous	11 (2) (3) 10	DT acid plant - - ST acid plant	None - - CaO slurry	98
Onahama: Onahama Smelting & Refining Co.	240	furnace Reverberatory furnace P-S converters	2-2.5 7- 9	1/2 to MgO scrubber, then strong SO ₂ to DT acid plant, 1/2 to CaO scrubber ST acid plant	CaO slurry	99
Sagaroseki: Nippon Mining Co.	150	Flash furnace O ₂ enriched, P-S converters	10-12 4- 6	DT acid plant ST acid plant	None NaOH solution	97
Tamano: Iishi Kyodo Smelting Co.	80	Flash furnace P-S converters	7- 8 (1)	DT acid plant	None	99
Toyo: Sumitomo Metal Mining Co.	120	Flash furnace P-S converters	7- 8 (1)	ST acid plant	NaOH solution	99

DT = Double train P-S = Peirce-Smith ST = Single train

- 1) Combined with flash furnace gas
- 2) Combined with continuous furnace gas
- 3) Combined with roaster gas

TABLE 7 HEALTH PROTECTION STANDARDS FOR SULPHUR DIOXIDE AND
SUSPENDED PARTICULATES IN URBAN ATMOSPHERES (E.E.C.) (9)

SULPHUR DIOXIDE

Reference period	Maximum concentrations	Associated concentrations of suspended particulates
Year	Median of daily means $80 \mu\text{g}/\text{m}^3$	Annual median of daily means $> 40 \mu\text{g}/\text{m}^3$
Year	Median of daily means $120 \mu\text{g}/\text{m}^3$	Annual median of daily means $< 40 \mu\text{g}/\text{m}^3$
Winter (October to March)	Median of daily means $130 \mu\text{g}/\text{m}^3$	Winter median of daily means $> 60 \mu\text{g}/\text{m}^3$
Winter (October to March)	Median of daily means $180 \mu\text{g}/\text{m}^3$	Winter median of daily means $< 60 \mu\text{g}/\text{m}^3$
24 hours	Arithmetic mean $250 \mu\text{g}/\text{m}^3$	Arithmetic mean of concentration over 24 hours $> 100 \mu\text{g}/\text{m}^3$
24 hours	Arithmetic mean $350 \mu\text{g}/\text{m}^3$	Arithmetic mean of concentration over 24 hours $< 100 \mu\text{g}/\text{m}^3$

SUSPENDED PARTICULATES

Reference period	Maximum concentrations
Year	Median of daily means $80 \mu\text{g}/\text{m}^3$
Winter (October to March)	Median of daily means $130 \mu\text{g}/\text{m}^3$
24 hours	Arithmetic mean $250 \mu\text{g}/\text{m}^3$

TABLE 8 EXCEPTIONAL CONCENTRATIONS FOR SULPHUR DIOXIDE AND
SUSPENDED PARTICULATES IN URBAN ATMOSPHERES (E.E.C.) (9)

SULPHUR DIOXIDE

Reference period	Maximum concentrations	Associated concentrations of suspended particulates
24 hours	Arithmetic mean $350 \mu\text{g}/\text{m}^3$	Arithmetic mean of concentration for 24 hours $> 100 \mu\text{g}/\text{m}^3$
24 hours	Arithmetic mean $500 \mu\text{g}/\text{m}^3$	Arithmetic mean of concentration for 24 hours $< 100 \mu\text{g}/\text{m}^3$

SUSPENDED PARTICULATES

Reference period	Maximum concentrations
24 hours	Arithmetic mean $300 \mu\text{g}/\text{m}^3$

Between 1982 and 1987, if unfavourable meteorological conditions exist, the daily levels given in Table 7 may be exceeded for 3 consecutive days before measures must be taken to reduce emissions, provided the levels given in Table 8 are not exceeded.

gases in two single absorption acid plants (51.5% S recovery as acid) and by scrubbing surplus gases with alkaline mill tailings (19.5% S fixation). A further 1% sulphur is contained in discard slag while 28% of the input sulphur is released to atmosphere.

3.3.5 West Germany

The Norddeutsche Affinerie copper flash smelter is located in Hamburg.

3.3.5.1 SO₂ Ambient Air Quality Standard

The Federal ambient air quality standard (9) is $140 \mu\text{g SO}_2/\text{Nm}^3$ on a yearly average, and $400 \mu\text{g SO}_2/\text{Nm}^3$ for (undefined) short-term exposure.

The valid ambient air quality and emission standards were not used as the basis for local government's permission to Norddeutsche Affinerie to build and operate the smelter. It was necessary to erect a 150 m high stack downstream of the double contact acid plant in order to disperse emissions which must be less than 240 kg/h. The stack is higher than would have been necessary to meet the Federal standards. Some 99.45% of the total sulphur entering the smelter is captured; as acid (95.3%), in slag (1.7%), in flue dusts and by products (1.3%), and in washing acid to the neutralization plant (1.15%). It is estimated that 0.40% of the sulphur is contained in the stack off-gas and 0.15% is lost in in-plant emissions.

3.3.6 Other Areas

Countries such as Chile, Peru, Zambia and Zaire have a well-established copper smelting industry employing, in general, traditional technology. Certain plants are, however, equipped with flash furnaces or electric furnaces. Whilst these countries are significant producers of copper, air pollution control regulations have not been formulated. However, where grass-roots or expansion smelter projects are funded by international financing agencies such as the World Bank, conditions are likely to be imposed whereby compliance with regulations similar to those in the U.S. will be required.

Canada produces the major share of the world's nickel supply from smelting nickel-copper sulphide concentrates. The study of Canadian smelters is outside the scope of this report. Other sulphide nickel-copper smelters are located in Australia, the Republic of South Africa, Botswana and Zimbabwe.

Regulations in these countries, where they exist, are not as severe as those in the U.S.A. or Japan. Some of these smelters treat off-gases in an acid plant whilst others discharge all gases to the atmosphere.

3.4 Particulate Emissions

As in the case of gaseous emissions, several countries have developed standards for ambient particulate concentrations and emissions in order to protect the workplace and environment. Regulations in some of the more important areas are outlined in the following sections.

3.4.1 U.S.A.

In the U.S.A. the following standards have been formulated:

3.4.1.1 Ambient Standard - as suspended particulates (6,8)

Federal Standard

The U.S. Department of Health, Education and Welfare estimates that adverse health effects begin when the dust content is higher than $80 \mu\text{g}/\text{m}^3$, while adverse effects on materials and vegetation can begin at $60 \mu\text{g}/\text{m}^3$ (11). This forms the basis of the following EPA guidelines:

1. Primary:

- (a) $75 \mu\text{g}/\text{m}^3$, annual geometric mean of 24-hr concentrations
- (b) $260 \mu\text{g}/\text{m}^3$, annual maximum of 24-hr concentrations

2. Secondary

- (a) $150 \mu\text{g}/\text{m}^3$, maximum 24-hr concentration, not to be exceeded more than once per year.
- (b) $60 \mu\text{g}/\text{m}^3$, annual geometric mean (as a guide to be used in assessing implementation plans to achieve the 24-hr standard).

State Standards

In general, the various States have adopted the same ambient standards as the national standard. Three States have adopted more stringent standards as shown in Table 9 (8). The standards in Arizona are the most severe.

3.4.1.2 Emission Standards - as particulates (6,8)

Federal Standard

As in the case for gaseous emissions, the Federal government sets the standard for new sources, and the various States regulate existing sources. The New Source Performance Standard (NSPS) for copper smelters is 0.05 gm/m^3 .

State Standards

The States have chosen different ways to regulate particulate emissions. A few States have standards aimed directly at smelters, but in most cases, smelters are included in a general category of industrial processes. Eleven of the sixteen States with non-ferrous smelters set the standards for existing industrial processes by the following formulae:

$$E = 4.10 (P^{0.67}) \quad (\text{process weight rate up to } 30 \text{ st/hr})$$

$$E = 55.0 (P^{0.11}) - 40.0 \quad (\text{process weight rate over } 30 \text{ st/hr})$$

where E = allowable emission rate (lb/hr)

P = process weight rate (s.t/hr)

Table 10 (8) presents the particulate emission standards for the five States with smelters that do not adhere to the above formulae. The U.S. regulations are typically based on the production rate and not the volume of particulate in the exhaust gas. New Mexico and Washington have set their emission standards in a manner similar to the Japanese, i.e. on the particulate content of the exhaust gas, and both States have more stringent standards than the Japanese national standards.

TABLE 9 U.S. AMBIENT SUSPENDED PARTICULATE STANDARDS ($\mu\text{g}/\text{m}^3$) (8)

	National primary	National secondary	Arizona	Montana	New Mexico
Maximum 24- hour geometric mean	260	150	100		
Maximum 24- hour average (annual)	75	60		200	
Maximum 24- hour average, not to be exceeded more than 1% of days in year					90
Maximum 30- day average					110
Maximum 7- day average					

TABLE 10 U.S. PARTICULATE EMISSION STANDARDS (8)

Illinois

New sources are regulated by the following formulas:

$$E = 2.54 (P^{0.534}) \text{ (Process weight rate up to 450 tons/hr)}$$

$$E = 24.8 (P^{0.16}) \text{ (Process weight rates over 450 tons/hr)}$$

where E = allowable emission rate (lb/hr), and

P = process weight rate (tons/hr)

New Mexico

Particulate emissions from nonferrous smelters cannot exceed 0.03 grain per standard cubic foot (0.074 g/m³)

Pennsylvania

All industrial sources are regulated by the following formula:

$$A = 0.76 E^{0.42}$$

where A = allowable emissions

E = emission index (F x W lb/hr)

F = process factor (lb/unit)

W = production or charging rate (units/hr)

The process factors (F) are given as follows for primary lead and zinc smelting:

Process	Primary lead	Primary zinc
Roasting	0.004 lb/ton ore feed	3 lb/ton ore feed
Sintering-windbox	0.02 lb/ton sinter	2 lb/ton product
Reduction	0.5 lb/ton product	10 lb/ton product

TABLE 10 (CONTINUED) U.S. PARTICULATE EMISSION STANDARDS (8)Tennessee

New sources are regulated by the following formulas:

$$E = 3.59 (P^{0.62}) \text{ (Process weight rates up to 30 tons/hr)}$$

$$E = 17.31 (P^{0.16}) \text{ (Process weight rate over 30 tons/hr)}$$

Texas

All sources not covered by other standards are regulated by the following formulas:

$$E = 3.12 (P^{0.985}) \text{ (Process weight rate up to 20 tons/hr)}$$

$$E = 25.4 (P^{0.287}) \text{ (Process weight rate over 20 tons/hr)}$$

Utah

85 percent particulate control is required for process units or systems emitting one ton or more of particulate annually, based on zero control.

Washington

Particulate emissions from industrial sources cannot exceed 0.10 grain per standard cubic foot (0.25 g/m^3).

3.4.2 Japan

3.4.2.1 National Ambient Standard - as suspended particulate (8)

The Japanese national standards for suspended particulate matter are:

- (a) Average of hourly values as measured in 24 consecutive hours should be $100 \mu\text{g}/\text{m}^3$ or less.
- (b) Any hourly value should be $200 \mu\text{g}/\text{m}^3$ or less.

The Japanese standards are more stringent than the U.S. national standards, as in the case with the NAAQS for SO_2 . More stringent standards may exist in Japanese prefectural and local standards than at the national level.

3.4.2.2 Emission Standards

The Japanese national particulate emission standards are given in Table 11 (8). The standards depend on gas emission rates, and for smelter processes they are:

$0.40 \text{ g}/\text{Nm}^3$ for less than $40,000 \text{ Nm}^3/\text{hr}$ gas

$0.30 \text{ g}/\text{Nm}^3$ for more than $40,000 \text{ Nm}^3/\text{hr}$ gas

New sources in heavily polluted districts must meet the special emission standard of $0.20 \text{ g}/\text{Nm}^3$. These source standards are probably not adequate to meet the present ambient standards, although regulation at the prefectural and local levels is more severe.

3.4.3 European Economic Community (E.E.C.)

The standards covering concentration of suspended particulates have been referred to in Section 3.3.3 and are given in Tables 7 and 8 (9).

TABLE 11 JAPANESE PARTICULATE EMISSION STANDARDS (8)

(June 24, 1973)

(in g/Nm³)

Name of Facility	New Standard			
	Ordinary Emission Standard		Special Emission Standard	
	Large Scale	Small Scale	Large Scale	Small Scale
Boiler (Heavy oil is used as fuel)	0.10	0.20 0.30	0.05	0.20
(Coal is used as fuel)	0.40		0.20	
Blast furnace	0.10		0.05	
Converter (combustion furnace) Open-hearth furnace Roasting furnace, sintering furnace, calcination furnace	0.30	0.40	0.20	
Heating furnace Cement sintering furnace, smelting furnace Electric furnace for steel-making Direct fire furnace, reaction furnace, drying furnace	0.20	0.40	0.10	0.20
Waste incinerator (continuous furnace)	0.20	0.70	0.10	0.20
Waste incinerator (others)	0.7		0.40	

Notes:

1. Nm³ denotes normal cubic meters (at 0°C and 1 atmospheric pressure).
2. The new standards specify standard values for each scale. Facilities are classified into two scales (three scales for heavy oil boiler). Strict standards are applied to large scale facilities.
3. The gas emission rate of 40,000 Nm³/h is the criterion used for scale classification. However, heavy oil boilers alone are classified into three scales with the criteria of 200,000 Nm³/h and 40,000 Nm³/h for ordinary emission standards.
4. The special emission standards apply to those facilities which are newly installed in polluted districts.

4 MAJOR SMELTERS - LOCATION, CAPACITY, SO₂ CONTROL

The location, capacity (greater than 25,000 tpa) and methods of SO₂ control at many of the major world copper smelters are given in Table 12 (5,8). Nickel and nickel-copper smelters are also shown in the table. Only those smelters treating sulphide concentrates are listed.

The greatest concentration of copper smelters occurs in Japan and in Arizona and that State's immediate neighbourhood. Other major copper smelting areas are Chile, Peru, Zambia and Zaire. Canada and the U.S.S.R. also have major copper smelters. Other smelters, generally of smaller capacity, are scattered worldwide.

The major nickel and nickel-copper sulphide smelter capacity is located in Canada. Other significant nickel smelters are located in South Africa, the U.S.S.R. and Australia.

Table 12 illustrates that production of sulphuric acid is the accepted control approach for recovering SO₂ from smelter gases. Older smelters, consisting of reverberatory furnaces and Peirce-Smith converters, are able to capture from 50-70% of the sulphur entering the smelter in concentrates when converter gases are treated in an acid plant. Modern flash smelters are able to capture in excess of 99% of the sulphur in feed material when flash furnace and converter gases are treated in an acid plant and tail gases from the latter are scrubbed.

TABLE 12 MAJOR SMELTERS - LOCATION, CAPACITY, SO₂ CONTROL (5)

COPPER SMELTERS	TPY Cu	SMELTING PROCESS	TYPE OF CONTROL	% S CAPTURE
NORTH AMERICA:				
United States:				
Asarco	100,000	MHR	acid	75
Asarco	170,000	R	acid	55
Asarco	100,000	MHR	acid	45
Cities Service	82,000	FBR	acid	93
Copper Range	80,000	R	PSC	-
Inspiration Cons.	140,000	EF	HC	87
Kennecott Copper	250,000	N	acid	88
Kennecott Copper	70,000	R	acid	91
Kennecott Copper	80,000	R	acid	65
Kennecott Copper	50,000	R	PSC	-
Magma Copper	180,000	R	acid	60
Phelps Dodge	60,000	R	acid	60
Phelps Dodge	100,000	R	-	-
Phelps Dodge	180,000	R	acid	60
Phelps Dodge	150,000	FF	acid	90
El Paso, Texas				
Hayden, Arizona				
Tacoma, Washington				
Copperhill, Tennessee			liq SO ₂	
White Pine, Michigan				
Inspiration, Arizona				
Garfield, Utah				
Hayden, Arizona				
Hurley, New Mexico				
McGill, Nevada				
San Manuel, Arizona				
Ajo, Arizona				
Douglas, Arizona				
Morenci, Arizona				
Playas, New Mexico				
Canada:				
Falconbridge	30,000	FBR	acid	64
INCO	180,000	IFF	PSC	70
Noranda Mines	220,000	N/R	PSC	-
Gaspe Copper	80,000	R	acid	64
Hudson Bay	60,000	MHR	PSC	-
Afton Mines	27,000	R	d. alk	95
Texasgulf*	59,000	M	acid	99
Falconbridge, Ontario				
Copper Cliff, Ontario				
Noranda, Quebec				
Murdochville, Quebec				
Flin Flon, Manitoba				
Kamloops, British Columbia				
Timmins, Ontario				
Mexico:				
Industrial Minera	40,000	BF	acid	-
Min. de Cananea	70,000	R	PSC	-
SOUTH AMERICA				
CHILE:				
Compania de Cobre	60,000	R	PSC	-
Compania de Cobre	250,000	R	PSC	-
Minera de Teniente	180,000	R	PSC	-
Empresa Nacional	70,000	R	PSC	-
Empresa Nacional	60,000	R	HC	-
Paipote			acid	
Potrerillos				
Chuquibambilla (including e.w.)				
Caletones				
Las Ventanas				
Paipote				
Peru:				
Southern Peru Copper	100,000	R	PSC	-
Centromin	57,000	R	PSC	-
Ilo				
La Oroya				

*commissioning mid - 1981

TABLE 12 MAJOR SMELTERS - LOCATION, CAPACITY, SO₂ CONTROL (5) (CONTINUED)

COPPER SMELTERS	LOCATION	TPY Cu	SMELTING PROCESS	TYPE OF CONTROL	% S CAPTURE
<u>AUSTRALIA:</u>					
Mt. Isa Mines	Mt. Isa	160,000	FBR	-	-
Elect. Ref. & Smelting	Port Kembla	30,000	S	-	-
Peko Wallsend	Tennant Creek	35,000	FF	-	-
<u>ASIA:</u>					
Japan:					
Dowa Mining	Kosaka	50,000	FF	acid	99
Furukawa Mining	Ashio	40,000	FF	acid	91
Mitsui Mining	Tamano	60,000	BF	acid	
Hibi Kyodo	Tamano	122,000	FF	acid	99
Mitsubishi Metal	Naoshima	160,000	FF	acid	98
Nippon Mining	Hitachi	80,000	R/M	acid	
Nippon Mining	Saganoseki	170,000	FF	acid	97
Onahama Smelting	Onahama	190,000	FF	acid	99
Rasa Industry	Miyako	30,000	R	acid	
Sumitomo	Toyo	180,000	FF	acid	99
India:					
Hindustan Copper	Khetri	30,000	FF	acid	
Korea:					
Korea Min. & Smelting	Chang Hang	50,000	BF	-	-
Turkey:					
Black Sea Copper	Samsun	40,000	FF	acid	
<u>SOVIET UNION (Sutulov 1973)</u>					
Balkhash					
Dzhezkazgan	Kazakhstan	400,000			
Karsakpai					
Irtysk					
Almalyk	Uzbekistan	120,000			
Krasnouralski					
Kirovogradski					
Sredneuralski	Urals	350,000			
Karabanski					
Mednogorski					
Alaverdi	Armenia	100,000			
Norylsk	Siberia				
Pechenga	Kola Peninsula	120,000			

TABLE 12 MAJOR SMELTERS - LOCATION, CAPACITY, SO₂ CONTROL (5) (CONTINUED)

COPPER SMELTERS	LOCATION	TPY Cu	SMELTING PROCESS	TYPE OF CONTROL	% S CAPTURE
<u>EUROPE:</u>					
Austria:					
Montanwerke Brixlegg	Brixlegg	30,000	FBR EF	acid	
Belgium:					
Metallurgie Hoboken	Hoboken	30,000	BF HC	acid	
Finland:					
Outokumpu Oy	Harjavalta	50,000	FF PSC	acid	95
Poland:					
Kombinat GMHL	Glogow	300,000	BF/FF HC	acid	96
Kombinat GMHL	Lignica	100,000	BF HC		
Spain:					
Rio Tinto Patino	Huelva	90,000	BF FF PSC	acid	90+
Sweden:					
Boliden Aktiebolag	Ronnskar	60,000	MHR EF PSC TBRC	acid liq SO ₂	
West Germany:					
Norddeutsche Affinerie	Hamburg	80,000	FF PSC	acid	99
Duisburger Kupferhutte	Duisburg	30,000			
Yugoslavia:					
Rudarsko-Topioncarski	Bor	150,000	MHR R PSC	acid	70
<u>AFRICA:</u>					
Republic of South Africa:					
O'Okiep Copper	Nababeep	40,000	R PSC		
Palabora Mining	Phalaborwa	140,000	R PSC	acid, tgs	72
Zimbabwe:					
Lomagundi Smelting	Alaska	40,000	R PSC		
South West Africa:					
Tsumeb Corp.	Tsumeb	70,000	R PSC		
Zaire:					
Gecamines	Lubumbashi	160,000	BF PSC	-	-
Zambia:					
Nchanga Consolidated	Kitwe	300,000	R PSC	acid	
Roan Consolidated	Luanshya	120,000	R PSC	-	-
Roan Consolidated	Mufulira	200,000	EF PSC	-	-

TABLE 12 MAJOR SMELTERS - LOCATION, CAPACITY, SO₂ CONTROL (5) (CONTINUED)

NICKEL SMELTERS	LOCATION	TPY Ni-Cu	SMELTING PROCESS	TYPE OF CONTROL	% S CAPTURE
<u>NORTH AMERICA:</u>					
Canada:					
Falconbridge	Falconbridge, Ontario	70,000	FBR	acid	64
INCO	Copper Cliff, Ontario	250,000	MHR	-	-
INCO	Thompson, Manitoba	46,000	FBR	-	-
<u>AUSTRALIA:</u>					
Western Mining	Kalgoorlie, W.A.	60,000	FF	-	-
<u>SOVIET UNION:</u>					
Norilsk	Norilsk	160,000	FF	PSC	
<u>EUROPE:</u>					
Finland:					
Outokumpu Oy	Harjavalta	10,000	FF	PSC	95
<u>AFRICA:</u>					
Republic of South Africa:					
Impala Platinum	Impala	10,000	EF	-	-
Rustenburg Platinum	Rustenburg	9,000	EF	acid	90+
Western Platinum	Marikana	3,000	EF	-	-
Zimbabwe:					
Empress Nickel	Gatooma	5,000	R	PSC	-
Bindura Nickel	Bindura	7,000	EF	PSC	-
Botswana:					
BCL	Selebi-Pikwe	32,000	FF	PSC	-

Legend

FBR - fluid bed roaster
 MHR - multi-hearth roaster
 S - sinter plant
 BF - blast furnace
 R - reverberatory furnace
 EF - electric furnace
 FF - Outokumpu flash furnace
 IFF - Inco oxygen flash furnace
 N - Noranda reactor
 ELT - El Teniente reactor
 M - Mitsubishi continuous smelting process
 PSC - Peirce-Smith converter
 HC - Hoboken converter
 TBRC - top blown rotary converter
 tgs - tail gas scrubbing

SMEETING TECHNOLOGY

In general, the pyrometallurgical processes and technology used for the extraction of nickel from sulphide concentrates are similar to those used in copper smelting, although in the latter, a far wider range of smelting processes are in use, due mainly to the structure of the industry and number of process licensors vending technology. The continuous smelting processes have not yet been applied to the nickel industry.

Common thermodynamic principles apply in the smelting of copper concentrates to blister copper, regardless of which smelting process is employed. The principal difference between processes is of an engineering nature, i.e. the design and characteristics of the particular furnaces used. The overall smelting process is divided into a number of unit operations.

With the exception of roasting and sintering where desulphurization of concentrate takes place in the solid state, concentrate is first smelted to produce a liquid copper-iron sulphide matte of varying grade, depending on concentrate composition and on the characteristics of the process used. In certain cases, matte grade is determined by metallurgical constraints such as impurity content. The resulting matte is further oxidized to blister copper, generally in another furnace or converter. Both smelting and converting are essentially iron removal and desulphurization processes. In smelting, the sulphur present in concentrate as complex mineral sulphides (and occasionally as labile sulphur) is oxidized to SO_2 , while in converting the sulphur present as a constituent in liquid sulphide matte is also converted to SO_2 . At the same time as desulphurization is taking place, iron sulphides are oxidized to FeO (and a certain amount of magnetite) which enters a slag phase on the addition of fluxes. In certain smelting processes, the quantity of iron in the matte can be controlled by adjusting the degree of oxidation of the charge. After the oxidation of any labile sulphur present, the amount of sulphur removed as SO_2 is proportional to the amount of iron oxidized.

In the case of nickel smelting, the metal is also present in association with iron and sulphur, and usually copper and cobalt are present to a varying but lesser extent. The thermodynamic properties of the sulphides and oxides of these metals are such that in the presence of oxygen, each of

the sulphides is unstable with respect to its corresponding oxide (13). In addition, iron has the greatest affinity for oxygen, followed by cobalt, nickel and copper. This thermodynamic relationship explains the minor differences that exist between copper and nickel smelting technology. The furnaces used to smelt nickel concentrates to matte are similar to those used in the copper industry. However, because of the relatively high affinity of nickel for oxygen, on conclusion of the slag blow metallic nickel can only be produced from the remaining nickel sulphide under conditions of high temperature (1500°C), an oxygen atmosphere and intimate contact between the reactants. These conditions would be very difficult to achieve in the conventional (Peirce-Smith) converter used in the copper industry. The reaction conditions in the Peirce-Smith converter would favour the formation of nickel oxide which would enter a slag phase and could only be reduced to metallic nickel with great difficulty, the end-point being difficult to control. The favoured treatment route in a nickel smelter is the production of a high-grade Bessemer matte (essentially a nickel sulphide containing any copper and cobalt present as sulphides, and a residual amount of iron) in a Peirce-Smith converter. This matte undergoes further treatment and refining to produce metallic nickel. Metallic nickel can be produced from nickel sulphide directly in a top-blown rotary converter (TBRC) which uses an oxygen atmosphere and a reaction temperature of around 1500°C .

This review of smelting technology addresses itself to the principal differences between the various smelting processes in terms of the matte grade produced, the resulting tenor ($\% \text{SO}_2$), volume and continuity of the gas streams emitted from the oxidation reactions taking place in the various furnaces, and the effect thereof on SO_2 pollution control technology.

5.1 Roasting

In the pyrometallurgical extraction of copper, low grade concentrates (i.e. those concentrates containing less than 20% Cu and correspondingly large quantities of pyrite) are generally partially roasted to form a calcine prior to being smelted in a reverberatory furnace or an electric furnace. Roasting, which involves oxidation of any labile sulphur present followed by partial oxidation of iron sulphides, increases the concentration of

copper in the matte produced from smelting the calcine, as compared with smelting 'green' concentrate where a 'natural' matte grade is produced. A further benefit of roasting is that the charge is dried and preheated prior to smelting, which results in reduced fuel or power requirements for smelting. Typically, from 40 to 50% of the sulphur present in concentrate is oxidized during partial roasting by control of the air:concentrate ratio. Roasting may be carried out in multiple hearth or fluid bed roasters, the latter being more modern, at a temperature in the range of 500 - 700°C. Roasting is often autogenous, depending on the degree of oxidation and matte grade desired, but the heat balance may dictate the addition of hydrocarbon fuel to the roaster to compensate for a heat deficit.

Roasting of sulphide copper concentrates is also carried out prior to the extraction of copper by hydrometallurgical methods. The sulphide minerals of copper are not easily leached but its sulphates (partial roast) are soluble in water and its oxides (dead roast) are soluble in dilute sulphuric acid. Thus a controlled roasting of sulphides can produce a readily leachable calcine. Gas strength is typically in the range of 3-7% SO_2 in these fluid bed roasting processes.

Due to low oxygen utilization and the ingress of dilution air into multiple hearth roasters, much of which is deliberate in order to control roasting conditions, the effluent gas strength is typically less than 5% SO_2 , whereas in fluid bed roasters, where oxidation conditions are more closely controlled due to high gas-solids contact efficiency, the off-gas may contain 10 - 15% SO_2 . Above 5% SO_2 , the gas strength is sufficiently high for economic conversion to sulphuric acid. The gas volume is essentially constant and continuous.

The design of multiple hearth roasters, with their many openings at each hearth level, is such that the fugitive dust and gaseous emissions can become particularly severe in the plant, especially when accretions of sticky sulphates adhere to the flues causing a back pressure in the system. As a result of this and low unit capacity, the multiple hearth roaster has been gradually replaced by the fluid bed roaster which is a fully encapsulated vessel which also produces a higher strength gas. Advances in mineral dressing techniques in recent years have enabled concentrates to be upgraded considerably

by the rejection of pyrite. The introduction of flash and other new, energy-efficient smelting technologies which incorporate the roasting stage in the primary smelting process, have reduced the need for separate roasting units. In a few cases, where low-cost power is available, roasting followed by electric smelting may be competitive with other modern smelting processes and would merit serious consideration. In addition, when concentrates contain significantly large amounts of volatile impurities (eg. Bi, As) a roasting stage is likely to be required. These impurities are volatilized and collected in flue dust which is not recycled to the smelting process. (Bi and As dissolve readily in matte during smelting and are subsequently difficult to eliminate by volatilization during converting once the formation of copper commences).

The multiple hearth roaster is fed with filter cake whereas the fluid bed roaster may be fed with either filter cake or slurry. In the latter case, owing to the large amount of water vapour in the gases, the SO_2 concentration is lower on a wet basis.

Similar conditions prevail in roasting of nickel concentrates, although slight oxygen enrichment of reaction air is sometimes used. This results in an off-gas strength at the upper part of the range previously mentioned. In the partial roasting of nickel concentrates, it is mainly pyrrhotite (Fe_7S_8) that is oxidized.

5.2 Sintering

Sintering, which is essentially a partial roasting and agglomeration operation carried out on a travelling grate, is used to prepare charge for smelting in a blast furnace. The process is now virtually obsolete in the copper and nickel smelting industries and would not be considered for any new smelter because of the environmental problems associated with fugitive dust and gas emissions and also because of the difficulty of capturing high strength gases from the sinter machine for sulphur fixation. In addition, the blast furnace has largely been replaced by more efficient, economical, and environmentally acceptable smelting processes, thereby rendering the sinter machine obsolete for this application.

In certain cases, mixed sulphide-oxide ores (of around 1 cm size and less) used to be sintered for desulphurization prior to being smelted in a blast furnace. Flotation concentrates need to be pelletized before being sintered to prevent large dust losses on the sinter strand and in the blast furnace and to keep the charge in the latter open. Desulphurization is typically around 40 to 50% and undersize material from the sinter strand is recycled in order to control temperature and sulphur content of the final sinter product. The large ingress of air around the sinter strand leads to a heavily dust-laden off-gas containing about 2% SO_2 which is too lean for economic sulphur capture and fixation. The few remaining sinter strands are generally at small operations in lesser developed countries where environmental regulations are not in existence.

5.3 Blast Furnace

As mentioned in the previous section, blast furnace smelting in both the copper and nickel industries has largely been superseded by more energy-efficient, economic and environmentally acceptable processes. The occurrence of high-grade lump ores, suitable for direct smelting in a blast furnace, has also diminished significantly and with the advent of flotation technology for sulphide ores, blast furnaces have been replaced by more energy-efficient and modern smelting processes capable of treating fine-grained concentrates. The unacceptably high fugitive dust and gas emissions from sinter machines used for partial roasting and agglomeration of charge for the blast furnace, and from the blast furnace itself, have contributed towards closure of most blast furnace - sinter plants. The high cost of metallurgical coke, which typically comprises about 10% of the blast furnace burden, has adversely affected the economics of the process. Productivity in blast furnaces is low compared with that in the modern smelting processes.

Air is injected through tuyeres above the blast furnace crucible for combustion of the coke which provides the heat for smelting the charge. Some desulphurization of the iron sulphides also takes place, thereby increasing the matte grade slightly above the 'natural' grade. The degree of desulphurization is, however, only moderate and because of the large volume of air

blown through the tuyeres together with the large amount of dilution air ingressed into the top of the furnace through the charging doors and into the off-gas flue, the gas strength is low and generally in the range 2-5% SO_2 . Oxygen enrichment of tuyere air to about 26% O_2 has been practised which, with minimum ingress of dilution air, produces a gas strength at the upper limit of this range. The off-gases are heavily laden with dust which is recovered in cyclones and electrostatic precipitators. The gases are generally unsuitable for sulphur capture and fixation and the low gas temperature does not permit recovery of waste heat. The Momoda-type blast furnace, which incorporates modifications to design and charging practise, has enabled SO_2 to be recovered as sulphuric acid.

Blast furnaces may be circular or rectangular in cross-section. In copper smelting blast furnaces, matte and slag are tapped separately from the forehearth, whereas in copper-nickel smelting, it is more usual to employ an external forehearth where increased residence time and more quiescent bath conditions improve the settling of matte from slag and reduce metal losses in the slag accordingly. Since the forehearth requires external heating, adequate off-gas handling and ventilation systems are required.

5.4 Reverberatory Furnace Smelting

Reverberatory furnaces, for many years, until the development of flash smelting technology was fully commercialized, were the mainstay of the copper smelting industry. Many of these older smelters are still in existence and it is principally these smelters which are unable to comply with ambient air quality and emission standards. As a result, many plants are under pressure to adopt modern technology or to curtail production.

Reverberatory furnaces are either fed with flotation concentrate filter cake (green charge) or with calcine from roasters (hot charge). Melting of the fluxed charge takes place by firing with hydrocarbon fuel, separately from the material being smelted. Only a minor amount (10-15%) of desulphurization of the charge takes place in the freeboard, and in the bath from reduction of magnetite, and so effectively a 'natural' matte grade is produced.

Because the process does not make use of the inherent energy in the concentrate by oxidation of iron sulphides, as in modern processes, the gas strength is low in SO_2 (0.5 - 2%). The off-gas essentially results from combustion of the fuel and from the ingress of dilution air which can be considerable. Rigidly controlling furnace draught and tight sealing of flues and dust collection systems minimizes the infiltration of dilution air, but the effect on gas strength is not generally significant. Gas flow is continuous and the gases are suitable for waste heat recovery due to their high volume and temperature (1250°C) but they are too lean to permit economic recovery of SO_2 as sulphuric acid. The gases are therefore generally vented directly to atmosphere after dust removal. As an alternative to discharging furnace gases to the atmosphere, if a high degree of oxygen enrichment of combustion air is used, it may be feasible to combine the gases with converter and/or roaster gases to achieve an aggregate concentration of about 5% SO_2 which is suitable for sulphuric acid manufacture. However, the inclusion of a large volume of dilute reverberatory furnace gases would greatly increase the size of the acid plant. Oxygen enrichment of combustion air (to about 30% O_2) is frequently employed but the increase in gas strength is only marginal. The Onahama smelter in Japan produces reverberatory furnace gas at 2½% SO_2 using this technique and recovers the SO_2 as sulphuric acid in a modified acid plant, but uneconomically (14).

In smelting of nickel concentrates, the charge is generally roasted first to produce a calcine but the gas strengths are similar to those in copper smelting.

The process is thermally inefficient because the energy content of the concentrate is not utilized, despite the recovery of waste heat from the off-gases which carry up to 50% of the heating value of the fuel as sensible heat.

In copper smelting, the matte grade varies in the range 25 - 60% Cu which means that a large part of the overall oxidation to blister copper must take place in the converters, a batch operation with variable and intermittent gas flow. In nickel smelting, matte grades are in the range 15 - 20% Ni + Cu.

New smelting capacity, either greenfield or plant expansions, is unlikely to include reverberatory furnaces because the process represents a serious pollution problem. In addition, because the process relies on large amounts of high cost hydrocarbon fuel to melt the charge, process economics are poor. Exceptions are likely to be very small capacity plants of around 20,000 tpy Cu in countries where there are no environmental regulations and where fuel is relatively cheap and isolated from world prices.

5.5 Electric Furnace Matte Smelting

Electric furnaces treat either concentrate or calcine, performing a similar function to the reverberatory furnace, and smelt to matte of 'natural' grade in the range of 35 - 60% Cu, or in the nickel industry in the range 15 - 30% Ni + Cu. The energy for smelting is generated in the form of resistance heating produced by the passage of electric current through electrodes submerged into the slag layer. Because fuel is not burnt in the furnace, gas volumes should be low compared with reverberatory furnace and other smelting methods. However, in order to maintain sufficient furnace draught, a certain amount of dilution air is ingressed through furnace openings. The amount of infiltration air determines the SO_2 content of the effluent gases because the SO_2 is derived from desulphurization of charge in the freeboard as well as from magnetite reduction in the bath. The SO_2 content of effluent gases may vary in the range 0.5 - 5% SO_2 , depending on the amount of infiltration air and whether calcine or concentrate is charged. The higher strength gas may be combined with roaster and/or converter gases for recovery of SO_2 as sulphuric acid. Electric furnaces operating in South Africa smelting low-grade nickel-copper concentrates typically have a gas strength of around 0.5% SO_2 (5).

Electric smelting will continue to be attractive in locations where the power cost is low and where there is a projected low cost escalation factor compared with fossil fuels, and where high temperatures are required to effect smelting, as in the case of concentrates containing significant quantities of MgO or Al_2O_3 which demand high slag temperatures. Electric furnace matte smelting

is very versatile in that it can smelt all materials.

Dried charge is fed through the roof of an electric furnace to form 'black top' conditions, i.e. a complete covering of the slag layer, such that the furnace gases are at a low temperature (400°C) and maximum heat transfer between the slag and the charge takes place. This is generally easy to achieve when charging calcine, but in the case of dried concentrate 'black top' conditions may be difficult to maintain, particularly if the concentrate exhibits pyrophoric properties. In this instance, the gas temperature may rise to 800°C due to roasting of sulphides in the charge in the furnace free-board. The ingress of dilution air promotes roasting and the 'stack effect' produced by the long charge pipes and hot gases can lead to serious fugitive dust and gas emission problems above the furnace in the building. In addition, because electric furnace gases are at a low volume and low temperatures, gas cooling and waste heat recovery facilities are not provided. Combustion may therefore arise in the electrostatic precipitator if the gas temperature rises too high.

The principal technical disadvantage of electric smelting, as in the case of reverberatory smelting, is that it does not make use of the energy which is potentially available from oxidizing the sulphide minerals of the charge. Production of a 'natural' matte grade also means that most of the oxidation, and hence liberation of SO_2 , takes place in the converters, a batch process with variable and intermittent gas flow. Compared with other modern processes, electric furnace smelting is not the most suitable for capture and recovery of SO_2 as sulphuric acid and its application will probably be determined on economic rather than technical grounds.

5.6 Flash Smelting

Two basic flash smelting processes have been developed independently by Outokumpu in Finland and Inco in Canada. The Outokumpu process is being used to smelt Cu, Ni and Cu-Ni concentrates in various parts of the world. Variants of the basic process are in use in Japan (Furukawa) and Australia (Western Mining). The Inco process smelts Cu concentrates although a successful campaign smelting Ni concentrates has been reported.

A common feature is that the processes make use of the energy available from oxidizing part of the sulphide minerals in the concentrate. This results in upgrading of the matte above its 'natural' grade and in the production of a continuous stream of effluent gases suitable for the recovery of SO_2 as sulphuric acid, elemental sulphur or liquid SO_2 . Energy costs are considerably lower than those in reverberatory and electric smelting. The quantity of iron in the matte (and hence the matte grade) can be controlled by adjusting the degree of oxidation of the charge (i.e. the oxygen:concentrate ratio). The amount of sulphur removed as SO_2 is proportional to the amount of iron oxidized. It is possible, by suitable adjustment of the oxygen:concentrate ratio, for the smelting reactions to become autogenous, i.e. oxidation is carried to the point where smelting is sustained without the addition of fuel to the furnace. Oxygen enrichment of combustion air is used to achieve autogenous smelting and the gas strength is increased accordingly because of the reduced nitrogen input in the air to the furnace.

5.6.1 Outokumpu Flash Smelting

Outokumpu have continuously developed flash smelting technology since 1949 when their first commercial furnace was built in Finland. This process is generally regarded as the modern standard against which other processes are compared and flash furnaces have accounted for most of the new smelting capacity since 1965.

Concentrate is smelted in the furnace reaction shaft in association with air (which may be preheated), or oxygen-enriched air. Matte and slag separate in the furnace settler. Depending on oxidation conditions, the matte grade varies between 45 - 65% Cu, with modern practice tending towards the upper part of the range. Fuel may be burnt in the reaction shaft and settler depending on the heat deficiency as determined by the respective heat balances. The autogenous point is reached when combustion air contains about 35% O_2 when smelting a chalcoppyritic copper concentrate. When smelting nickel concentrate, the autogenous point occurs at about 55% O_2 in air.

Dust-laden off-gases leave the furnace via an uptake shaft which leads into a waste heat boiler where the gases are cooled and part of their sensible heat content is recovered. Electrostatic precipitators collect the dust for recycling to the furnace.

Oxidation to as high a matte grade as practicable in the flash furnace, consistent with impurity elimination constraints, magnetite formation and smooth converter operation, is desirable from emission control considerations. The maximum amount of SO_2 will be evolved in the primary smelting process giving a continuous, relatively high strength gas flow. Effluent gases from the Outokumpu flash smelting process contain from 10 - 15% SO_2 , or if oxygen-enriched combustion air is used, up to 30% SO_2 can be achieved. These gases are eminently suitable for SO_2 capture and fixation.

5.6.2 Inco Oxygen Flash Smelting

The Inco oxygen flash smelting process differs in detail from the Outokumpu process. In the case of the Outokumpu process, oxygen is employed to give a selected matte grade, while in the Inco process, the matte grade is a consequence of using tonnage oxygen (98% O_2) and the concentrate composition. The process uses only tonnage oxygen instead of air to bring about oxidation. Concentrate and oxygen are blown horizontally into the furnace above the molten bath at each end of the furnace whilst the off-gases leave the furnace via a central offtake. The smelting reactions are auto-genous and, because the nitrogen content of air is entirely replaced by oxygen, together with the absence of fuel combustion products, the gas volume (per tonne of charge) is much lower and of higher strength (70 - 80% SO_2) than in the Outokumpu variant of flash smelting.

The Inco flash furnace is steel-encased and so it is virtually gas-tight. This prevents cooling of the gases due to air infiltration and maintains the effluent gas at high strength. Although the off-gas temperature is high (1250°C), the small gas volume means that the sensible heat content of the gases is not large enough to justify a waste heat boiler to cool the gases and recover heat.

Because nitrogen in the combustion air is replaced by oxygen, there is naturally no nitrogen in the waste gases. As a result, the Inco flash furnace is unable to dissipate in waste gas the heat generated from the oxidation reactions to the same extent as the Outokumpu furnace. The total heat content of the gases is much less and so the autogenous point is reached at a matte grade of between 45 - 50% Cu, as compared with 60 - 65% Cu in the Outokumpu furnace with about 35% O_2 in air, depending on concentrate composition. This means that in an Inco flash smelter, a greater amount of oxidation has to be carried out in the converters. Depending on the amount of dilution air ingressed into converter hoods, the overall gas volume in an Inco flash smelter may be larger than in the Outokumpu case. However, the high strength gas from an Inco furnace is suitable for collecting as liquid SO_2 , or for conversion to sulphuric acid after conditioning and dilution. The low gas volume results in a lower dust carry-over into the electrostatic precipitators which accordingly can be of smaller rating.

5.6.3 Furukawa Flash Smelting

The Furukawa flash furnace is very similar in design to the Outokumpu furnace except that there are three electrodes in the settler. This practice may eliminate the need for a separate slag cleaning furnace when operating at moderate matte grade, since reducing conditions can be maintained in the settler. Electric power is used to maintain control over slag temperature and viscosity which obviates the need to burn fuel in the settler to maintain bath temperature. However, considerable quantities of fuel are used in the process in the reaction shaft and in preheating combustion air to $450^{\circ}C$. The matte grade at the Tamano smelter in Japan, where the Furukawa process is in operation, averages 50% Cu. The gas strength is around 10% SO_2 . A similar furnace with electrodes in an extended settler smelts Ni concentrates at the Western Mining smelter in Australia.

5.7 Mitsubishi Continuous Smelting and Converting

Most copper smelting processes comprise several unit operations, some of which are batch in nature, in producing blister copper from sulphide concentrates. The result is that certain gas streams are discontinuous and

gas volumes and strengths from the various stages are variable. This is undesirable with respect to the capture and fixation of SO_2 .

The Mitsubishi process is a continuous, multi-step process, which produces a continuous, uniform strength of effluent gas permitting efficient collection for SO_2 recovery. The smelting, slag cleaning and converting furnaces are interconnected by heated, enclosed launders, thereby eliminating matte tapping and transfer by crane and the fugitive emissions that emanate therefrom. Liquid products flow by gravity from one furnace to another along the launders.

The Mitsubishi process is in operation on a small commercial scale in Japan and the first full-scale (65,000 tpy) plant will be brought into operation in Timmins by Texasgulf in 1981.

Dried concentrates are smelted in an oxygen-enriched (35% O_2) air blast in an oval-shaped furnace which is also fired with oil to compensate for the heat deficit. Both charge materials and oxygen-enriched air are blown through vertical lances above the bath. A matte (65% Cu) - slag emulsion flows by gravity into an elliptical-shaped electric slag cleaning furnace where discard slag is produced and granulated. After settling, the matte flows to a converting furnace for continuous oxidation into blister copper. In this furnace, oxygen-enriched air (26% O_2) is blown through vertical lances above the bath.

The gas strengths from the smelting and converting furnaces are about 17% and 19% SO_2 , respectively, and since the gas flows are continuous, they are suitable for recovery of SO_2 as sulphuric acid. The gas strength entering the acid plant, after dilution, would typically be 14% SO_2 with a range of 10 - 16% SO_2 . Because matte transfer by crane is eliminated, the Mitsubishi process would appear to offer one of the best solutions in overcoming the problems associated with process and fugitive emissions.

The Mitsubishi continuous smelting process has been developed for smelting copper concentrates. Impurity content of concentrates may limit wide-scale application of the process.

5.8 Noranda Process

The Noranda process was originally conceived as a single-step process to produce blister copper from flotation concentrates. The process is currently operating at Noranda's Horne smelter and at Kennecott's Garfield smelter, but in each case a high-grade matte (70 - 75% Cu) is being produced for further oxidation to blister copper in converters. In the Horne smelter, the process still operates in conjunction with reverberatory furnaces and converters which existed prior to the installation of the reactor. The Noranda process is capable of operating in the matte mode or blister mode (if the concentrates are relatively free from deleterious impurities) but for impurity reasons, it is only operating in the matte mode at present.

Concentrates containing about 9% H_2O are charged by belt slinger through one end wall of the reactor where they are dried and smelted in the furnace freeboard. The molten particles separate into matte and slag in the bath, the former being oxidized by oxygen-enriched air (23.5% O_2 at Noranda, 34% O_2 at Kennecott) blown in through tuyeres to a high-grade matte (73% Cu at Noranda, 70% Cu at Kennecott). Matte is tapped intermittently without interrupting reactor operation and transferred in ladles to converters. Slag is skimmed from the opposite end-wall to the charging end and is slow-cooled before being retreated to produce a flotation concentrate to recover entrained copper.

As in all smelting processes which in part utilize the energy content of the concentrate, the control parameter in the Noranda process is the oxygen:concentrate ratio which can be set to produce matte of the desired grade, or copper. Fuel is added as required to compensate for the heat deficit. Depending on concentrate composition, the smelting reactions become autogenous at about 40% oxygen enrichment.

Effluent gases leave the reactor via a close-fitting hood, their strength depending on the degree of oxygen enrichment. At Noranda, gases contain about 10% SO_2 before dilution, whilst at Kennecott, the gas strength is about 21% SO_2 due to the higher level of oxygen enrichment. Infiltration of air around the hood is unavoidable and is about 75 - 100% of the process gas

volume. At Noranda, reactor gases are cooled in an evaporative cooler and then combined with converter gases. After dilution the gases are discharged to atmosphere containing about 4% SO_2 . At Kennecott's Garfield smelter, the reactor gases are cooled in a waste heat boiler and then combined with converter gases. They pass to a sulphuric acid plant in a stream containing about 8% SO_2 . Dust is removed from the gas streams by electrostatic precipitators. Careful design of reactor and converter hoods can minimize the dilution effect of infiltrated air such that the combined gas streams are suitable for the recovery of SO_2 as sulphuric acid.

5.9 Top-Blown Rotary Converter

The top-blown rotary converter (TBRC) was developed in the nickel industry to achieve the higher temperatures (1500°C) required using tonnage oxygen to produce crude nickel by the oxidation of molten nickel sulphide matte. The high temperatures are required to minimize the formation of nickel oxide. In copper smelting the same high temperatures are not required, as has previously been discussed.

The TBRC is a cylindrical vessel, similar to the BOF used in steel-making, which is rotated about its longitudinal axis. Air or oxygen is blown onto the surface of the liquids via a suspended water-cooled lance. Since copper converting is autogenous without oxygen enrichment of air, the TBRC is unlikely to be applied extensively in the copper industry. It has found application in scrap melting and in converting bismuth-contaminated mattes.

The TBRC was installed at the Peko-Wallsend smelter in Australia to facilitate impurity elimination (Bi, As) from copper matte. Off-gases contained about 15% SO_2 . After a period of closure, the smelter is understood to be reopening with Peirce-Smith converters having replaced the TBRC units.

A unique application of the TBRC is in the smelting of high-grade chalcocitic concentrates associated with native copper, as practised at Afton Mines in British Columbia. The vessel is used as the primary smelting unit, but because the sulphur input to the process is very low, the off-gases only

contain about 7% SO_2 during the oxidation stage. After scrubbing, the gases are discharged to the atmosphere.

At Boliden, in Sweden, the TBRC is used to smelt complex copper concentrates containing several deleterious impurities (Bi, As, Sb, Zn, Pb) so that their elimination in the vapour phase can be maximized. The original vessel was installed for the treatment of converter slags, thereby alleviating the need to return them to the electric furnace for copper recovery. Subsequently the process was extended to treat concentrates as well as cleaning of converter slags (15). Off-gas strength is variable, depending on the input sulphur and the stage of the converting cycle. After cleaning, the gases ultimately flow to a sulphuric acid plant.

At Inco, the TBRC is used to treat nickel sulphide residues in an oxygen atmosphere to produce crude metallic nickel. Effluent gases contain up to 15% SO_2 , depending on the stage in the blowing cycle, input sulphur, and amount of dilution air.

5.10 Kivcet Process

The Kivcet process was developed in the U.S.S.R. for smelting copper concentrates. The dual compartment furnace design was developed in response to the requirement for smelting copper concentrates with high lead and zinc contents. Two furnaces are in operation in the U.S.S.R. smelting some 600 tpd (at Irtysh) and 1000 tpd of copper concentrates and a third plant of 2000 tpd capacity is understood to be in the construction stage.

Smelting of concentrates takes place in a cyclone above the furnace bath using a 100% oxygen atmosphere. As a result, the effluent gas is rich in SO_2 , (about 80 - 85%), as in the case of Inco oxygen flash smelting (16). Gases leave the furnace via a large uptake shaft at one end of the furnace. Because of the high zinc content of the concentrate, the matte grade is limited to 50% Cu, but the range would normally be 45 - 60% Cu, depending on process conditions. As in the case of the Inco flash furnace, the matte grade produced, and hence the proportion of sulphur removed in the smelting stage, is related to the heat removal capacity of the furnace.

A water-cooled partition wall adjacent to the cyclone opposite to the gas uptake separates the reducing zone from the rest of the furnace. Here the slag is reduced by three electrodes before being tapped for discard and any zinc may be removed as a vapour.

The Kivcet process, along with the other modern processes, would appear to offer a suitable solution to environmental problems. The Kivcet process produces a gas of particularly low volume and high strength which may be converted to liquid SO_2 , sulphuric acid, or elemental sulphur. However, the process has a limited operating record and compared with other alternatives the furnace is of complex construction.

5.11 Peirce-Smith Converter

The Peirce-Smith converter is a well established and proven unit for converting copper and nickel-copper mattes to blister copper and Bessemer matte, respectively, and was developed at a time when there was less concern with SO_2 emissions.

The vessel is cylindrical, generally 4 - 4.3m diameter, by 9 - 10.5m long, and air or oxygen-enriched air (up to 30% O_2) is blown in through tuyeres located horizontally along the shell. Copper matte, of varying grade (25 - 65% Cu) depending on the primary smelting process, is converted to blister copper. Iron sulphide in the matte is first oxidized into a slag phase with the addition of silica flux. Molten converter slag may, or may not, be returned to the primary smelting furnace for recovery of entrained copper, depending on the smelting process.

In the case of reverberatory and electric furnace smelting, molten converter slag is returned to the smelting furnace. In Outokumpu flash smelting, converter slag is either returned molten to an electric slag cleaning furnace, or slow cooled, crushed, milled and returned to the flash furnace as a slag concentrate. In the Noranda process, converter slag is also returned to the reactor as a slag concentrate. Following iron removal, the remaining copper sulphide or 'white metal' is oxidized to blister copper which contains from 98.5 - 99.5% Cu, the balance being oxygen, sulphur and a minor amount of impurities. Blister copper is transferred to anode furnaces for fire refining into

anode grade copper which is subsequently electrolytically refined. The oxidation reactions take place at a temperature of 1150 - 1250°C and are auto-genous with atmospheric oxygen.

The gases leaving the converter after dilution by air infiltrated around the hood typically contain from 5 - 12% SO_2 , depending on the stage in the blowing cycle, the degree of oxygen enrichment and the amount of dilution air ingressed. At the end of the copper blow, the SO_2 content gradually falls to zero on a per converter basis. Converter operations are scheduled and blending of gases in common flues minimizes fluctuations in gas volume and SO_2 content, maintaining the latter at about 5% SO_2 .

Converter hoods may in time fall into a state of disrepair and allow progressively increasing amounts of dilution air to infiltrate the main process gas stream. With tight-fitting, water-cooled converter hoods, as installed in modern smelters, dilution may be kept below 100%, but where considerable inleakage occurs, particularly in older smelters where ingress of air is allowed in order to cool the gases, this may increase to 300 or 400%. In the case where gases are treated in a sulphuric acid plant, dilution must be kept to a minimum so that the gas strength can be maximized in order to keep the size and cost of the acid plant to a minimum. Flue dust is first extracted from the gas stream by settling in a balloon flue, settling chamber or cyclones and then by electrostatic precipitators.

Peirce-Smith converters used in the nickel industry employ the equivalent of the slag blow (i.e. for iron removal) in the copper industry, the end point occurring just before all iron is removed. Typical gas strength also varies between 5 - 12% SO_2 depending on the amount of dilution and the stage of the blow.

In smelters where the matte grade produced from the primary smelting furnace is low, the major portion of the oxidation of matte to blister copper is carried out in the converters. From an environmental standpoint, this is clearly a disadvantage. Converting is a batch process which means that the gas flow is intermittent. Volumetric gas flow and strength are variable, the latter in particular, varying with the stage in the blowing cycle. As a result, scheduling of converter operations is critical when there is an acid plant, because it depends on a constant gas volume and strength for efficient operation.

In such a case, smelter operations may appear to be geared more for the production of acid than for copper. Unavoidable dilution of the gas strength from infiltration of air around the converter hoods and in the flues are a further disadvantage in that the size and cost of sulphur fixation facilities are increased. It would appear to be advantageous to opt for a primary smelting process which produces as high a matte grade as practicable, and use oxygen enrichment of reaction air in order to produce a continuous, high strength gas of minimum volume as the major source of SO_2 flowing to sulphur fixation facilities. In this way, the environmental control problems associated with converter operations will be minimized. Computer control is used in several modern smelters to schedule converter operations in order to produce a continuous flow of gas to an acid plant.

Because converters have to be rotated in and out of the 'stack' position for charging of matte, and pouring of slag and blister copper, a low matte grade increases the number of occasions of rotation. The use of large ladles, compatible with overhead crane capacity will, however, assist in reducing crane movements. Since converter operations are the major source of in-plant fugitive emissions, production of high matte grades in the primary smelting furnace is advantageous in that the number of matte taps and crane movements is minimized.

5.12 Hoboken Converter

The Hoboken syphon converter was developed in Belgium and attempts to offer an improved solution in overcoming the fugitive emissions and dilution of the process gas stream problems encountered in the Peirce-Smith converter.

Similar in shape, but different in dimensions from the Peirce-Smith converter, the Hoboken converter draws off the gases through a flue connected axially to the converter by a syphon. The latter enables the gases to flow from the converter into the flue during all phases of operation while reducing to a minimum, liquid spillage through splashing into the gas-collection system. The design does not incorporate a hood over the converter mouth, as in the case of the Peirce-Smith converter. The gas collection system is regulated such that zero pressure is maintained at the converter mouth. This

prevents SO_2 escape as fugitive emissions and minimizes dilution of the converter gases by infiltrated air. Charging of matte, reverts and copper scrap can be carried out during the blow which increases converter availability and results in a less interrupted gas stream for acid-making. However, pouring of products still necessitates rotation of the vessel during which time blowing ceases. The Hoboken converter depends on a critical tuyere velocity for its successful operation (i.e. to minimize splashing) and this is achieved at a lower blowing rate (and therefore, productivity) than in its traditional counterpart. Overall, for similar sized units, production capacities of the Hoboken and Peirce-Smith converters are comparable.

Whilst the smaller sized Hoboken converter in Belgium operates in a generally trouble-free mode, operating techniques with the larger size vessels at Inspiration (U.S.A.) and Glogow (Poland) have caused problems with molten material splashing into the syphon and gas-tight joint. Build up of accretions in the syphon restricts draught in the flue system and converter and can result in fugitive emissions and disruption to acid plant operations. The problems experienced at Inspiration have resulted in a decision being taken to remove the syphon and replacing it with a gas offtake and hood system. Gas strength is typically in the range 7 - 11% SO_2 (Inspiration) and 13 - 17% SO_2 (Glogow) prior to gas cooling which is carried out in radiation cooling towers.

The Hoboken syphon converter would appear to offer an improved solution to environmental control over the Peirce-Smith converter. However, significant differences in design principles necessitate its being operated in a different manner to the Peirce-Smith converter in order for the benefits to be realized.

5.13 Comparative Gas Strengths

Table 13 summarizes typical gas strengths (% SO_2) from the various smelting processes used in the copper and nickel smelting industries.

TABLE 13 TYPICAL COMPARATIVE GAS STRENGTHS

	% SO ₂ BY VOLUME	
	Copper Smelting	Nickel Smelting
Roasting - multiple hearth	2.0 - 5.0	2.0 - 5.0
- fluid bed	3.0 - 15.0	3.0 - 15.0
Sintering	1.0 - 2.0	1.0 - 2.0
Blast Furnace	2.0 - 5.0	2.0 - 5.0
Reverberatory	0.5 - 2.5	0.5 - 2.0
Electric Furnace	0.5 - 5.0	0.5 - 2.0
Flash Smelting - Outokumpu	10.0 - 30.0	10.0 - 15.0
- Inco	80	N/A
- Furukawa	10	N/A
Mitsubishi Process	15.0 - 20.0	N/A
Noranda Process	10.0 - 20.0	N/A
TBRC	1.0 - 15.0	1.0 - 15.0
Kivcet Process	80.0 - 85.0	N/A
Peirce-Smith Converter	5.0 - 12.0	5.0 - 12.0
Hoboken Converter	7.0 - 17.0	N/A

The SO₂ contained in off-gases is at the high end of a range in processes where oxygen enrichment of reaction air is used. Figures at the low end of a range represent the worst case of ingress of dilution air. Processes employing oxygen smelting have a gas strength around 80% SO₂. Because converting is a batch process having two distinct blowing cycles, the gas flow is discontinuous and varies in strength within the range shown in the table. As removal of sulphur from the molten bath progresses, the SO₂ content of the gas falls and approaches zero for each individual converter. In a multi-unit operation fluctuations in gas strength are evened out and careful scheduling of converter operations enables a gas of nearly constant volume and strength (5% SO₂) to be delivered to an acid plant.

6 PARTICULATE EMISSIONS

6.1 Particulate Emission Control Technology

Before SO₂-laden gases from copper and nickel smelting processes can have their SO₂ content fixed as a stable product, it is first necessary, after capturing the gases emitted from the processes, to remove the dust or particulate content as completely and efficiently as possible. Particulate emission control technology also constitutes a significant part of overall air pollution control technology as evidenced by the allowable emissions in the regulations.

All particulate collection mechanisms involve either a gravitational or an applied force, the simplest one being gravitational force as occurs in a settling chamber (17). If this is insufficient, centrifugal force may be exerted on the particles in cyclones. In filtration, three separate primary effects, all force-related, are involved: impaction, interception and diffusion. The same collection mechanisms also occur in wet scrubbers.

The three collection mechanisms involved in filtration can be illustrated by considering an individual fibre in a fabric filter. If a particle is so large that it cannot follow the gas streamline around the barrier (fibre), the particle impacts on the barrier. Interception is a collection mechanism in which the smaller particles just graze the barrier, enter the laminar boundary layer which surrounds each element of the barrier, lose kinetic energy, and are thus removed from the gas phase. Diffusion is generally effective for particles below 1 μ m in aerodynamic diameter. This mechanism governs removal of particles which are so small that they can be affected by the motion of the molecules in the gas stream. Diffusion is not very important for the major mass of particles.

The other primary particulate removal mechanism involves electrostatic forces. The particles, whether solid or as liquid aerosol, are first charged and then immediately collected in the same equipment after migration to an oppositely charged electrode. This is the basic principle of both electrostatic precipitators and charged droplet scrubbers. In the former, particle collection occurs strictly by application of an electric field. In the

latter, removal occurs by the combined effects of impaction, interception, diffusion and electrical interaction. The charging of the water droplets enhances the ability of the water droplet to capture fine particles by attracting them to the interface so that diffusion and interception occur more effectively.

The methods and equipment, and characteristics of the latter, used for air pollution control are summarized in Table 14. (17). The equipment described in this study is shown against the air contaminants 'dust, fumes, smoke, mist'.

6.1.1 Settling Chambers

For gravity settling chambers, (e.g. balloon flues) to be effective, a long residence time is necessary so that the particles have time to settle out of the gas stream. The gas flow in such devices should be essentially laminar. Turbulence would cause re-entrainment of the particulates. This approach is restricted to particles greater than $50\mu\text{m}$ in diameter. Gravity settling is a very simple technique and if large masses of large size particles must be controlled (e.g. a burden of $100 - 1500\text{ gm/m}^3$), this approach is a good choice for an initial separation if the necessary space is available and temperature loss permits. These units have no moving parts. Periodic cleanout or a hopper on the bottom for particle removal by a screw-conveyor, drag-link conveyor or even a simple dump hopper is all that is necessary for a properly sized chamber.

Use of a baffled settling chamber can increase the collection efficiency with very little increase in cost. This approach increases the opportunity for particles to be collected by impaction. Large particles will impinge on the baffles and thereby lose enough kinetic energy to drop out of the gas stream. These units are best suited for particles larger than 20 to $30\mu\text{m}$. The advantage of the baffled chamber over the simple open chamber is the decrease in size of the equipment as a result of adding the impaction surfaces. There is virtually no difference in the pressure drop between the open chamber and the baffled chamber.

TABLE 14 METHODS AND EQUIPMENT FOR AIR POLLUTION CONTROL (17)

Name of Device			Air Contaminants	Optimum Size Particles—Micron	Optimum Concentration gr/cu ft	Temperature Limitations F	Utility Requirements HP, Water, KW, BTU	Face Velocity	
General	Specific Type	Description						FPM	Location
Industrial Filters	Cloth bag	Bags made of synthetic or natural fiber fabrics		> 0.3	> 0.1	0-180-500		1-30	Fabric
	Cloth envelope	Envelopes made of natural or synthetic fibers, fabrics over screen cages		> 0.3	> 0.1	0-180-500		1-30	Fabric
Electrostatic Precipitators (High Voltage)	Single stage (plate)	Ionizing (-) wires between parallel collecting (+) plates		> 0.3	> 0.1	0-850	0.2-0.6kw/1000 cfm	180-600	Plates
	Single stage (pipe)	Ionizing (-) wires inside concentric collecting (-) pipes		> 0.3	> 0.1	0-1200	0.2-0.6kw/1000 cfm	180-600	Pipes
Dry Inertial Collectors	Settling chamber	Straight chamber expansion (without baffles)		> 50	> 5	0-700		60-600	Chamber
	Baffle chamber	Straight chamber expansion (with baffles)		> 30	> 5	0-700		1000-2000	Inlet
	Skimming chamber	Scroll shaped chamber w/peripheral slots		< 20	> 1	0-700		2000-4000	Inlet
	Cyclone	Chamber with spiral flow		> 10	> 1	0-700		2000-4000	Inlet
	Multiple cyclone	Small cyclones in parallel		> 5	> 1	0-700		2000-4000	Inlet
	Impingement	Alternate stages of baffles and nozzles		> 10	> 1	0-700		3000-6000	Nozzles
Scrubbers	Dynamic		Dust, Fumes, Smoke, Mist	> 10	> 1	0-700	1/2 hp/1000 cfm	2000-4000	Inlet
	Cyclone	Cyclone collector same as dry inertial type with coarse sprays		> 10	> 1	40-700	2-10 gpm/1000 cfm	1500-3000	Inlet
	Impingement	Impingement collector w/wetted baffles		> 2-10	> 1	40-700	3-5 gpm/1000 cfm 2-4 hp/1000 cfm	4000-6000	Nozzles
	Submerged	Dynamic collector w/coarse sprays		> 1	> 1	40-700	1 gpm/1000 cfm	2000-4000	Inlet
	Fog	Cyclone collector w/fine tangential sprays		< 2	> 0.1	40-700	3-5 gpm/1000 cfm 350 psig sprays	3000-4000	Inlet
	Pebble bed	Tower w/counter-currently wetted coarse packing		> 5	> 0.1		3-5 gpm/1000 cfm	500-1000	Bed
	Multi dynamic	Power driven normal and reverse flow fan stages w/coarse sprays		< 0.5	> 0.1	40-700	10-30 gpm/1000 cfm 10-20 hp/1000 cfm	2000-3000	Inlet
	Venturi	Venturi w/coarse sprays at throat		< 2	> 0.1	40-700	3-5 gpm/1000 cfm	12000-24000	Throat
	Crossflow	Packed bed, liquid and gas flows at 90°		> 3	> 0.1	40-250		1500-3000	Bed
	Jet	Water activated jet pump		> 2	> 0.1	40-700	50-100gpm/1000 cfm	2000-3000	Inlet
Afterburners	Direct	Combustion chamber with supplemental fuel firing		Any	Combustible Only	2000	1.1 Btu/cfm° ΔT	500-1000	Chamber
	Catalytic	Combustion chamber with catalyst with supplemental fuel firing		Any	Combustible Only	1500		500-1000	Chamber
Gas Absorbers	Spray tower	Vertical up flow chamber with downward sprays		Molecular	> 0.001	40-100	2-10 gpm/1000 cfm	120 (superficial)	
	Packed tower	Tower with counter-currently wetted Rashig rings, berl saddles, etc. packing		Molecular	> 0.001	40-100	3-6 gpm/1000 cfm	60 (superficial)	
	Fiber cell	One or more stages of cocurrently wetted fiber cells		Molecular	> 0.001	40-100	5-15 gpm/1000 cfm	200 (superficial)	
Gas Adsorbers	Deep bed (1-3 ft)	Activated charcoal bed in regenerative recovery equipment		Molecular	> 0.001	125		30-100	Bed
	Shallow bed (1/4 in.)	Activated charcoal beds in cells or cartridges		Molecular	< 0.001	125		50-120	Bed

TABLE 14 (CONTINUED) METHODS AND EQUIPMENT FOR AIR POLLUTION CONTROL (17)

Name of Device		Air Resistance WG (inches)	Efficiency % by Weight	Space	Description of Collected Pollutant	Application	Limitations
General Industrial Filters	Cloth bag	> 4	> 99	Large reverse type	Discharged into hoppers when dislodged from bags	Dry collection possible Decrease of performance is noticeable	Sensitivity to filtering velocity High temperature gases must be cooled to 200F to 550F
	Cloth envelope	> 4	> 99	pulse type moderate Large	Discharged into hopper when dislodged from fabric face	Collection of small particles possible High efficiencies possible	Affected by relative humidity (condensation) Susceptibility of fabric to chemical attack
Electrostatic Precipitators (High Voltage)	Single stage (plate)	< 1	> 99	Large	Dry dust on plates—dislodged into hopper	99+ percent efficiency obtainable Very small particles can be collected	Relatively high initial cost Precipitators are sensitive to variable dust loadings or flow rates
	Single stage (pipe)	< 1	> 99	Large	Dry dust on pipe—dislodged into hopper	Particles may be collected wet or dry Pressure drops and power requirements are small compared to other high efficiency collectors Maintenance is nominal unless corrosive or adhesive materials are handled Few moving parts	Resistivity causes some material to be economically uncollectible Precautions are required to safeguard personnel from high voltage Collection efficiencies can deteriorate gradually and imperceptibly
Dry Inertial Collectors	Settling chamber	< 0.1	< 50	Large	Dry dust or liquid into hopper	Low pressure loss, simplicity of design and maintenance	Much space required
	Baffle chamber	< 0.5	< 50	Large	Dry dust or liquid into hopper	Simplicity of design and maintenance	Low collection efficiency
	Skimming chamber	< 1.0	< 70	Moderate	Dry dust or liquid into hopper	Little floor space required Dry continuous disposal of collected dusts	Much head room required Low collection efficiency of small particles
	Cyclone	< 2.0	< 80	Moderate	Dry dust or liquid into hopper	Low to moderate pressure loss	Sensitive to variable dust loadings and flow rates
	Multiple cyclone	4.6	< 90	Moderate	Dry dust or liquid into hopper	Handles large particles	
	Impingement	4.6	< 80	Small	Dry dust or liquid into hopper	Handles high dust loadings Temperature independent	
Scrubbers	Dynamic	-8 developed	< 80	Moderate	Dry dust or liquid into hopper		
	Cyclone	1.5-3	< 90	Large	Slurry sludge with water	Simultaneous gas absorption and particle removal Ability to cool and clean high-temperature, moisture-laden gases	Corrosion, erosion problems Added cost of wastewater treatment and reclamation
	Impingement	2/stage	< 95	Large	Slurry sludge with water		Low efficiency on submicron particles
	Submerged	3.6	< 95	Small	Slurry sludge with water	Corrosive gases and mists can be recovered and neutralized	Contamination of effluent stream by liquid entrainment
	Fog	> 2.0	< 99	Moderate	Slurry sludge with water	Reduced dust explosion risk Efficiency can be varied	Freezing problems in cold weather
	Pebble bed	> 4.0	< 90	Large	Slurry sludge with water		Reduction in buoyancy and plume rise
	Multi-dynamic	2.4	< 99	Small	Slurry sludge with water		Water vapor contributes to visible plume under some atmospheric conditions
Afterburners	Venturi	> 10	< 99	Small	Slurry sludge with water	Gas and particulate removal	
	Crossflow	-8 developed	< 95	Small	Slurry sludge with water		
	Jet	-8 developed	< 90	Small	Slurry sludge with water		
Afterburners	Direct	< 1	< 95	Moderate	Innocuous flue gas out stack	High removal efficiency of submicron odor-causing particulate matter Simultaneous disposal of combustible gaseous and particulate matter Direct disposal of nontoxic gases and wastes to the atmosphere after combustion Possible heat recovery Relatively small space requirement Low maintenance	High operational cost Fire hazard Removes only combustibles Catalysts subject to poisoning Catalysis require reactivation
	Catalytic	> 1	< 95	Moderate	Innocuous flue gas out stack		
Gas Absorbers	Spray tower	< 1	< 95	Large	Solution in water		
	Packed tower	1.5-4 in. WG/ ft of packing	> 98	Compact	Solution in water		
Gas Absorbers	Fiber cell	< 4	< 95	Moderate	Solution in water		
Gas Absorbers	Shallow bed (1.4 in.)	0.5-2	95	Small	Adsorbed on charcoal	Solvent recovery	
	Shallow bed (2.4 in.)				Discharged w/charcoal	Removal of toxic/odorous organics	

* 2 (extended surface packings)
20-30 (filamentous packings)

The balloon flue is the most common form of settling chamber used in the copper and nickel industry and is the first item of equipment in the gas cleaning plant, occasionally after reverberatory furnaces, but most often after converters where dust particle size is comparatively large. Sometimes spray cooling nozzles are installed at the inlet of a settling chamber to cool the gases. The radiation chamber of a waste heat boiler acts as a settling chamber because the large cross-sectional area causes sufficient decrease in gas velocity to cause fall-out of the largest size particles. Settling chambers may collect up to 50% of the total dust loading in a gas stream. There has been a trend on the part of some smelters to replace balloon flues with high velocity flues (with no settling) and cyclones because of corrosion problems, fugitive dust handling and high maintenance costs. Balloon flues, because of their large surface area, frequently give rise to a large fall in gas temperature. Modern smelters are usually equipped with high velocity flues.

6.1.2 Cyclones

In cyclones, the primary mode of collection is centrifugal acceleration of the gas stream which throws the particles to the wall. The velocity steadily increases as the gas descends from the cylindric body into the conical section of the cyclone. The increasing centrifugal force causes smaller particles to enter the viscous fluid zone at the wall where they also suffer a decrease in kinetic energy. Such particles and those already falling down the inner wall, are unable to make the turn into the inner spiral and are removed from the bottom of the conical section.

Cyclones are low efficiency devices for small particles. They have higher efficiencies for large particles. The cut diameter is about $10\mu\text{m}$ but may range from 5 to $15\mu\text{m}$ depending on the cyclone type, diameter, body length, taper, inlet velocity, etc. The cut diameter is defined as that diameter at which 50 percent of the particles of that size are collected and 50 percent are not.

Cyclones can be operated either wet or dry, although the latter prevails in the copper and nickel smelting industries. Wet operation might be a reasonable approach for the removal of large hygroscopic particles if a serious water pollution problem does not result. In wet operation water is

injected into the cyclone inlet. The entering gas velocity diffuses the water droplets over the entire inside surface of the unit. The wall is continually flushed clean so that deposits of sticky particulates should not occur.

Cyclones are usually operated in parallel sets of identical units rather than using one huge collector for treating large gas flows. The pressure drop may be greater through a group of small cyclones, but the local velocities are higher, which results in a lower cut diameter. Cyclonic removal of small particulates becomes more effective as the velocity through the collector increases. If the volume rate is increased for a given cyclone, higher gas rotation and viscous energy losses (pressure drop) will result.

As in the case of settling chambers, cyclones are usually the first item of equipment in the gas cleaning plant and may replace the settling chamber or balloon flue. Dust collection efficiencies of up to 80% are possible for a single unit, or up to 90% for a bank of multiple cyclones, depending on particle size. In smelters where fluid bed roasters are used, some 80% of the product calcine leaves the roaster as bed overflow and is collected in a bank of cyclones. Dust is removed continuously by screw or drag-link conveyor or by simple tote box if the amount of material collected is small.

6.1.3 Bag Filters

Bag filters are devices in which particulates are removed from a gas stream by retention in or on a porous structure through which the gas flows. Fabric filters have the advantage of being positive collectors, i.e. the fibres of the filter medium are interposed between the particulates and the clean environment and form a physical barrier to prevent escape of the dust. The mechanisms of particle capture are impaction, interception and diffusion. Natural or synthetic fibre fabrics are usually used, but woven, pierced or sintered metal barriers are occasionally required for high temperature service. Deep beds of randomly oriented fibre or solid particles may also be effective for particulate control in special circumstances. The pressure drop through the filter medium depends on the filter velocity (more specifically, on the ratio of volumetric gas flow rate to gross filter medium area), the inlet particulate loading, the filter medium characteristics, and the frequency and effectiveness of the filter cleaning method in use.

A new filter cloth is not very effective as a filtering medium because the true filtering surface is formed only when particles begin to bridge the open areas between the fibres of the filter. It is impossible to remove all of the particles which have been deposited on the filter, so even when the bulk of the particulate mass (>98 percent) is removed in the cleaning cycle, most of the interstitial area in the filter remains bridged by previously collected particles.

The resistance to gas flow steadily increases with time until some predetermined pressure drop is reached. At that point, the cleaning cycle is initiated. This gives a sudden decrease in filter resistance which is measured in terms of pressure drop. There is a small region where the pressure drop is quite low, indicating that the cake has not been completely formed. There are some open interstitial areas through which fine particles can pass. The period between the end of the cleaning cycle and the reformation of the effective filtering surface is the cake repair period and is a time of low capture efficiency. The solution for this potential loss of control is to divide the dirty gas flow into a number of compartments. The compartments are then cleaned one by one, so that at no time will more than one compartment be operating at a low efficiency as a result of filter cleaning. Cleaning of the filter bags may be accomplished by a mechanical shaking mechanism, or by means of a reverse air pulsing mechanism (high pressure or low pressure). An alternative to the pressure drop method of initiating the cleaning cycle is to use a timing device. The pressure drop method of filter cleaning can lead to uneven wear on the bags and may, in the event of a torn bag going unnoticed, give no cleaning at all. This method is more complicated than the timing method and is dependent on draught conditions.

Filters may be constructed of woven or felted fabrics. These two classes of filters have vastly different characteristics. To collect a highly abrasive particle, a slick finish woven fabric would be selected in order to minimize wear. If the emissions contain some tarry particulates, (an unlikely occurrence in copper and nickel smelting), a felted (nonwoven) fabric would be the best choice. Felted fabrics have another advantage in that they have a

high nap (small fibres projecting from the surface) compared to that on woven fabrics. The tarry particulates can be captured on the projecting fuzz fibres without blinding the bulk of the surface of the filter medium itself. Although other types of filter media are used for air pollution control, fabric filters are the most important. Copper and nickel concentrates which contain significant quantities of lead and zinc cause sticky oxide and sulphate particles which can 'blind' the filter fabric.

Bag filters do not enjoy wide application in the copper and nickel smelting industries. They are best suited to dust and fume collection from gas streams containing highly volatile impurities such as Pb, Zn, As, Bi, etc. Bag houses are more commonly used for removal of dust from in-plant fugitive emission gas streams where dust loading is small and particle size is very fine. They are also installed on concentrate and flux storage bins when pneumatic transport of these materials is used. Dust is removed from hoppers at the bottom of a bag house by means of a screw-conveyor, drag-link conveyor, or tote box. Collection efficiencies of bag filters may be upwards of 99% and even as high as 99.9%. Depending on the filter fabric, operating temperature is limited to about 260°C. This necessitates cooling the gases before the gas filter inlet.

6.1.4 Electrostatic Precipitators

Electrostatic precipitators are devices in which a high-density electric field is created, causing any particulates in the gas stream to acquire an electric charge and to migrate subsequently to a collecting surface where the charge is neutralized. The field causes large numbers of oxygen molecules in the gas to become charged. As the 'gas ions' drift from the generation (discharge) electrode to the collection electrode, some fraction of the ions collide with the particles in the gas stream. Eventually, most of the dust becomes negatively charged to an equilibrium value.

As the charge on the particle builds up, it begins to repel the negatively charged 'gas ions' because they have like charges. Thus there is a limit to the amount of charge which can be transferred to any particle. The particle is accelerated in the electric field towards the collection electrode (plate)

which has zero or opposite polarity. In simple terms, when the charged particle reaches the collection electrode, the charge is neutralized and the particle falls into a collection hopper beneath the unit.

Particles continually arrive at the collection electrode. If the rate of charge neutralization is too low, other particles arriving at the plate can create a 'fishnet' effect. The second wave of particles may be attracted so strongly to the collection electrode that they tend to keep the first group of particles from falling into the collection hopper. Layers of particles begin to build up on the collection surface. In this situation, the driving force for charge neutralization is decreased because of the finite amount of energy needed to transfer a charge across any particles which are being held on the surface. The effective collection potential decreases as the thickness of the dust layer on the plates increases. The result is a steadily increasing power loss to maintain efficiency which is unacceptable from an operational point of view or a collection efficiency which approaches zero for fine particulates. To prevent this problem, the collection plates and the discharge wires are periodically agitated by striking them with mechanically or pneumatically operated hammers called rappers. The intensity and the frequency of rapping are adjusted to match the particle characteristics (hygroscopicity, density, resistivity, etc.).

Electrostatic precipitators have very wide application in the copper and nickel smelting industries and are installed at virtually all smelters. They are the penultimate dust collecting unit on roaster, primary smelting and converter gas streams when sulphuric acid or other sulphur fixation product is manufactured. Electrostatic precipitators are suitable for recovery of ultra-fine dust and fume particles from large volumes of gas at high efficiencies, from 98 - 99.9%. Dust is continuously conveyed from the hopper bottom, generally for recirculation to the primary smelting furnace, depending on volatile impurity content. Typical operating temperature is 350°C , so it is necessary to cool the gases to this temperature by water sprays or by radiation heat loss from the flues. Water sprays are frequently used since this conditions the particles for more efficient collection.

6.1.5 Wet Scrubbers

The last major class of particulate collectors is the wet scrubbers. Wet scrubbers are devices in which the primary means of collection is a liquid which is introduced into the unit and deliberately converted into countless microdroplets. Conversion of the scrubber liquid into an aerosol provides a large surface area for the collection of any soluble contaminants and also creates a large number of targets for any particulates present in the gas phase. A very important variable is the relative velocity of the particles with respect to the droplets. The particulates must have the higher velocity in order to increase the probability of collection. If the particle is moving fast enough, the droplets are relatively motionless, as are the fibers in a fabric filter. Even small particles will be unable to follow the streamlines around the droplets and will impact on the surface or be collected by interception.

Wet scrubbers operate by the contacting power principle which states that the smaller the particles being removed, the greater the energy which must be expended. If very small (submicron) particles are to be collected, a correspondingly high particle velocity must be attained which requires that the entire gas stream be accelerated. In any equipment with fixed dimensions, the pressure drop increases drastically with increasing velocity. Of major importance is that portion of the available fluid energy (pressure drop) which is actually used to achieve particle-droplet interaction. As the particles and the gas stream are accelerated, part of the available driving force (pressure drop) is expended in the viscous losses associated with getting the bulk gas stream through the control device. That part is lost as far as particle collection is concerned. Only that portion of the pressure drop which is converted into fluid energy to give the relative increase in particle velocity is applicable to particle removal.

Several varieties of wet scrubbers are available, such as packed towers, plate towers, spray chambers, venturists, crossflow units, etc. When a simple or baffled spray chamber is used for removal of particles larger than $25\mu\text{m}$, the sprays serve two functions. They condition the gas stream by adjusting its humidity to promote agglomeration and by cooling it. At the

same time, the sprays prevent particle buildup on the interior of the chamber. The spray chamber wet scrubber can be fairly effective for large particles but is ineffective for small particles.

Other scrubber designs have been developed to provide high removal efficiency in different particle size regions. For 10 to 20 μm particles, equipment more efficient than a spray chamber is needed, e.g. a wet cyclone. These units combine the operating characteristics of both a cyclone and a spray chamber. Increased particle collection efficiency is achieved as a result of added centrifugal motion. For 5 to 10 μm particles, a low energy device is needed, one which operates at a pressure drop of 25 to 50 cmwg. For smaller particles (e.g. 1 to 5 μ), self-induced scrubbers or other medium energy collectors are required. At 1 μm and below, high energy devices such as venturi scrubbers are necessary. The pressure drop through such units can be 150 to 200 cmwg.

Wet scrubbers are generally followed by a mist or entrainment separator to prevent loss of any scrubber liquid in the effluent. As the gas velocity is increased, the problem of preventing scrubber liquid carryover becomes more severe, which may require a demister. Every wet scrubber and entrainment separator or demister must have a sump into which the liquid and particles drain. The sump must be drained at regular intervals or, preferably, continually emptied by a slurry pump. The particles must be removed and the liquid recycled, especially if any reagents have been added to promote effectiveness in particle capture.

Wet scrubbers have wide application in the copper and nickel smelting industries, where they are used as the final gas cleaning and cooling step prior to conversion of SO_2 into sulphuric acid or other sulphur fixation product. The cleaned gas then passes through a mist precipitator before entering the acid (or other) plant. Collection efficiency in a wet scrubber may vary from 90 - 99% depending on type and specific application. Wet scrubbers are also used on tail gas streams and for recovering dust from fugitive emissions.

7 GASEOUS EMISSIONS

7.1 Sulphur Dioxide Emission Control Technology

Sulphur dioxide emission control technology in the copper and nickel smelting industries has been developed essentially to treat two types of gas stream: concentrated gas streams which arise from primary smelting furnaces and converters where the gas strength is greater than about 4.5% SO_2 , and dilute gas streams (containing generally less than 2% SO_2) which arise from multihearth roasters, reverberatory furnaces, fugitive emissions, and tail gases.

7.2 Concentrated Gas Streams

Sulphur dioxide emission control technology on smelter gas streams is both more technically and economically feasible, and most widely used, in the treatment of concentrated gas streams. Sulphur dioxide may be captured and fixed as elemental sulphur, (although this is technically complicated and economically unattractive), or alternatively used in the production of liquid SO_2 or sulphuric acid. Manufacture of sulphuric acid is the accepted control approach in the industry. Figures 2 and 3 (2), simplified copper and nickel-copper smelter flow sheets, show the disposition of sulphur fixation facilities in relation to the major SO_2 -containing gas streams. In both flow sheets, roasting of concentrates prior to smelting may be an optional unit operation, depending on smelting process used. A slag treatment stage may be required prior to discard, depending on smelting process and matte grade produced.

7.2.1 Elemental Sulphur Production

Reduction of SO_2 in smelter gases to elemental sulphur is both technically difficult to achieve and expensive because of the high cost of reductant, usually naphtha. For these reasons production of elemental sulphur has not been widely accepted in the metallurgical industry. Commercial facilities have been built at Phelps Dodge's Hidalgo copper flash smelter in New Mexico, BCL's copper-nickel flash smelter in Botswana, and at Outokumpu's pyrite roaster in Kokkola, Finland. The latter plant was permanently closed several years ago because the high cost of naphtha and competition from lower cost sulphur adversely affected the economics of pyrite roasting. Phelps Dodge's

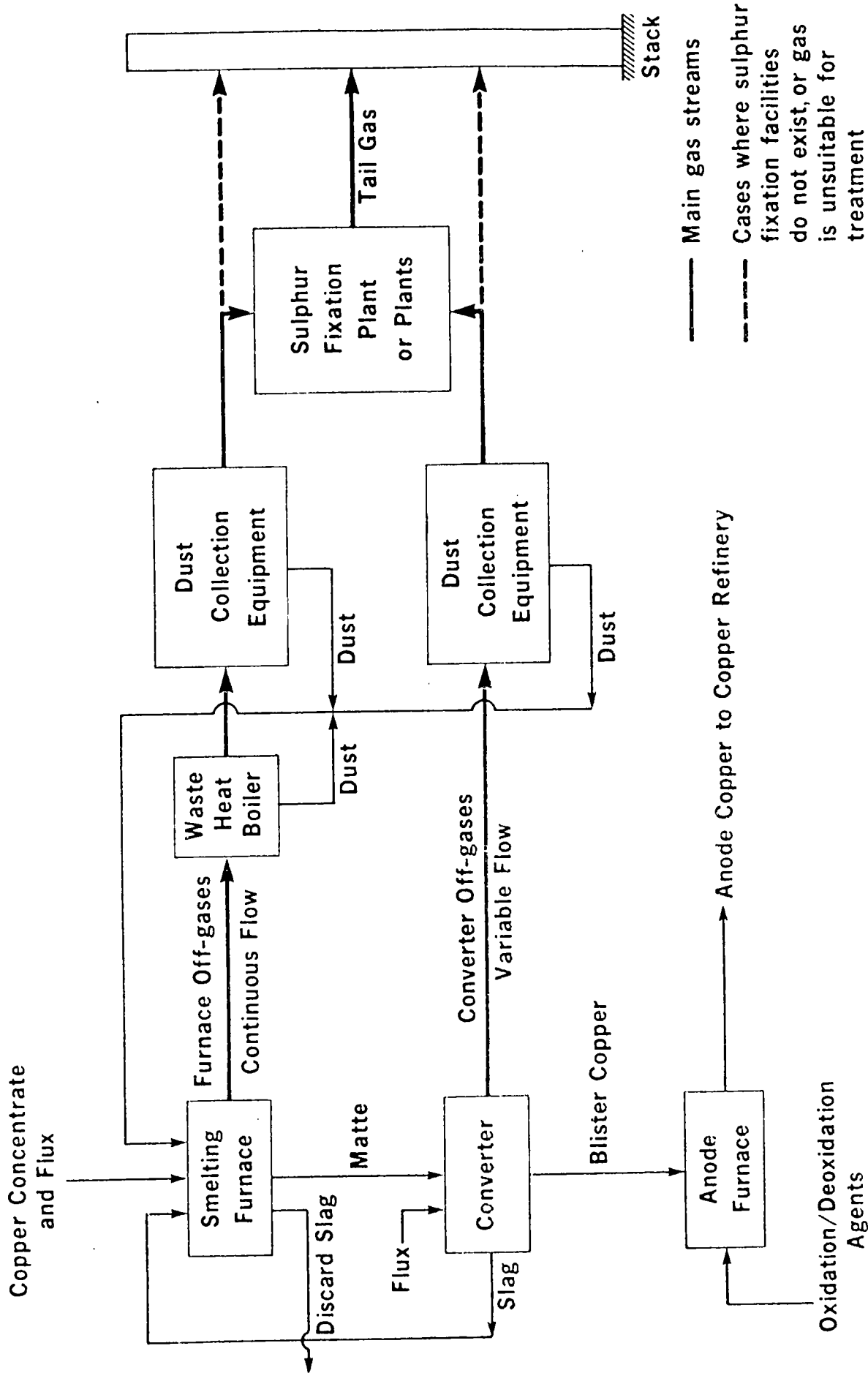


FIGURE 2 GENERAL FLOW DIAGRAM OF A COPPER SMELTER (2)

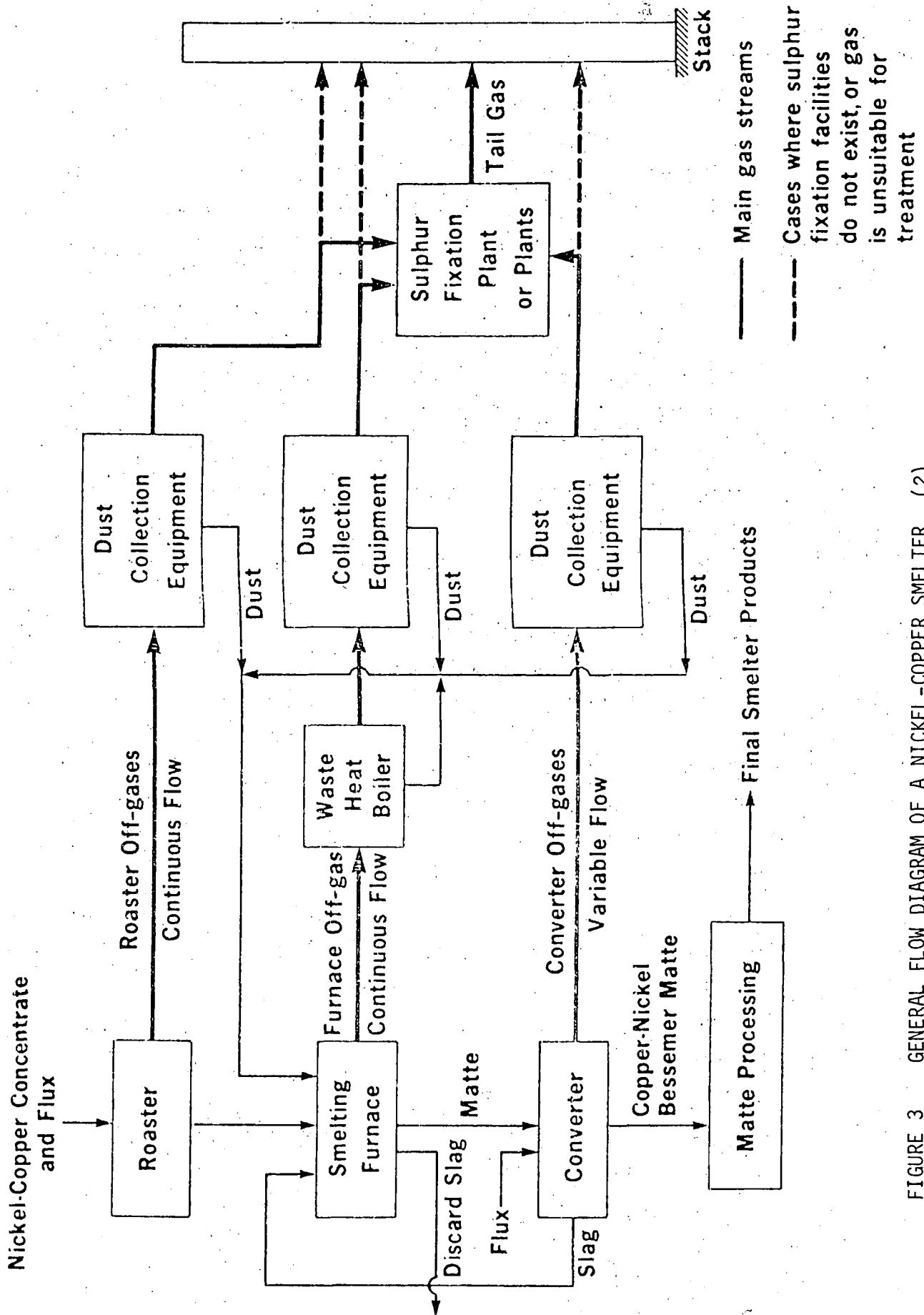


FIGURE 3 GENERAL FLOW DIAGRAM OF A NICKEL-COPPER SMELTER (2)

plant was never put into production owing to the high cost of reductant and was superseded by a sulphuric acid plant. This elemental sulphur plant would have had to compete with neighbouring supplies of Frasch sulphur in the marketplace. Because of technical problems encountered in its flash furnace and the resulting difficulties in producing sulphur of a commercially acceptable specification, the elemental sulphur plant in Botswana has not operated on a continuous basis and is now shut down. Metallurgical process problems and the high cost of reductant contributed towards closure of Allied Chemical's plant near Falconbridge, Ontario which was designed to treat roaster gases.

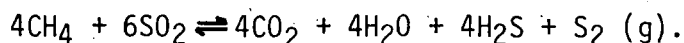
The production of elemental sulphur requires a continuous, high strength (preferably at least 12% SO_2) gas stream (2, 18). This means that converter gases are not suitable as feed to an elemental sulphur plant. In addition, for economic reasons it is necessary to have the lowest possible oxygen content (not greater than 1% O_2) since oxygen increases the consumption of reducing agent. It is customary for primary smelting furnaces to operate under slight negative pressure which results in the ingress of varying amounts of dilution air (containing oxygen) into the gas stream. However, when producing elemental sulphur the furnace has to be designed to be completely gas-tight so that it can be operated under a slight positive pressure to avoid ingress of air. Totally enclosing the furnace with steel casing is then necessary to prevent high strength process gas escaping from the furnace into the surrounding building. This complicates the design of the furnace to some extent.

Sulphur dioxide in smelter gas can be reduced by passing the gas stream through an incandescent coke bed. Processes of this type used to be operated by Boliden (Sweden), Cominco (Canada) and Orkla (Norway), but the high cost of coke rendered the plants uneconomic and they were shut down and dismantled several years ago.

Hydrocarbons such as natural gas, fuel oil, high-grade pulverized coal (which was used at BCL's smelter in Botswana) and naphtha (at Kokkola) are more commonly used as reducing agent.

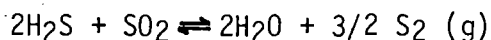
Elemental sulphur production takes place in three main stages when using hydrocarbon reductants (5):

- (a) Gas purification at 150°C, similar to sulphuric acid manufacture.
- (b) Catalytic reduction of SO₂ at 500°C with hydrocarbons by reactions of the type



Liquid elemental sulphur (30-40% of that in the original gas) is condensed at this point by cooling the gases to 170°C.

- (c) Catalytic Claus reaction at 240°C (one or two stages) in which elemental sulphur is produced from the remaining SO₂, according to the reaction



and then condensed by cooling.

Conversion to elemental sulphur is only about 90% complete which means that the basic process must be improved if it is to be used for compliance with the most stringent ambient air quality and emission standards. Other gaseous components are formed through side reactions which result in a tail gas containing hydrogen sulphide (H₂S) and carbon oxysulphide (COS) in addition to about 1% SO₂. The gas mixture can be passed through additional catalyst beds at a lower temperature where H₂S and COS react with the remaining SO₂ if it is required to increase the overall sulphur yield. This also removes the greatest amount of the hazardous side reaction gases which are more toxic than SO₂. In the metallurgical industry, in order to further reduce emissions, it is usual to oxidize H₂S and COS in an incinerator before discharging the tail gas to atmosphere, but only at the cost of additional fuel. In the natural gas and petroleum industries Claus plant technology is well developed and processes are available by which the unreacted sulphur compounds can be reduced to H₂S, absorbed in sodium carbonate solutions, and oxidized to elemental sulphur by sodium vanadate. It is estimated that the SO₂ concentration can be reduced to 0.03% by these techniques (5). Figure 4 illustrates a typical flowsheet for recovering elemental sulphur from smelter gases by reduction of SO₂ (5).

In the Outokumpu flash furnace, partial reduction of SO₂ is carried out in the uptake shaft at 1350°C by the addition of reductant, upstream of the sulphur recovery plant.

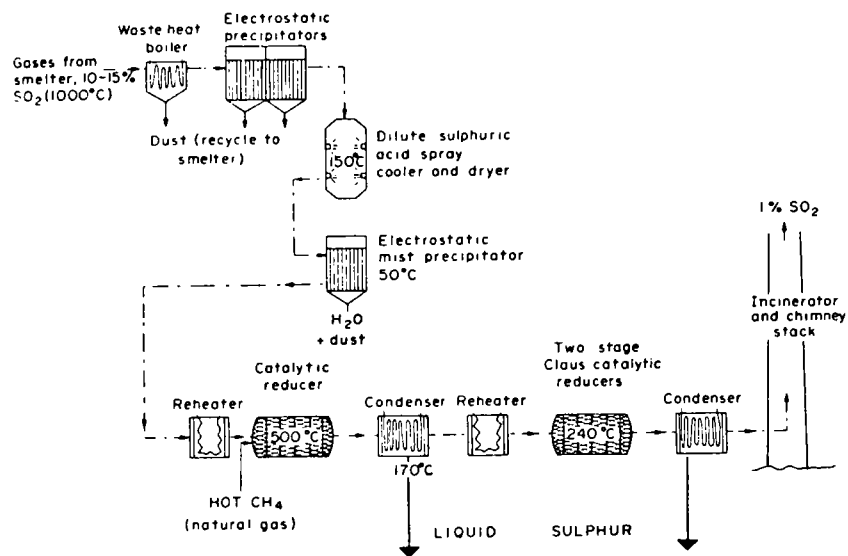


FIGURE 4 FLOWSHEET FOR RECOVERING ELEMENTAL SULPHUR FROM SMELTER GASES (5)

The complex technology used coupled with the high cost energy requirement (about 500 Nm³ CH₄/tonne of S) for SO₂ reduction, mitigate against the production of elemental sulphur from smelter gases gaining wide acceptance. However, in certain cases the production of elemental sulphur may warrant serious consideration when taking into account smelter location relative to acid markets, transportation costs, and the ease of storing elemental sulphur.

7.2.2 Liquid SO₂ Production

Gas with the highest possible SO₂ content is necessary for the economic recovery of sulphur in the form of liquid SO₂, and the gas flow must be continuous with minimum variations in strength. There are two main types of liquid SO₂ recovery processes (2, 18):

(a) Physical Recovery Processes

These include processes such as pressure absorption in water and dry compression - refrigeration. Because the gas has to be compressed, its SO₂ content is the prime economic factor because of the high energy requirement and costs of compression. Fluid bed roaster and flash furnace gases are suitable for economic processing by water pressure absorption, as practised by Boliden in Sweden. Oxygen flash smelting gas can be economically processed directly by dry compression and refrigeration as evidenced by CIL's plant at Copper Cliff which treats gases containing 80% SO₂ from Inco's oxygen flash furnace smelting copper concentrate.

An important consideration in connection with these processes is that the clean gas must be thoroughly dried before compressing and refrigeration. The only practical and economic drying agent for this purpose is concentrated sulphuric acid. For this reason it is highly desirable to combine liquid SO₂ production by physical recovery processes with a sulphuric acid plant. In such a combination the moisture in the smelter gas provides the dilution water for the sulphuric acid plant, while the tail gas from the liquid SO₂ plant is processed in the acid plant.

(b) Chemical Absorption Processes

These processes are operated at atmospheric pressure and use chemical absorption for SO_2 extraction from the gas stream. Of the several processes in existence the two best known are the Cominco and the DMA (dimethyl aniline) processes. The Cominco process uses a solution of ammonium bisulphite as the absorbent and strips the SO_2 as a strong (25% SO_2) gas by acidifying with sulphuric acid. Ammonium sulphate is a by-product. Figure 5 illustrates a simplified flowsheet of the Cominco process (7). Sulphur dioxide - bearing gas, free from sulphur trioxide and particulates, is absorbed by an ammonium sulphite-bisulphite solution. The SO_2 in the gas reacts with ammonium sulphite to form the bisulphite. Ammonia is added to convert part of the bisulphite to sulphite and recycled to the absorption scrubbers. The remainder of the bisulphite solution is diverted to the stripper, acidified with sulphuric acid, and stripped with air to produce about a 25% SO_2 gas and a solution of ammonium sulphate containing about 10% of the feed sulphur. The process recovers about 90% of the SO_2 from dilute flue gases, even at concentrations as low as 0.5%. Tail gases contain as little as 0.03% SO_2 . A serious disadvantage of the process is the high cost of ammonia make-up since large quantities of ammonium sulphate are produced. Because of this it is not an economic method of producing ammonium sulphate.

The DMA process was developed by ASARCO and is used at its Tacoma, Washington copper smelter. The process was used at the Selby lead smelter in California, and is still used by Cities Service Company in Tennessee, Asturiana de Zinc in Spain, and at Falconbridge's nickel refinery in Norway.

The DMA process is used for recovering SO_2 from smelter gases containing from 4 to 10 percent SO_2 . Basic steps of the process are shown in Figure 6 (7). After the gas is cleaned, the sulphur dioxide is absorbed by dimethyl aniline in a bubblecap tower which contains an absorption section, a soda scrubber and an acid scrubber. Tail gases from the DMA absorption section in the bottom of the tower are scrubbed with a dilute sodium carbonate solution in the middle section of the absorption tower, thereby

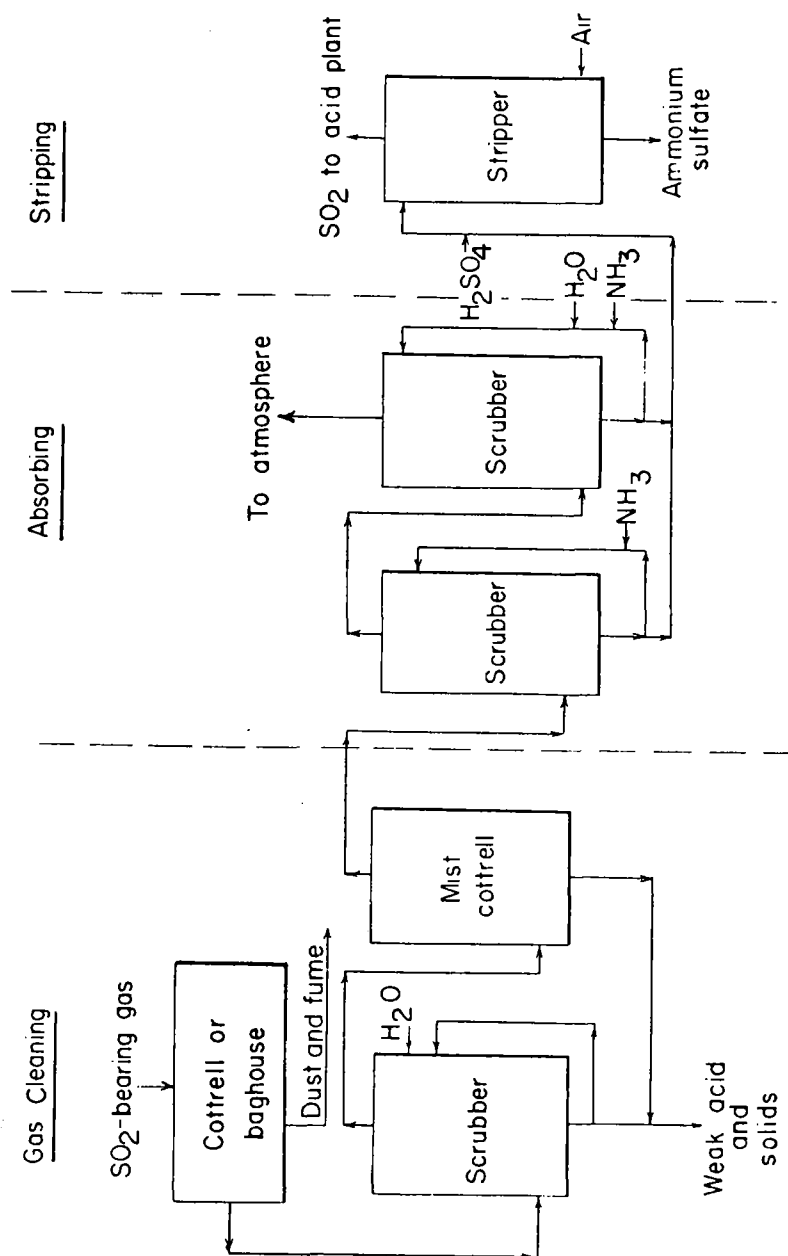


FIGURE 5 COMINCO ABSORPTION PROCESS (7)

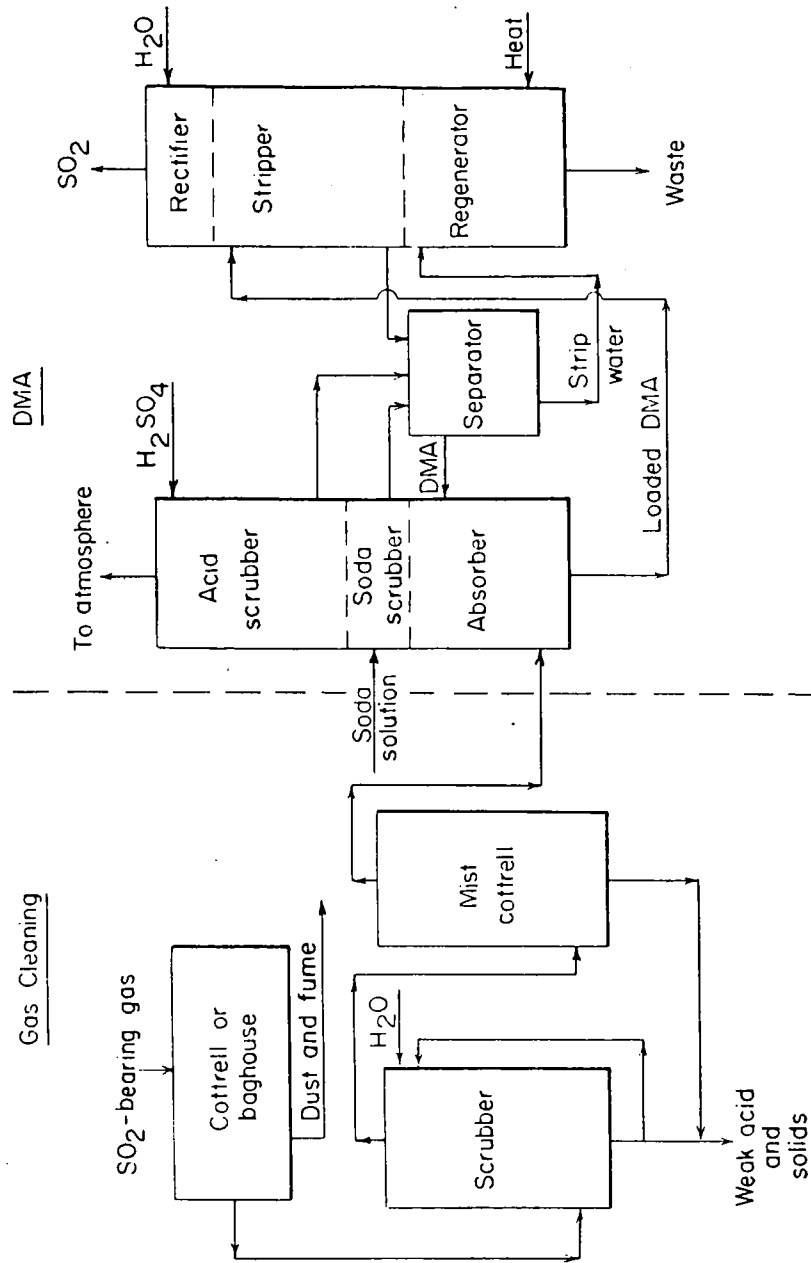


FIGURE 6 DMA PROCESS (7)

recovering residual SO_2 from the gas stream. However, the sodium carbonate serves the more fundamental purpose of neutralizing the sulphuric acid used for DMA vapour recovery as well as any acid formed through SO_2 oxidation. Neutralization of this acid is essential to permit recovery of dimethyl aniline which otherwise would be lost as water-soluble DMA sulphate in waste water discharged from the stripping column. In the upper section of the absorption column tail gases are scrubbed with dilute sulphuric acid to recover DMA vapour which would otherwise escape to the atmosphere.

The loaded DMA solution is stripped with steam in the stripper section of the stripping column. Dimethyl aniline and SO_2 are recovered from the combined aqueous scrubber solutions, by steam distillation in the lower section of the stripping tower. The hot gas stream leaving the stripper, containing SO_2 , steam, and dimethyl aniline vapour, is cooled in the upper or rectifier section of the stripping column. In the presence of the SO_2 , DMA vapour is recovered as water soluble dimethyl aniline sulphate. This leaves essentially pure SO_2 , which can be liquefied.

Chemical absorption processes are considerably more expensive than physical recovery processes with respect to both capital and operating costs, but they have the advantage of being applicable to gases with comparatively low SO_2 content, and giving much higher extraction yields than the physical processes. Thus, it is quite possible to extract 98% by chemical absorption processes, whereas it is only economically feasible to extract 90% by physical recovery processes.

7.2.3 Sulphuric Acid Production

Sulphuric acid is the most common sulphur-containing product recovered from metallurgical gases and is the accepted control approach in the industry. The technology used in the conventional contact acid plant is well proven and there are fewer restrictions on the characteristics of gases from which acid can be made than in the case of alternative products. Sulphuric acid is also the most common form in which industry consumes sulphur, and its manufacture is the least expensive method of efficiently removing SO_2 from smelter gases. Compared with sulphur burning plants, the manufacture of sulphuric acid from metallurgical gases, is however, more difficult and costly.

For the manufacture of sulphuric acid by the contact process to be economic the feed gas strength must normally not be less than about 4% SO_2 because below this gas strength the oxidation reaction is not auto-thermal. In Japan, sulphuric acid is made from weaker reverberatory furnace gases containing about 2.2% SO_2 but energy-intensive gas pre-heating and refrigeration cycles make the process uneconomic (14). Typically, approximately 2 - 3% of total sulphur oxides are present as SO_3 but occasionally copper converter gases may contain as much as 5%, depending on ingress of dilution air and cooling methods (19). It is important to minimize SO_3 formation in the gases before the acid plant and this is best achieved by rapid cooling to about 350°C and excluding ingress of air. Tight-fitting water-cooled converter hoods are generally used to achieve these conditions.

There are three basic steps in making sulphuric acid from smelter gases by the contact process as described below (2,5,14,18,19). Figure 7 shows a schematic diagram of a single or double contact acid plant (14).

1. Gas purification - in which gases are first cleaned by removing dust in electrostatic precipitators. This step is essential because dust will choke the catalyst beds in the converter and impurities present in the dust will poison the catalyst and contaminate the acid. Table 15 shows estimated maximum limits (in terms of total loading without reference to particle size distributions) at the acid plant proper for various objectionable impurities (20). These limits correspond to the maximum amounts of catalyst fouling that can be accommodated with a plant shut-down once per year to screen catalyst and repair equipment. Adding some fresh catalyst to make up for screening losses normally compensates for any slight catalyst deactivation which may occur.

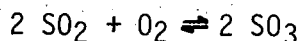
TABLE 15 ESTIMATED UPPER IMPURITY LIMITS (DRY BASIS) FOR CLEANED 7% SO₂ GAS (20)

	<u>Mg/Nm³</u>
Chlorides (as Cl)	1.20
Fluorides (as F)	0.25
Arsenic (as As ₂ O ₃)	1.20
Pb	1.20
Hg	0.25
Se	50.00
Total Solids (dust)	1.20
H ₂ SO ₄ (mist as 100%)	50.00

Due to harmful effects of mercury and selenium in agriculture, they are subject to extremely low limits in acid used for fertilizer manufacture.

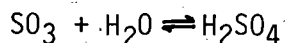
After preliminary cleaning, the gases are then cooled and cleaned in wet scrubbers. The gas must be cooled to reduce its moisture content. Final cooled temperature is determined by the SO₂ concentration, product acid strength desired, cooling water temperature, and plant elevation above sea level. The gas then enters mist precipitators for final cleaning and mist removal to produce an optically clear gas. A weak acid bleed may be necessary to keep impurities at tolerable concentrations. The gases are dried by scrubbing with 93% to 96% H₂SO₄. The heat generated by the absorption of water in the circulating acid is removed in heat exchangers cooled with water, reducing acid temperature to about 40°C. The main gas blower usually follows the drying tower to provide sufficient suction to pull the air required through the purification system and sufficient pressure to blow the gas through the converter heat exchange system and the absorption tower. The gas leaves the blower at about 55°C.

2. Conversion - in which SO_2 is oxidized to SO_3 in contact with a catalyst (usually V_2O_5) by the exothermic reaction



The conversion is normally carried out in a flowing gas stream in the approximate temperature range of 425 to 625°C with excess oxygen present. At temperatures less than about 400 to 425°C, the catalyst is essentially ineffective and reaction does not proceed at any appreciable rate. At temperatures of 600°C and above, there is a tendency towards lower conversion efficiencies due to chemical equilibrium limitations. Catalytic converters are therefore designed to contain a number of adiabatic catalyst beds in series with gas cooling and heat exchange between beds to remove the heat of reaction. In this way, a stepwise approach to high conversion is achieved. Conversion is normally about 97% complete at 450°C. The catalyst deteriorates over time and the acid plant must be shut down for catalyst screening or replacement. As conversion efficiency decreases, the SO_2 content of the tail gas increases. Replacement of the catalyst is made when SO_2 emissions are about 30% above normal. Very dilute gases would require supplemental heating prior to the conversion stage.

3. Absorption - in which the SO_3 is absorbed in a circulating stream of 98.5% H_2SO_4 , to which water or weaker acid is added to react with SO_3 , to produce 99.6% H_2SO_4 according to the exothermic reaction



This reaction proceeds almost completely to the right at temperatures less than about 260 to 300°C. The operation is typically carried out in countercurrent flow packed towers. The reason for using 98.5% H_2SO_4 as an absorbing medium is that this concentration is a maximum boiling point azeotrope (i.e. has a minimum vapour pressure of both SO_3 and H_2O). If water

or weaker acid were to be used, the water vapour above these solutions would react with incoming SO_3 vapour to form micron and sub-micron sized particles of H_2SO_4 in the gas phase. Such particles are not easily absorbed and will pass out of the exit stack as an objectionable fog or aerosol. Cast iron and alloy steels do not corrode at these high acid levels which simplifies pumping and recirculation equipment design. Control of the acid concentrations is carried out automatically using electrical conductivity as the control parameter. Gases leaving the absorbing tower contain sulphuric acid mists which must be removed by a mist eliminator. Tail gases from a single contact acid plant generally contain about 0.16% SO_2 giving an overall SO_2 removal efficiency of up to 98%. For higher conversion efficiencies, double absorption acid plants are used that can achieve overall SO_2 conversion efficiencies in excess of 99% and where the tail gas contains as low as 0.05% SO_2 . Double-absorption acid plants are necessary where compliance with the most stringent air pollution control regulations is required. In this type of plant, gas which has been partially converted to SO_3 by passing through 2 or 3 catalyst beds is cooled, passed through an intermediate SO_3 absorbing tower, reheated and then passed through another 1 or 2 catalyst beds to achieve a high overall conversion. The gas is then passed through a final absorbing tower for SO_3 removal. Lime neutralization of acid plant tail gas can further reduce the last traces of SO_2 to 0.01%, but sulphur fixation in this manner is likely to be expensive. Double-absorption plants are about 10 - 20% more expensive than corresponding single contact acid plants, and require more energy and may have lower on-line availability.

High strength acid (up to 99.6% H_2SO_4) is bled from the absorption system and diluted with water to 93% H_2SO_4 which is the usual market product.

The operating characteristics of copper and nickel smelters leads to several important design considerations in an acid plant for treating metallurgical gases, as compared with gases from a sulphur burning plant. This results from the fact that gases from a smelter may be variable in strength and flow rate. The gas strength will also be different according to smelting process and this will lead to a different set of design parameters. Thus, the design of an acid plant is unique to the smelter whose gases it is treating. A continuously flowing gas containing 5 - 8% SO_2 and 30 - 50% more oxygen than SO_2 is normal for a conventional contact acid plant (2). High concentrations of SO_2 are desirable to keep acid plant size and cost to a minimum. With conventional plant designs an upper limit of about 9 - 11% SO_2 exists, depending on oxygen concentration. The major factors limiting the use of higher SO_2 concentrations are catalyst behaviour and life, and the need for special construction materials to handle high temperatures in corrosive environments. A gas with intermittent flow or weak in SO_2 requires specially designed oversize heat exchangers and, in some cases, extra heat from external sources. Furthermore, an acid plant must be designed for the maximum or peak flow rate, and thus intermittent gas flow requires a larger design capacity plant for a given daily acid production.

Acid plants treating smelter gases are typically supplied with two gas streams; one from a roaster or modern (i.e. not reverberatory) primary smelting furnace, and a second from the converters. Reverberatory furnace off-gases are typically not suitable for acid plant feed because of their low SO_2 and O_2 concentrations. However, it is conceivable that some reverberatory furnace off-gas might be blended with other gases if the latter are unusually rich in SO_2 . The determining factor will be maintenance of a satisfactory acid plant gas composition, typically no less than 4.0% SO_2 and with an oxygen concentration no less than SO_2 concentration (in the range of about 7% to 11% combined SO_2 and O_2) (19). For single-contact acid plants, the $\text{O}_2 : \text{SO}_2$ ratio should be at least from 1.25 to 1.3:1. Double-contact plants require ratios of at least 1.18 to 1.22:1 (14). The two gas streams mentioned above are usually of different strength and flow rate. The primary smelting furnace gas stream is generally of constant composition and flow rate, whilst that from

the converters, because of their batch and two-stage nature of operation, is generally of variable flow rate and strength. Acid plant design must take account of several smelter operating characteristics. The operations of a smelter, particularly scheduling of converter operations on a staggered basis, are, to an extent, constrained by the design parameters and operating requirements of an acid plant. Where it is not possible to schedule converter operations to provide as nearly uniform gas flow and strength as possible to the acid plant, it is necessary either to shut down the acid plant and then restart it when gas is available (which is not really a viable alternative in a metallurgical plant), or to provide a continuously operating fired heater at the acid plant to keep flowing process gas (or air) hot.

Design specifications fix many parameters within the acid plant which can affect operation once on line. The design basis must be realistic and allow for normal variations in operation of the smelter. For example, the maximum design volume governs equipment size, including the acid plant blower.

The SO_2 and O_2 contents of the feed gas influence the design of the acid plant converter and associated heat exchangers. A gas strength lower than the design minimum, caused by excessive in-leakage or operating problems, may result in the acid plant being no longer autothermal in which case fuel must be burned. If the gas strength is too low, there may be difficulty in making acid of acceptable strength. Since the basis used for designing an acid plant governs the subsequent operation of the smelter, it is prudent to be conservative in the design of the former.

Conversion efficiency of an acid plant is usually lower than normal during start up. It is essential that the operation of the smelter is stabilized to produce an off-gas that is within the acid plant design specifications. Depending on the smelting process employed, it could take from 4 to 16 hours to produce an acceptable gas for the acid plant. A further 8 hours are then required to stabilize the acid plant and achieve design conversion. As a result, the tail gas emission could well exceed the design level, by a factor of 2 to 4, for 12 to 24 hours after plant start-up. Installation of an auxiliary sulphur burner can be used to control smelter feed gas composition to maintain the tail gas composition within design limits (2).

7.3

Weak Gas Streams

Weak gas streams originate from the following sources in copper and nickel smelters:-

1. process gas streams, where the SO_2 content is generally around 0.5 to 2.0% SO_2 , eg. from sinter machines, blast furnaces, multihearth roasters, reverberatory furnaces, electric furnaces, and fire refining furnaces.
2. tail gas emissions from sulphur fixation plants treating in general, the concentrated process gas streams.
3. fugitive emissions, which arise from
 - transfer of hot calcine from multihearth roasters to smelting furnace
 - leakage through furnace refractories
 - uncovered tapholes and launders when tapping matte, and from its transport in the converter aisle
 - converters when rotating in and out of the stack position for charging and pouring of materials.

Fugitive emissions leak into the smelter building itself. This not only creates unpleasant working conditions but also causes SO_2 to be emitted into the outside atmosphere at ground level which may have deleterious effects in the immediate vicinity of the smelter. The quantity of sulphur lost as fugitive emissions represents about 1-2% of the total S input to the smelter (5). Fugitive emissions in the building can be minimized by adopting the following engineering and operating practices:-

- complete sealing of calcine cars and charging system
- sealing furnace refractories tightly and operating furnaces at a slightly negative pressure, or steel encasing the furnace (eg. Inco flash furnace)
- providing adequate ventilation around tapholes and launders by installation of gas collection hoods, covers, ducting and fans

- maintaining strong draught conditions in converter hoods and ensuring that hoods and flues are preserved in a good state of repair. Some smelters (in Australia and Japan) have installed secondary hooding around the converters to ventilate emissions during pouring. Installing tight-fitting converter hoods
- enclosing the smelter building sufficiently to permit collection of leakage gases through hoods installed in various parts of the smelter, as practised at some plants in Japan. These gases can be scrubbed with water followed by neutralization with lime.

Technology for the control of weak SO_2 gas streams has been largely developed for thermal power plants. In some cases certain processes may be applicable in the metallurgical industry. Although a few systems have been developed specifically for metallurgical operations, the technology has not enjoyed wide acceptance or application in the metallurgical industry for treatment of weak process and tail gas streams, due in part to the fact that many of the proposed flue gas desulphurization (FGD) systems are not yet commercially proven and secondly, because a salable product generally cannot be produced economically. The systems are generally expensive to install, particularly when considered in terms of the incremental amount of sulphur recovered from a metallurgical gas after the majority of sulphur has been recovered as sulphuric acid. In addition, at many smelter locations (outside of Japan), air pollution control regulations are not sufficiently stringent as to necessitate installation of FGD systems. Thus, with few exceptions outside of Japan where frequently special conditions prevail, weak SO_2 gas streams, i.e. those not amenable to direct processing in sulphuric acid plants, are currently uncontrolled.

Two overall approaches, either singly or in combination, have been adopted in efforts to develop applicable technology for the control of weak SO_2 gas stream emissions (14). These are:-

1. increasing the concentration of SO_2 by using a regenerative absorption system, to a range where it is feasible to produce sulphuric acid or other usable by-products.
2. neutralizing the effluent as a stable waste product by using a nonregenerative absorption or scrubbing system.

The major source of weak, uncontrolled SO_2 emissions from smelters is the off-gas generated by the reverberatory furnace. For reasons previously mentioned, sinter machines, blast furnaces and multihearth roasters are now virtually obsolete in the industry and are unlikely to be considered for any new smelter. The reverberatory furnace is, however, still one of the major primary smelting units and it is towards control of these gas streams that technological developments have been addressed. In the U.S.A., approximately 22% (on an average basis) of the sulphur input to copper smelters is emitted from the reverberatory furnace as uncontrolled weak gas streams. For any given plant, the range can be from 9 to 34%, depending on whether the furnace is charged with calcine or concentrate, respectively (14).

Construction, operation and maintenance of the reverberatory furnace are important factors in concentrating the SO_2 content of the gases. Minimizing dilution effects by sealing of all openings in furnaces, flues and ductwork; close control of draught conditions; reduction of excess burner air; and also oxygen enrichment of combustion air and more uniform charging practice can increase the gas strength to about 2.5% SO_2 . While in general this gas is insufficiently concentrated for direct processing to sulphuric acid, it is a sufficient increase over conventional practice to provide significant reduction in subsequent size and complexity of retrofit concentration or neutralization systems.

Using oxygen enrichment to 60% O_2 in air through special oxy-fuel roof burners, the El Teniente smelter in Chile has increased the gas strength to between 5.8 - 7.3% SO_2 (14). As in the case with the Ni-Cu reverberatory furnaces at Inco's Copper Cliff smelter where similar results have been obtained, this technique was adopted primarily to increase production and reduce fuel requirements rather than for environmental reasons.

In Japan, from 1971-1973 the Onahama smelter used oxygen enrichment to increase the gas tenor to 2.5% SO_2 for direct treatment, without further concentration, in a single contact sulphuric acid plant of modified design. However, considerable energy was expended for gas reheat to promote catalytic reaction and for refrigeration for water balance to the extent that the acid plant was not economic. The plant achieved efficiencies of 96% conversion of SO_2 to SO_3 even at low (1.5%) concentrations of SO_2 . Product acid strength was 93-94% H_2SO_4 . A simplified flowsheet of the remodelled acid plant is shown in Figure 8 (14).

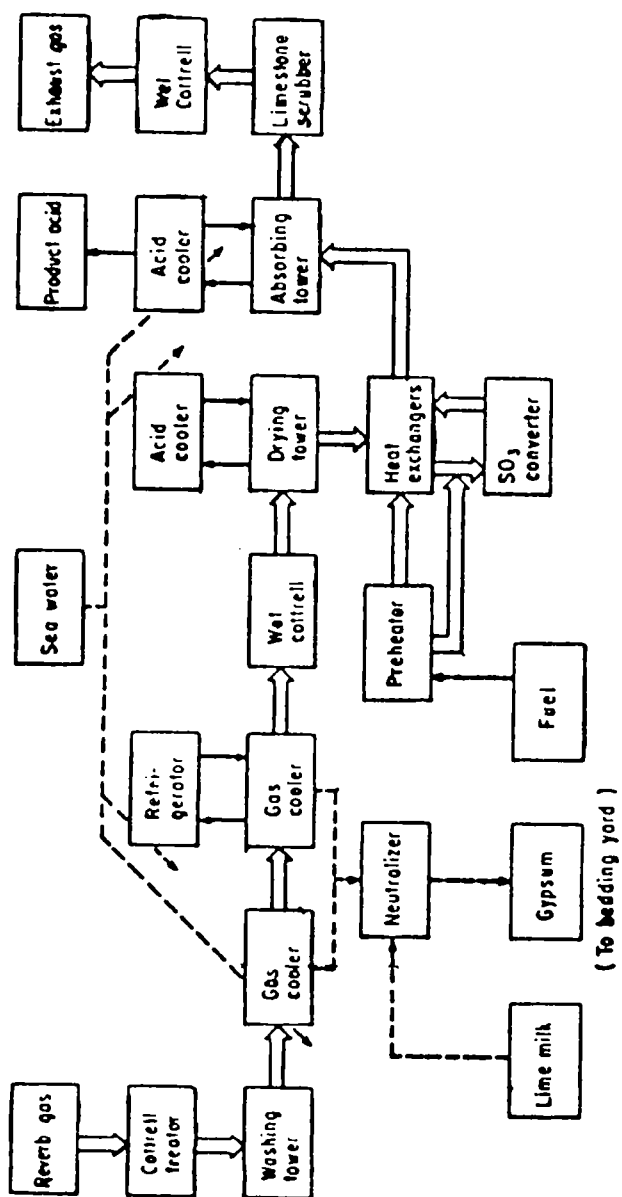


FIGURE 8 FLOWSHEET OF REMODELLED ACID PLANT (14)

In certain cases, reverberatory furnace gas may be concentrated to a strength which, when combined with converter gases, produces an aggregate gas strength (greater than 4% SO_2) which is suitable for treatment in a conventional acid plant.

The technology developed for, and applied to, the treatment of weak reverberatory furnace gas streams is equally applicable to the treatment of gas streams from multihearth roasters. These gases vary in strength from about 2 - 5% SO_2 , depending on the amount of dilution air ingressed. The multihearth roaster has now largely been replaced by the fluid bed roaster, or the roaster-reverberatory furnace combination has been replaced by a more modern and environmentally acceptable primary smelting process, such as flash smelting.

Combining a FGD system with an acid plant, even when the gas strength is high enough for direct processing in the latter, will tend to reduce the overall load and design requirements on the acid plant. Acid plant equipment size is reduced by reducing the volumetric gas flow rate and the efficiency of conversion is increased by increasing the SO_2 concentration. For example, when a magnesium oxide FGD system is used where 10-13% SO_2 concentration off-gas is produced, overall control system size is greater than when a citrate system with over 90% generated SO_2 gas is used (14).

Several FGD systems developed specifically for control of weak reverberatory furnace gases, or for gases from utilities, have demonstrated technical feasibility. With some adjustment in operating conditions, it has been concluded that there appears to be no major technical reason why experience with off-gases from utility boilers cannot be applied to reverberatory furnace off-gases (14).

The processes developed to control weak SO_2 emissions according to the two overall approaches previously mentioned, and their application in smelters, are described below (14).

7.3.1 Regenerative Absorption Systems

The following regenerative absorption systems have been developed:-

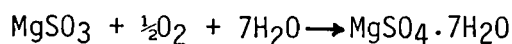
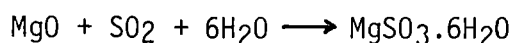
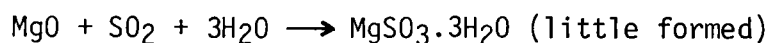
7.3.1.1 Magnesium Oxide Concentration System

The system developed at the Onahama copper smelter in Japan has been in use since 1973 and is shown in quantified flowsheet form in Figure 9 (14).

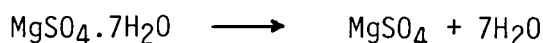
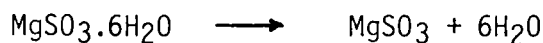
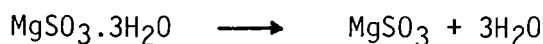
The MgO process was selected to concentrate SO₂ from the reverberatory furnace off-gas for direct acid plant processing because at the time, in comparison with other processes, less energy was required.

The process employs MgO in aqueous slurry as the scrubbing medium. The three major process areas are absorption, drying and calcining.

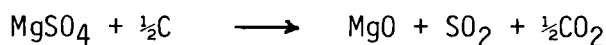
In the absorber the MgO is converted to magnesium sulphite by the SO₂ in the flue gases according to the following reactions:-



The magnesium sulphite and small amount of sulphate formed are then dried to liberate the water of crystallization as follows:-



The sulphite is then calcined where it is converted back to MgO and then to the hydroxide for reuse. The SO₂ is generated in more concentrated form (average 10% SO₂, maximum 13% SO₂) for conversion to sulphuric acid. Coke is used to reduce any magnesium sulphate which is formed.



The initial washing tower and the secondary sea water cooled gas coolers prior to the absorption tower are those used in the gypsum system at the Onahama smelter. The gaseous effluent from the absorber, after being cleaned, is discharged to atmosphere containing about 20 ppm SO₂.

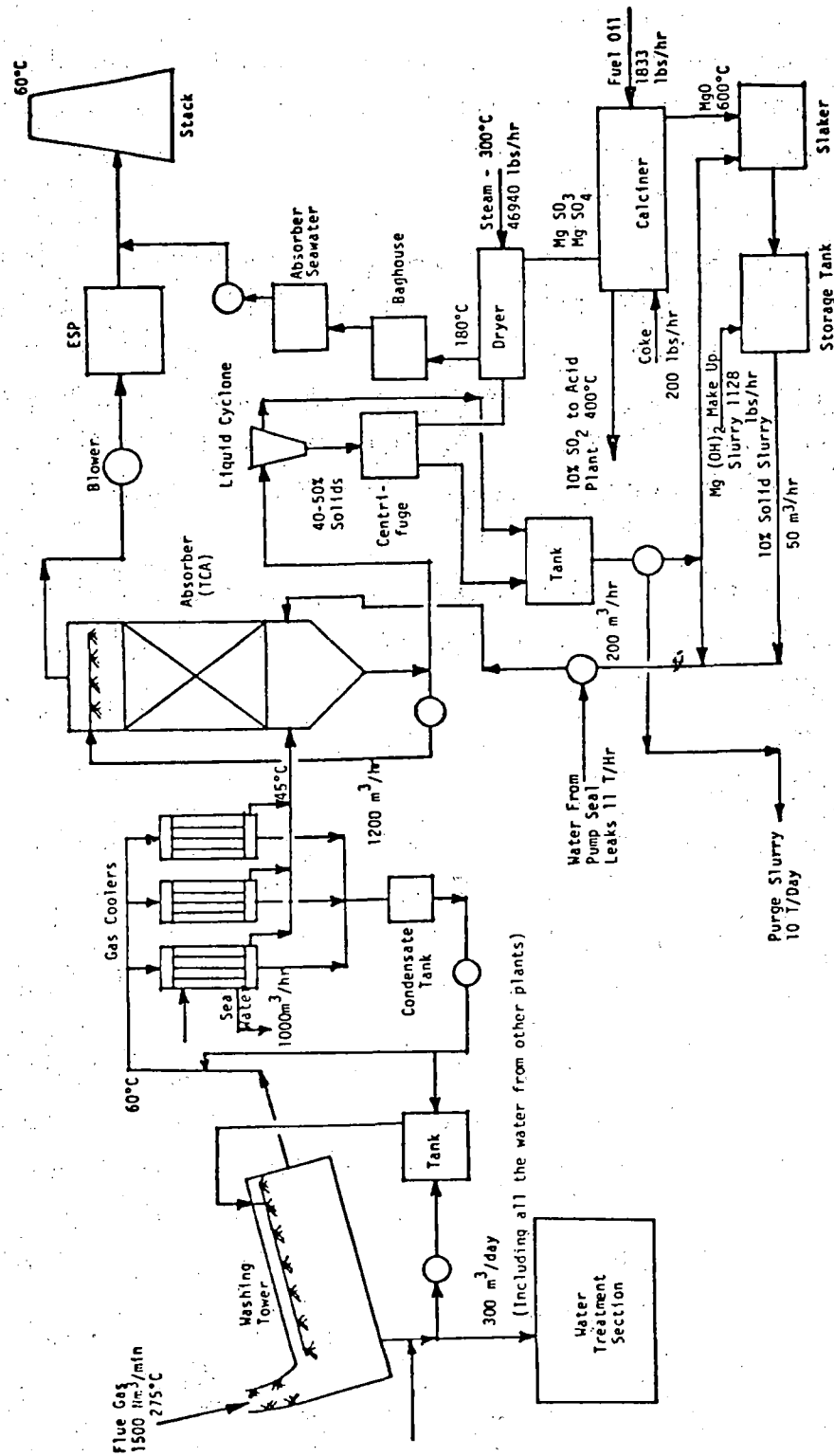


FIGURE 9 FLOWSHEET FOR MgO SYSTEM AT ONAHAMA SMELTER (14)

The system appears to have considerable capability for absorbing fluctuations in the SO_2 content from the reverberatory furnace. This is inherent because of the capacity of the absorbent, the supply of the absorbent, and the fact that the pH is maintained constant. Below a pH of 6, magnesium bisulphite begins to form and must be bled from the system, because it is not regenerable.

In the USA, an MgO absorption system has not been used for treating smelter gas streams although the technology has been applied to power plant gas streams. Whereas the Onahama smelter uses a TCA absorber, the U.S. plants use a venturi scrubber. Purchase of the MgO in the form of a ready-mixed magnesium hydroxide slurry is preferable to handling and mixing MgO and it is reported that recycled MgO slurry is more satisfactory from an SO_2 removal standpoint.

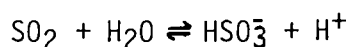
It appears that there is no major technical reason why the MgO system cannot be universally applied in the concentration of weak reverberatory furnace off-gases.

7.3.1.2 USBM Citrate Process

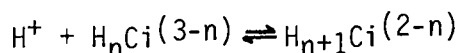
The USBM selected for development a buffered solution of citric acid and sodium citrate because of its chemical stability, low vapour pressure, and adequate pH buffering capacity (14). This system was originally designed on the laboratory scale to produce sulphur by using manufactured H_2S as a reducing agent. While pilot plant tests on reverberatory furnace gases at the San Manuel smelter encountered problems, the potential for absorbing SO_2 into the citrate solution was demonstrated, since 93 - 99% of the SO_2 was consistently removed from a gas stream containing 1.0 - 1.5% SO_2 . Most of the problems occurred in the SO_2 to sulphur conversion circuit, i.e. downstream of the absorption and regeneration sections of the plant.

Two other pilot plant tests using the USBM citrate process have been carried out (14). Stack gases from a coal-fired steam generating station containing 0.1 - 0.2% SO_2 were treated where 95 - 97% of the SO_2 was removed. Treatment of sinter machine gases containing 0.5% SO_2 at the Bunker Hill lead smelter proved inconclusive. In both cases, steady-state conditions were not achieved either due to equipment breakdown and/or difficulties with the SO_2 reduction system.

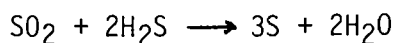
Figure 10 shows a generalized flowsheet for the USBM citrate process (14). Gases are cleaned of particulate matter and acid mist and cooled to between 46° and 65°C before passing to a countercurrent absorption tower. The liquid is an aqueous solution of sodium citrate and citric acid. Absorption of SO_2 in aqueous solution is pH dependent, increasing at higher pH. Dissolution of SO_2 forms bisulphite ion with resultant decrease in pH by the following reaction:-



However, by incorporating a buffering agent in the solution to inhibit pH decrease, high SO_2 loading and substantially complete SO_2 removal from the waste gases can be attained. The following reaction illustrates the buffering action performed by the citrate ion:-



The cleaned gas from the absorber is exhausted to atmosphere via a stack. The SO_2 rich citrate solution from the bottom of the absorber is fed to a reactor where SO_2 is reduced to sulphur by H_2S in aqueous solution according to the following reaction:-



The citrate solution is regenerated. Sulphur is removed by oil flotation, melted at 125°C , and decanted under pressure. The citrate solution (top layer) is discharged to a flash drum at reduced pressure. Sodium sulphate is removed from the citrate solution in a vacuum crystallizer by cooling to a temperature well above the freezing point of water.

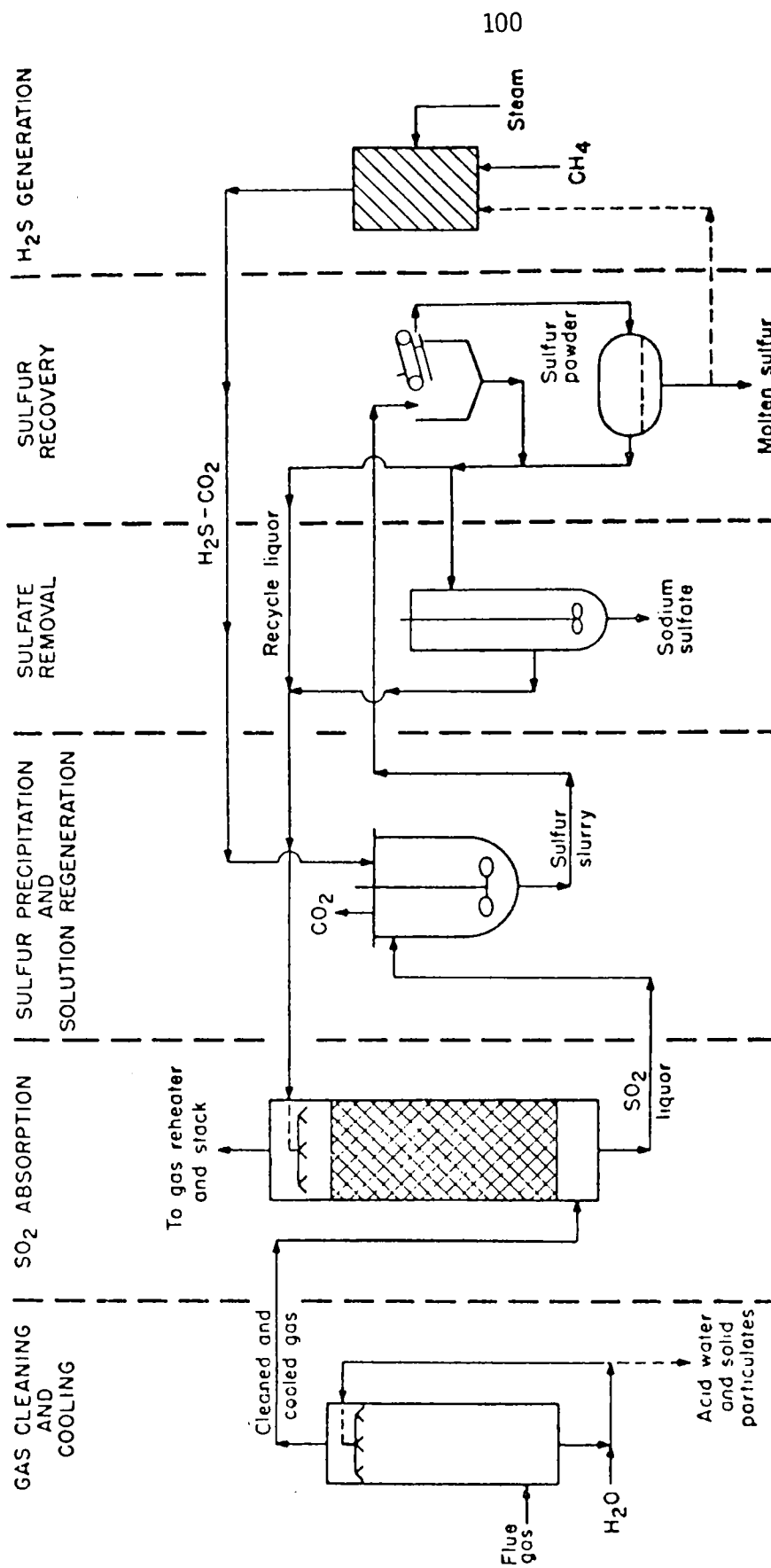
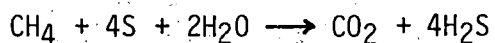


FIGURE 10 FLOW DIAGRAM FOR THE BUREAU OF MINES CITRATE PROCESS (14)

H₂S for regenerating the absorbent and precipitating elemental sulphur can be produced by reacting sulphur with methane and steam at about 630°C by the following reaction:-



Several problems were encountered with the process during the pilot plant test programme. These were:-

1. complexity of the process affecting its reliability
2. dependence on methane whose availability is uncertain
3. nearly 2 - 3% of the SO₂ is oxidized
4. high kerosene consumption
5. lack of development on the H₂S regenerating system and the sulphur handling system.

As an alternative to sulphur precipitation by H₂S, the USBM is investigating steam stripping of the pregnant absorbent solution to produce strong SO₂ gas for feed to a sulphuric acid plant. This alternative would simplify the process and probably eliminate most of the problems so far encountered. Process economics and widespread adoption of the USBM Citrate Process will depend primarily on the cost and availability of citric acid.

7.3.1.3 Flakt-Boliden Citrate Process

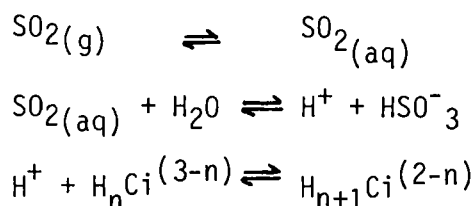
Since 1970, Boliden has been successfully using an SO₂ control system employing only low temperature water as absorbent to treat a blend of flue gases, varying in strength from 0.5 - 3% SO₂, from multihearth roasters, two electric furnaces, converters and a lead smelter (14). The absorbed SO₂ is stripped by heating with steam to produce liquid SO₂ (6t/hr). In 1976 a second, larger plant for liquid SO₂ production (16t/hr) was put into operation. To give flexibility, the liquid SO₂ can also be evaporated and fed to an existing acid plant in order to keep feed gas strength to the plant approximately constant.

In locations where cold water is not available year-round, it is desirable to improve the SO₂ absorption properties of water. This led to development of another absorbent - a brine solution of citric acid and sodium citrate which improved the flexibility of the system over cold water. The exact composition of the absorbent depends on a number of factors such as SO₂ concentration in the feed, gas temperature and required SO₂ outlet concentration and absorbent temperature. Citric acid has a very low vapour pressure and shows great chemical stability.

The Flakt-Boliden citrate process is based on an absorption stripping technique. The pregnant absorbent (brine of citric acid and sodium citrate) passes to a stripper where a mixture of SO₂ and water vapour is driven off. After condensing the main quantity of water, the SO₂ may be marketed in different ways. Since the absorbent is a solution rather than a slurry, scaling and plugging of equipment is minimized, and is far less than in the USBM citrate process.

Figure 11 illustrates a simplified flowsheet for the Flakt-Boliden citrate process (14). The incoming gas is cleaned and then cooled to saturation by direct water injection. In addition to dust, acid mist is removed in a mist precipitator before the absorption step to minimize sodium sulphate formation in the absorber which would increase purge requirements.

The reactions occurring in the absorption stripping operation are given below:



The forward reactions take place during absorption, and the reverse reactions during stripping.

Absorption of SO₂ in aqueous solution is pH dependent, increasing at higher pH. Because dissolution of SO₂ forms bisulphite (HSO₃⁻) ion with the resultant decrease in pH by the second reaction, the absorption of SO₂ in aqueous solution is self-limiting. However, by incorporating a buffering agent

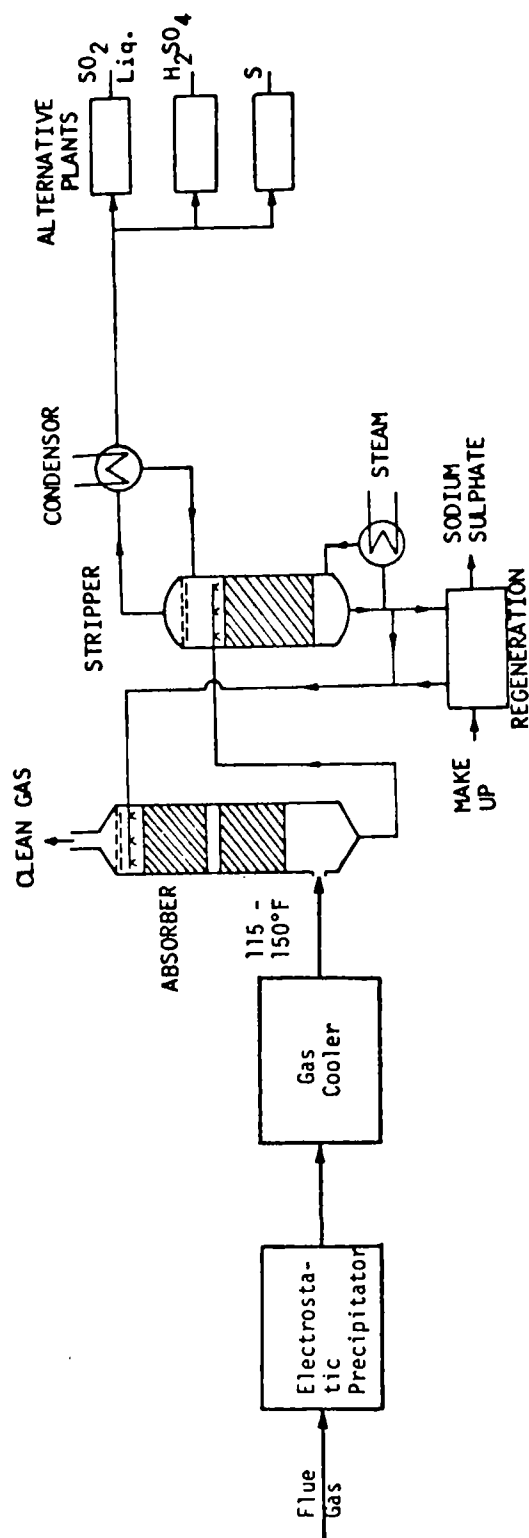


FIGURE 11 FLOW DIAGRAM FOR THE FLAKT-BOLIDEN CITRATE PROCESS (14)

in the solution to inhibit pH decrease (remove the hydrogen ions formed in the second reaction), high SO_2 loadings and substantially complete SO_2 removal can be attained. In the citrate process this is accomplished by the buffering action of the various citrate species by the third reaction. The buffering capacity is dependent on the concentration of citric acid and sodium hydroxide and the relation between them. The relationship depends on the raw gas composition, and generally the absorbent pH is between 4 and 5.

The important process variables at the absorption step are:

1. liquid-to-gas flow ratio in the absorber
2. SO_2 content of the incoming gas
3. composition of the solution
4. temperature of operation.

The absorption of SO_2 takes place under atmospheric pressure and close to equilibrium between the SO_2 concentration in the gas and that in the solution. The absorption efficiency is in the range 95 to 99%. The cleaned gas, after passing through a demister is passed to atmosphere via a stack.

Stripping is accomplished by steam treatment at reduced pressure in counter-contact to the liquid flow. Stripped absorbent, containing a residual amount of SO_2 , is recirculated to the absorber. The concentrated SO_2 gas which can be as high as 95% can be used for the production of sulphuric acid, elemental sulphur, or liquid SO_2 . The main impurity accumulated in the closed absorption loop is sodium sulphate which, although small in quantity, is removed by a bleed stream.

Gases from several sources in the copper and lead smelters were fed to the citrate process pilot plant at Boliden. The SO_2 content thus varied between 0.2 and 6.0% SO_2 because of the discontinuous nature of the operations.

A typical Flakt-Boliden SO_2 recovery process for green and calcine-charged reverberatory furnaces is proposed in Figures 12 and 13 (14). Inlet gas strengths specified are respectively 1.5% and 0.8% SO_2 , the product would be liquid SO_2 , and 90% removal of SO_2 from the input gases is predicated.

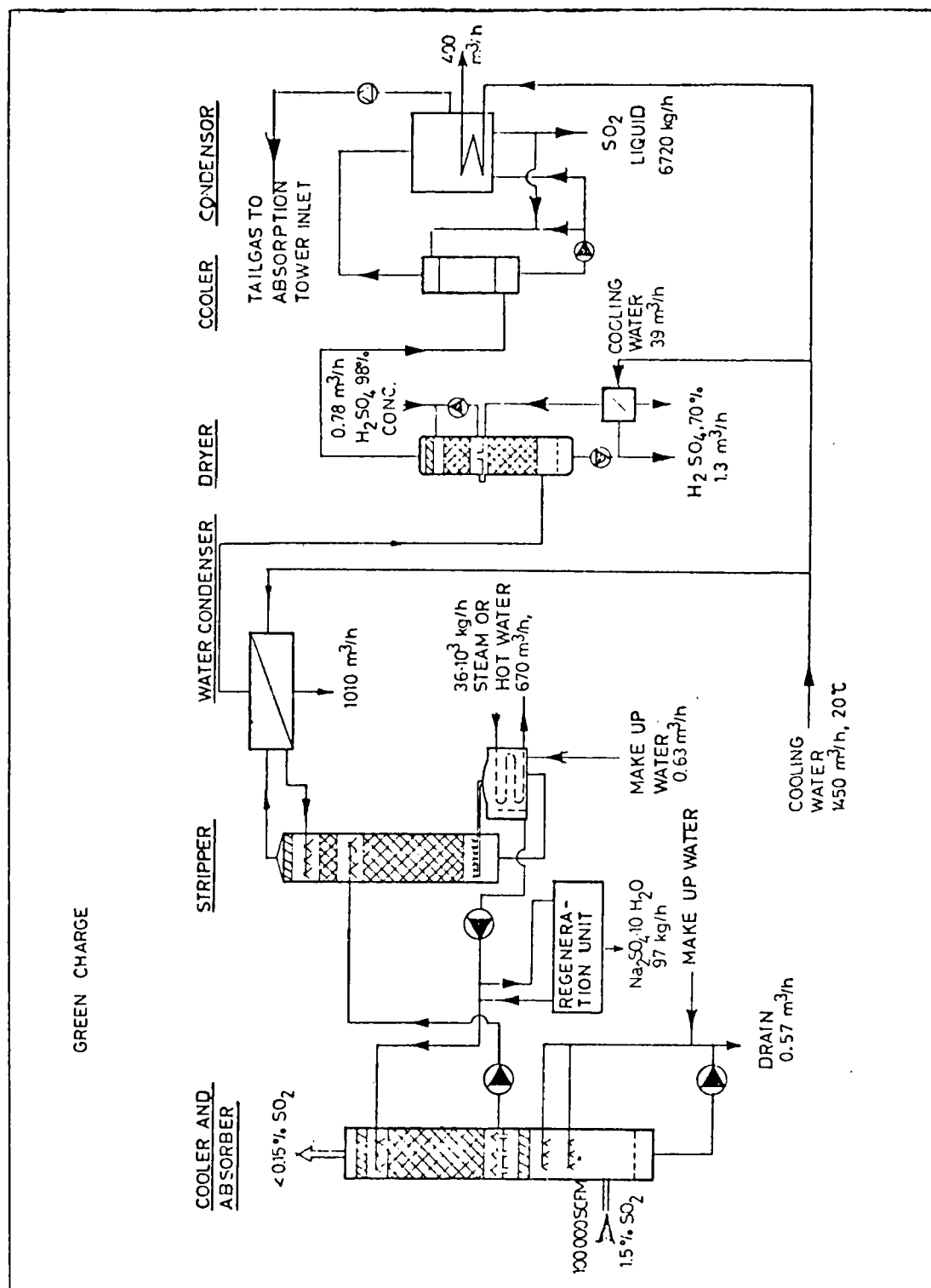


FIGURE 12 GREEN CHARGE REVERBERATORY FURNACE OFF-GAS FLAKT CITRATE SO₂ CONTROL SYSTEM (14)

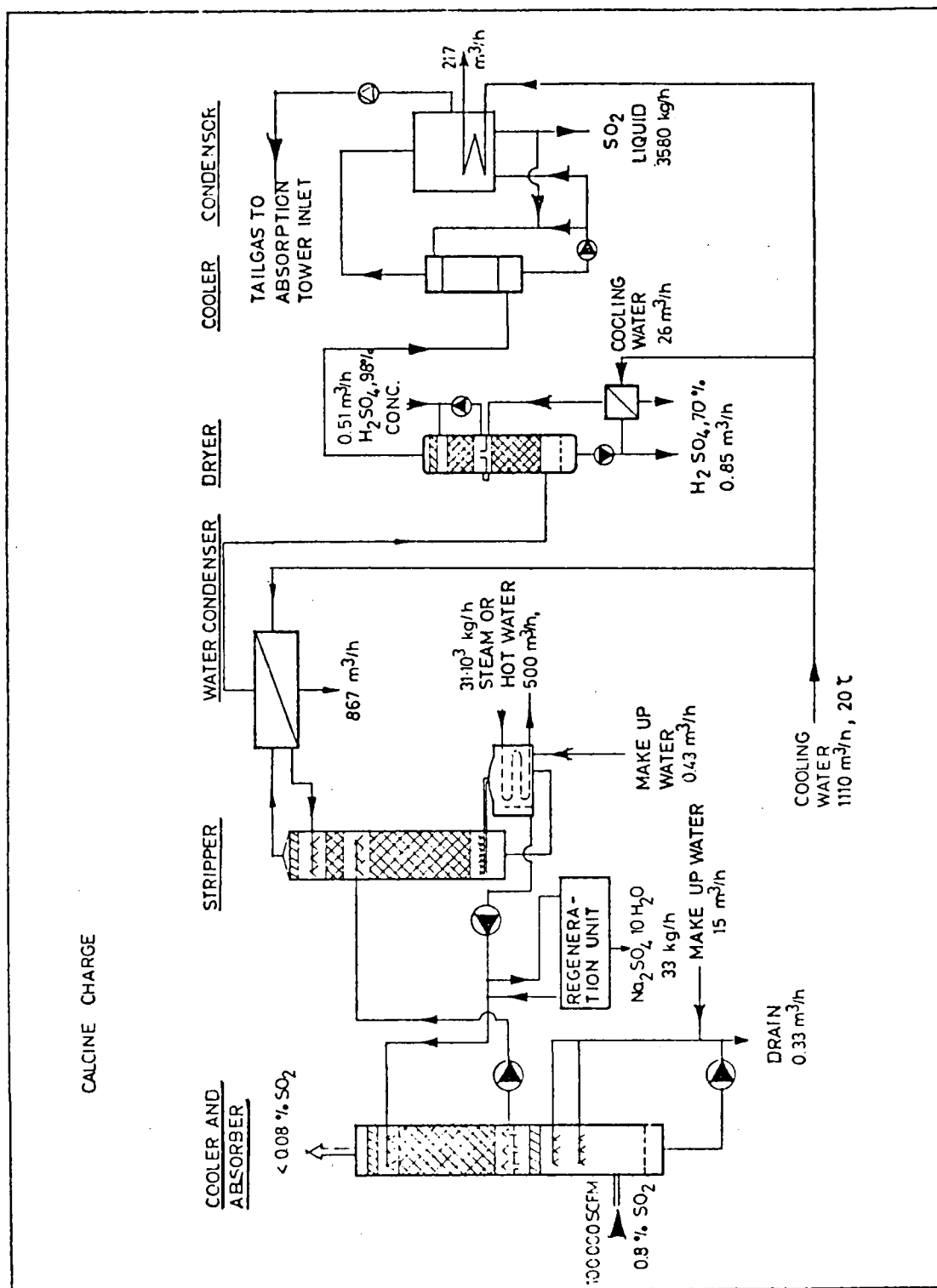


FIGURE 13 CALCINE CHARGE REVERBERATORY FURNACE OFF-GAS FLAKT CITRATE SO_2 CONTROL SYSTEM (14)

Operating experience on metallurgical gases, both at full-scale and particularly at pilot plant scale, indicate the feasibility of citrate as an absorbent. Whilst operation of a full-scale plant processing reverberatory furnace gases must still be demonstrated for long periods of time, problems encountered in testwork do not represent fundamental problems that would eliminate this system from consideration. Salts other than citrates (eg. phosphate buffers) may also be used.

The essential difference between the USBM and Flakt-Boliden processes is the method of recovering absorbed SO_2 ; i.e. as sulphur (USBM) or concentrated SO_2 (Flakt-Boliden).

7.3.1.4 Cominco Ammonia Scrubbing System

Ammonia-based scrubbing processes, although they have been studied for a long time, are not amenable to throw-away operation because of the cost of ammonia and the solubility and nitrogen value (with chemical oxygen demand) of ammonium salts.

The Cominco process can achieve high efficiencies of SO_2 removal over a wide range of SO_2 concentrations well within that encountered by copper reverberatory furnaces (14). Since the absorbent is a solution rather than a slurry, there are no scaling or plugging problems in the process. The system produces a concentrated SO_2 stream which can be used to produce sulphuric acid, elemental sulphur, or liquid SO_2 . The main problem with this process is the loss of ammonia from the system. The ammonia volatility may limit the minimum level of SO_2 emission to 200 to 300 ppm for practical operations and also introduces costs that could produce an economic problem.

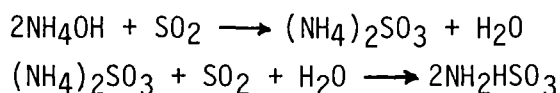
A semi-commercial ammonia base absorption plant operating on zinc roaster gas and a 40 t/day reduction unit went into production in 1936. A larger absorption plant operating on zinc roaster gas of 5.5% SO_2 with tail

gas less than 0.2% SO₂, a plant to treat the lead sintering machine gas of 0.75% SO₂ with tail gas of 0.10% SO₂, and two additional reduction units were added, bringing the total rated capacity to 150 t/day of sulphur.

In 1943, a number of changes were made to meet fertilizer requirements. The SO₂ reduction plants were closed down in 1943, and the 100% SO₂ was used to enrich the gas to the contact acid plants and increase the output. Presently, Cominco converts part of the SO₂ into sulphuric acid and part into ammonium sulphate.

The flowsheet of the ammonia scrubbing process for controlling SO₂ for the lead sintering plant at Trail is given in Figure 14 (14).

The process consists of absorbing the SO₂ from the flue gas in aqua ammonia, forming a solution that is essentially ammonium bisulphite, according to the following reactions:-



In addition, a small amount of ammonium sulphate is formed.

Gases containing 0.75% SO₂ pass through a humidifying tower and dust collector before entering the absorption plant which consists of two parallel systems. Gases are first cooled in a cooling tower where water and gas flows are countercurrent. Flow of gas and solution in the absorption towers is illustrated in Figure 14. Aqueous ammonia containing about 30% N₂ is added to the circulation in the absorption towers. The most significant operating parameters in the absorption step are:-

1. solution temperature
2. total concentration of SO₂ and NH₃ in solution
3. concentration of individual ammonium salts (sulphite, bisulphite, and sulphate) which also determines pH
4. ratio of liquid to gas flow
5. type of internal column construction.

The equilibrium absorption of SO₂ is enhanced by decreasing the solution temperature and by minimizing the total SO₂ concentration in the solution. Ammonia losses are reduced by decreasing the solution temperature and minimizing the total NH₃ concentration in solution.

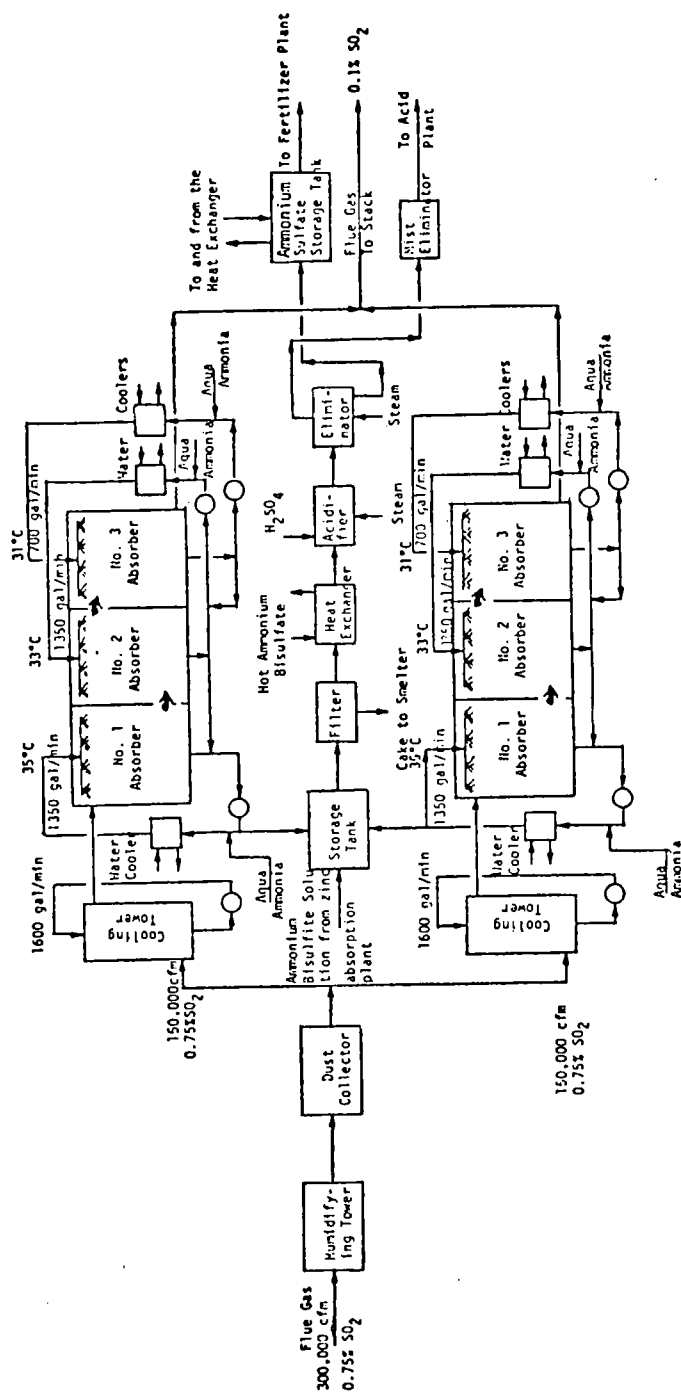
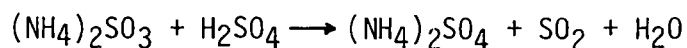
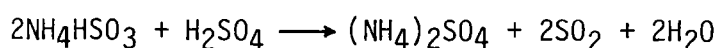


FIGURE 14 FLOW DIAGRAM COMINCO AMMONIA SCRUBBING PROCESS (14)

Mixed ammonium bisulphite solutions from the lead sintering and zinc roaster absorption plants are filtered, the filter cake being returned to the smelter, the filtrate being heated by hot ammonium sulphate solution in a heat exchanger, and then by steam and mixed with sulphuric acid in an acidifier. The evolved SO₂ gas and solution overflow into an eliminator where the remainder of the gas is boiled out of the ammonium sulphate solution with direct steam. These reactions are represented by the equations:-



Ammonium sulphate solution, substantially free of SO₂, is treated with aqueous ammonia to neutralize the free acid and produce a slightly ammoniacal solution to minimize corrosion of equipment. The ammonium sulphate solution is pumped to the fertilizer plant. The gas from the eliminator, containing SO₂ and water vapour, flow to an acid plant. Flue gas to the stack contains 0.1% SO₂.

Whilst the Cominco ammonia scrubbing process has been used at full scale to treat metallurgical gases from a lead and zinc plant, it has not been used to concentrate gases from a copper smelting reverberatory furnace, but indications are that technical feasibility could be established. However, a serious problem that has been encountered with most of the ammonia scrubbing systems is the formation of an opaque fume in the exit gas stream. The fume is partly attributed to gas phase reactions of NH₃, SO₂, and water forming ammonium sulphite, which, due to its small size, is not efficiently removed by a conventional mist eliminator. Establishing critical pH and temperature ranges within the primary scrubber can minimize the problem.

7.3.1.5 Wellman-Lord Process

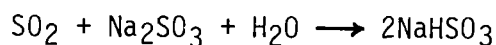
The Wellman-Lord SO₂ recovery process was developed by Davy Powergas in the late 1960's for the thermal power industry. Thirty commercial installations throughout the world are either in operation or in design or construction, half of these being in Japan. The process has been successfully applied to SO₂ absorption from sulphuric acid plants, Claus unit tail gases, as well as oil and coalfired boilers. However, it has never been applied to the metallurgical industry.

The installations operating in the U.S. have an SO₂ removal efficiency of greater than 90%, and an on-stream time of greater than 97% for the absorption step. The respective figures for the Japanese plants are 95% and 98% (14).

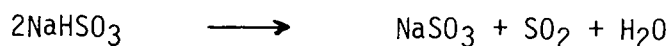
The process provides a method by which the SO₂ from a weak stream can be absorbed by chemical reaction with an alkaline scrubbing liquor. The SO₂ is later desorbed by a heating process in which the SO₂ appears in a concentrated form and the absorbing solution is regenerated for recycling to the scrubber. The resulting strong SO₂ gas can be further processed to sulphuric acid, elemental sulphur, or liquid SO₂.

Even though the Wellman-Lord process has considerable full-scale experience at power plants and refineries, its use for processing reverberatory furnace off-gas has not been demonstrated and would require additional confirmatory testwork.

Figure 15 gives the flowsheet for the Wellman-Lord process which is based on the chemistry of the sodium sulphite/bisulphite system (14). Flue gas containing SO₂ is scrubbed with a solution consisting of soluble Na₂SO₃, NaHSO₃, and Na₂SO₄. The SO₂ reacts with sodium sulphite to form sodium bisulphite according to the following reaction:-



In the regeneration cycle, the above reaction is reversed by the application of heat, releasing SO₂ and regenerating the sodium sulphite:-



Following cooling and removal of dust, the flue gas enters the SO₂ absorber which is a simple gas-liquid contacting device with two or more absorption stages. The absorber can be designed to reduce SO₂ concentration to the required level and can accommodate a wide range of turndown conditions. The absorber also produces some nonregenerable and therefore undesirable oxidation products. Contact of the scrubbing solution with oxygen in the flue gas will yield sodium sulphate, as would the presence of any SO₃, and this has to be purged from the system.

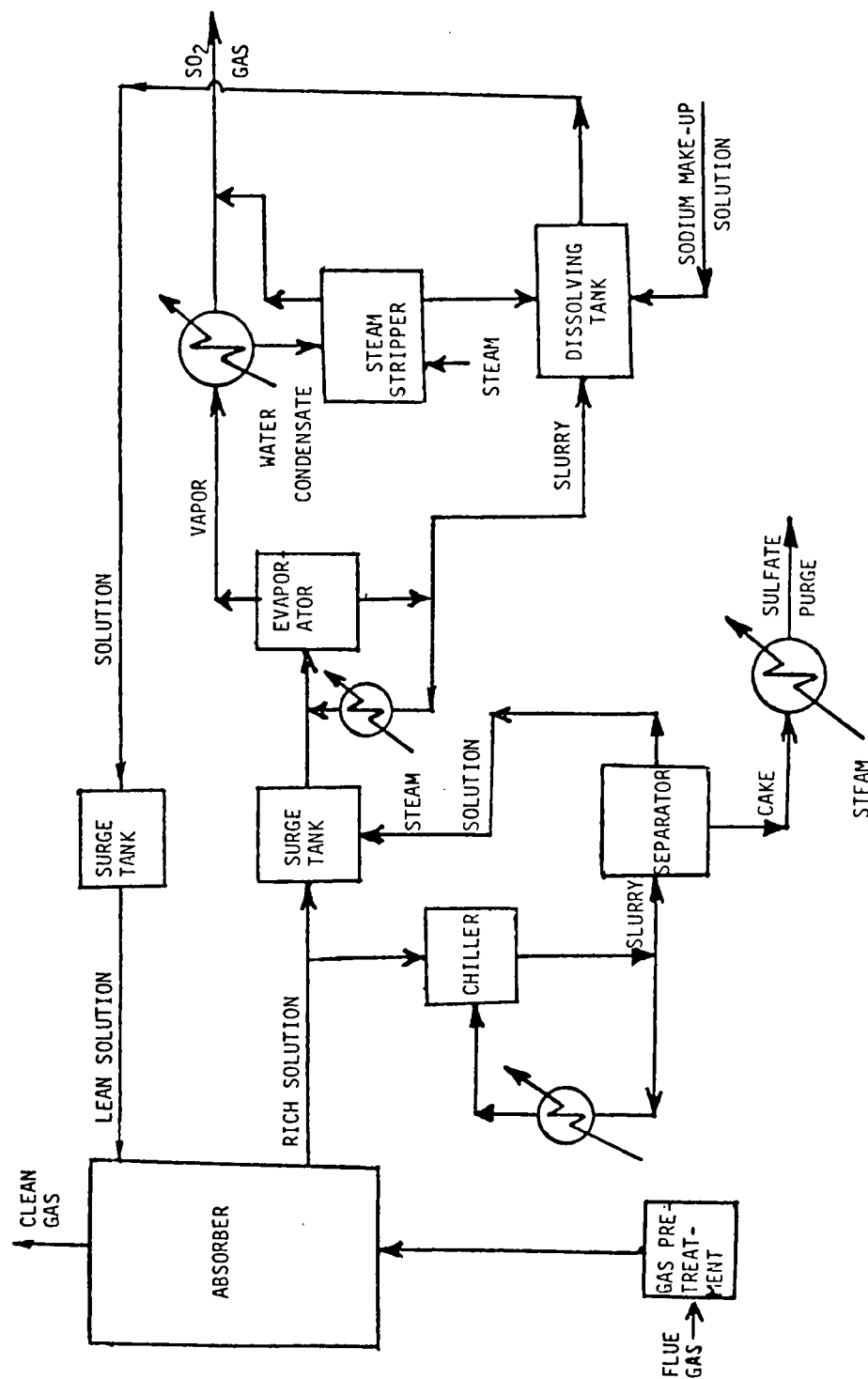


FIGURE 15 FLOW DIAGRAM FOR WELLMAN-LORD PROCESS (14)

Sodium bisulphite solution from the absorber goes to a forced-circulation evaporator-crystallizer which is heated by low pressure exhaust steam. Here the SO_2 is released from the bisulphite which is regenerated to the sulphite. A mixture of SO_2 and steam escapes through the top of the vessel. This gas is cooled to about 50°C . The condensed water is saturated with SO_2 and is steam stripped to remove the SO_2 . The SO_2 leaving the stripper combines with SO_2 from the evaporator and may be passed to a sulphuric acid plant, elemental sulphur plant, or liquid SO_2 plant for further processing. The sodium sulphite slurry produced in the evaporator is recycled to the absorber.

SO_2 absorption efficiency is controllable by adjusting processing parameters at the absorber with most operating systems producing 90 - 92% SO_2 recovery. The oxygen content in weak smelter gas streams is considerably higher than in power plant gases and this, together with the presence of SO_3 would result in higher sodium sulphate formation. Although applicability to weak smelter gas streams has not been commercially demonstrated, the following advantages to the Wellman-Lord process are foreseen:-

1. SO_2 absorption capability is excellent and there are no serious operating or maintenance problems.
2. the process generates a high purity stream of SO_2 , around 85%, or higher if appropriate drying facilities are added. This provides options between acid, elemental sulphur, or liquid SO_2 production.
3. the process has been commercially proven on treatment of power plant gas streams.
4. the process can handle wide variations in SO_2 concentration.

The principal disadvantages are:-

1. oxidation of absorbent, (Na_2SO_4), resulting in purging and loss of high cost sodium ions.
2. energy requirements in SO_2 regeneration are high.

7.3.2 Nonregenerative Absorption (Scrubbing) Systems

Whereas the processes described above are based on regenerative absorption systems which concentrate the SO_2 for subsequent processing to sulphuric acid, elemental sulphur or liquid SO_2 , a second category of processes are those based on neutralizing the SO_2 by scrubbing to produce a stable waste product. These processes are generally simpler, more technically developed and economical than regenerative absorption processes. Lime/limestone scrubbing systems in particular are well developed and are in widescale use for scrubbing gases from thermal power plants, especially in Japan.

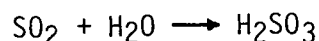
The following scrubbing systems have been developed, some specifically in the copper smelting industry (14):-

7.3.2.1 Onahama Lime/Limestone Scrubbing System

The development of the lime/limestone SO_2 control system to produce gypsum from copper reverberatory furnace gases has been carried out at the Onahama smelter in Japan over the last 20 years. Some 76% of sulphur input to the smelter is captured in sulphuric acid and 21% in gypsum. Scaling problems which occurred in the scrubbers and mist eliminators have largely been overcome by proper control of operating conditions of the absorbent, i.e. pH, temperature and concentration.

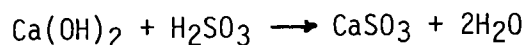
Figure 16 shows the flowsheet for the lime/limestone gypsum process at the Onahama smelter (14). Although the reactions in the scrubber are not completely understood and are quite complex, the overall effect can be simplified by the following reactions:-

1. formation of sulphurous acid

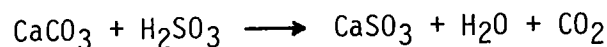


2. formation of calcium sulphite

- (a) lime scrubbing



- (b) limestone scrubbing



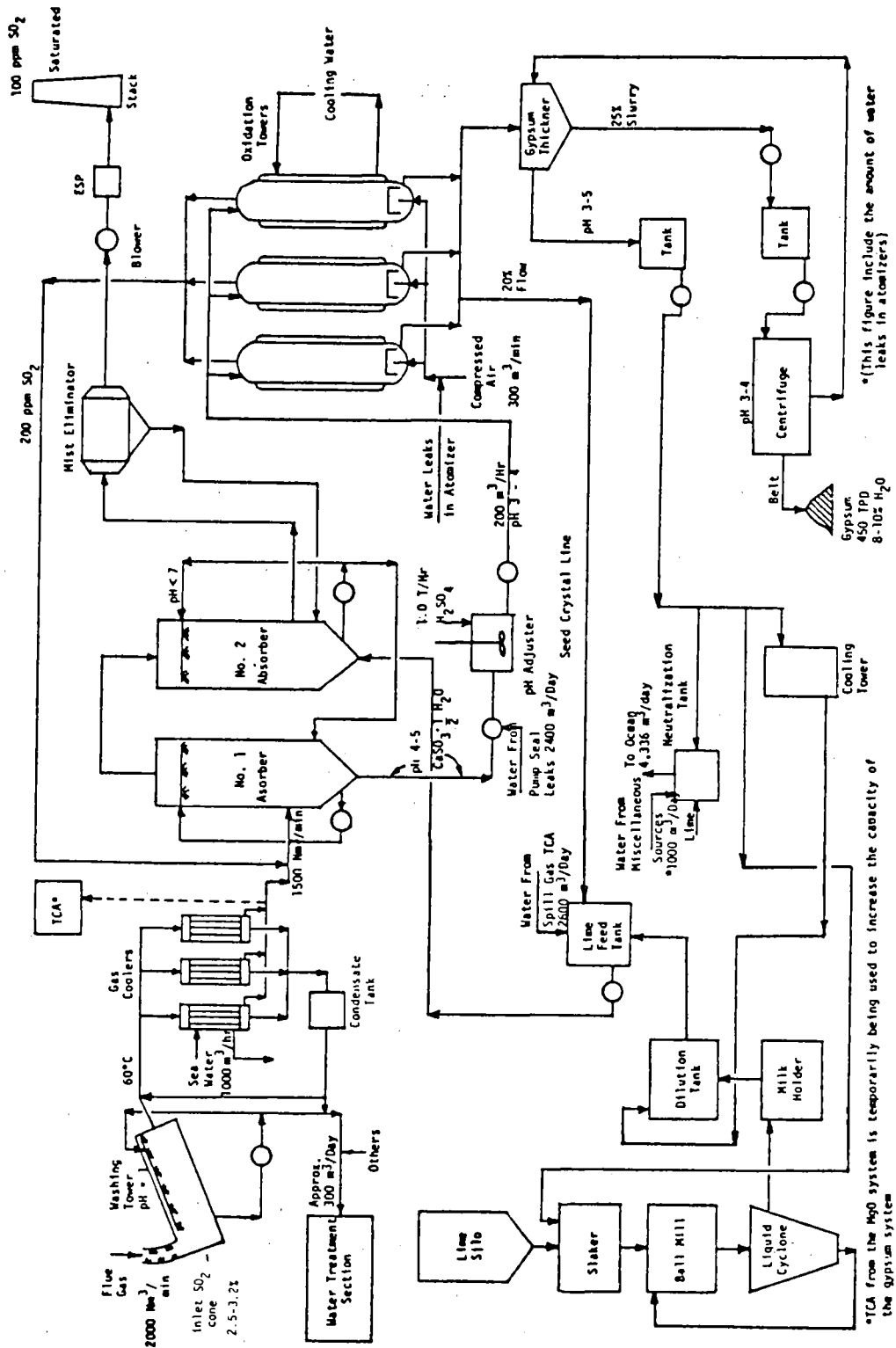
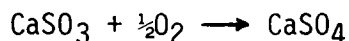


FIGURE 16 FLOWSHEET ONAHAMA LIME/LIMESTONE TO GYPSUM SYSTEM (14)

3. formation of calcium sulphate in the presence of oxygen



Unless the last reaction is forced by deliberate oxidation, the calcium sulphate content of the (sulphite) sludge will only be around 5 - 7%.

Inlet gas, containing 2.5 - 3.2% SO_2 , is washed and cooled to 60°C and then passed to five seawater-fed gas coolers to maintain absorption efficiency. The plant was designed so that after this point the gas could be separated, part going to the MgO absorption system (described in section 7.1.2.1) and part to the lime/limestone scrubbing system. The former system is currently not in use because of the lack of demand for acid, but its TCA absorber is being used on the lime/limestone system. Following the two absorbers which are in series, each absorbing about 50% of the SO_2 entering the system, the gas passes through a mist eliminator, blower, and precipitator before finally being discharged to atmosphere via a stack containing 40 - 60 ppm SO_2 .

Calcium sulphite slurry is taken from the first absorber at pH 4 - 5 and pumped into a pH adjuster where acid is added to reduce the pH to 3 - 4. Compressed air and slurry are mixed in indirectly cooled oxidation towers, following which slurry flows to a thickener from which approximately 20% of the flow is taken to a lime tank to supply seed crystals which enter the second of the two absorbers. Gas leaving the top of the oxidation towers contains less than 200 ppm SO_2 and is returned to the inlet of the first absorber.

The underflow from the gypsum thickener flows as a 25% slurry to centrifuges at a pH of 3 - 4. After centrifuging, the gypsum is stored for shipment. Thickener overflow passes either directly or indirectly via a cooling tower to the slaking system.

Any quick lime (CaO), slaked lime (Ca(OH)_2), or limestone (CaCO_3), can be used as absorbent, the reactivity of each decreasing respectively. The reaction rate of SO_2 absorption by lime slurry depends on the dissolution rate of the lime. If limestone is used it should be crushed to 300 mesh. Combinations of absorbent materials can be used, their reactivity and cost depending on the relative proportions of each present. Corrosion tends to occur when chlorides enter the system, but a chlorine ion concentration up to 1000 ppm in the liquid phase from the cooler can be tolerated.

The size, shape and colour of gypsum crystals are controlled according to end use, which in Japan is usually wallboard manufacture or as feed material for cement manufacture.

The lime/limestone scrubbing system is sufficiently well developed in Japan to be generally applicable to the neutralization of weak gas streams from reverberatory furnaces. The lower SO_2 content in the gas from a calcine-charged furnace, as compared with a green-charged furnace, would favour this process, although it has only been demonstrated on the latter. Widespread use of the process will depend on markets for gypsum product and costs of production. Other lime/limestone scrubbing systems have been developed and are used extensively in thermal power plants for scrubbing gases containing SO_2 .

7.3.2.2 Duval Sierrita Lime Scrubbing System

A lime slurry SO_2 scrubbing system is currently being used to control off-gases from two multihearth roasters processing Mo-Cu ores at the Duval Sierrita plant in Arizona (14). The scrubbing system receives gases containing 0.35 to 0.75% SO_2 from roasting MoS_2 and emits a tail gas to atmosphere containing less than 200 ppm SO_2 . Plant availability is 95% and an SO_2 removal efficiency of 92 - 96% can be achieved. The system has been under development since 1968.

Figure 17 shows the roasting-scrubbing flowsheet (14). Gases from the roasters are cleaned in cyclones and electrostatic precipitators before passing directly into a TCA type scrubber. The temperature is reduced by spraying in water to ensure dimensional stability of the polypropylene balls used as the mixing medium in the scrubber. The lime slurry is sprayed downward countercurrently to the gas flow.

After the 5% solids lime slurry has been sprayed into the scrubber and contacted the gases, it leaves from the bottom at pH 6. Scrubber effluent is disposed of into the tailings pond.

Before leaving the scrubber the gases pass through a vane type demister. A Brinks mist eliminator improves the removal of acid mist. Gases leave the stack at about 45°C containing 100 - 200 ppm SO_2 .

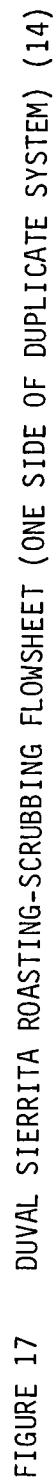


FIGURE 17

Operation of the system is primarily controlled by pH of the slurry leaving the bottom of the scrubber. However, the quantity of balls and their weight are also influencing factors. Low pH (around 4) is not conducive to high scrubber efficiency while high pH (> 7) leads to unstable conditions. Fluctuations in SO_2 content of the gas within the normal range does not affect operations adversely.

Reverberatory furnace gases are similar in strength to those from multihearth roasters. Since the Duval Sierrita scrubbing system has operated satisfactorily on roaster gases the technology should be transferable to the treatment of reverberatory furnace gases.

7.3.2.3 Palabora Scrubbing System

Reverberatory furnace gases at Palabora contain 15 - 20% of the smelter sulphur input, and at a strength of 0.5 - 1.0% SO_2 are unsuitable for acid production (21).

The primary hydroseparator overflow from the concentrator contains an abundance of alkaline calcium and magnesium carbonates in finely divided form. As an alternative to building a second acid plant it was calculated that capital cost savings would result from using this pulp to scrub gases surplus to acid plant requirements. This approach also led to an increase in copper recovery as an additional benefit, thereby making this scrubbing process unique. The mineral valleriite, a soft plate-like material, accounted for a major portion of the copper loss in concentrator tailings. Recovery of valleriite (containing 22.9% Cu at Palabora) under normal mill conditions is less than 20%. Although the mineral floats more easily under acidic conditions this was impractical in the main circuit. Due to its softness, most of the valleriite reports to the fine pulp in the hydroseparator overflow. Using this pulp to scrub smelter gases increases copper recovery because a temporary acidic condition arises immediately after absorption of the SO_2 , improving flotation characteristics of the valleriite which is returned to the concentrate thickeners.

In 1971, pilot plant testwork was carried out to determine absorption and flotation aspects of the proposed process. The conclusions of this work were that it was feasible to use hydroseparator overflow pulp for neutralization of excess smelter gases, and that tail gas SO_2 content could be reduced to less than 0.05% by two-stage countercurrent contact in grid packed towers. Recovery of copper from the pulp, although only averaging 25%, was economically significant.

Figure 18 shows a simplified flowsheet of the Palabora plant which was constructed in 1974 (21). Reverberatory furnace gases (0.5 - 1.0% SO_2), and converter gases (4 - 8% SO_2) surplus to acid plant requirements are routed to the scrubbing plant where they are humidified and cooled from around 300°C to 85°C in a spray tower by a circulating stream of sulphurous acid. Typical data for gases entering and leaving the scrubbing plant are given in Table 16.

TABLE 16 PALABORA SCRUBBING PLANT DATA

	<u>Reverb. Gas Only</u>	<u>Reverb.+ Converter Gas</u>
Gas flow (Nm^3/h)	150,000	171,000
inlet - % SO_2	0.3	2.0
outlet - % SO_2	0.01	0.14
inlet - $^\circ\text{C}$	230	270
outlet - $^\circ\text{C}$	35	45

Humidified gas passes to a scrubbing tower with some being bypassed into an activation tower, the amount being controlled by the pH of the pulp leaving the bottom of the latter.

Gas streams are recombined and contacted with the incoming pulp from the concentrator in the activation tower. Pulp distribution is achieved by manifolding onto a perforated plate situated above the gas outlet ducts. Grid type packing is used in both towers.

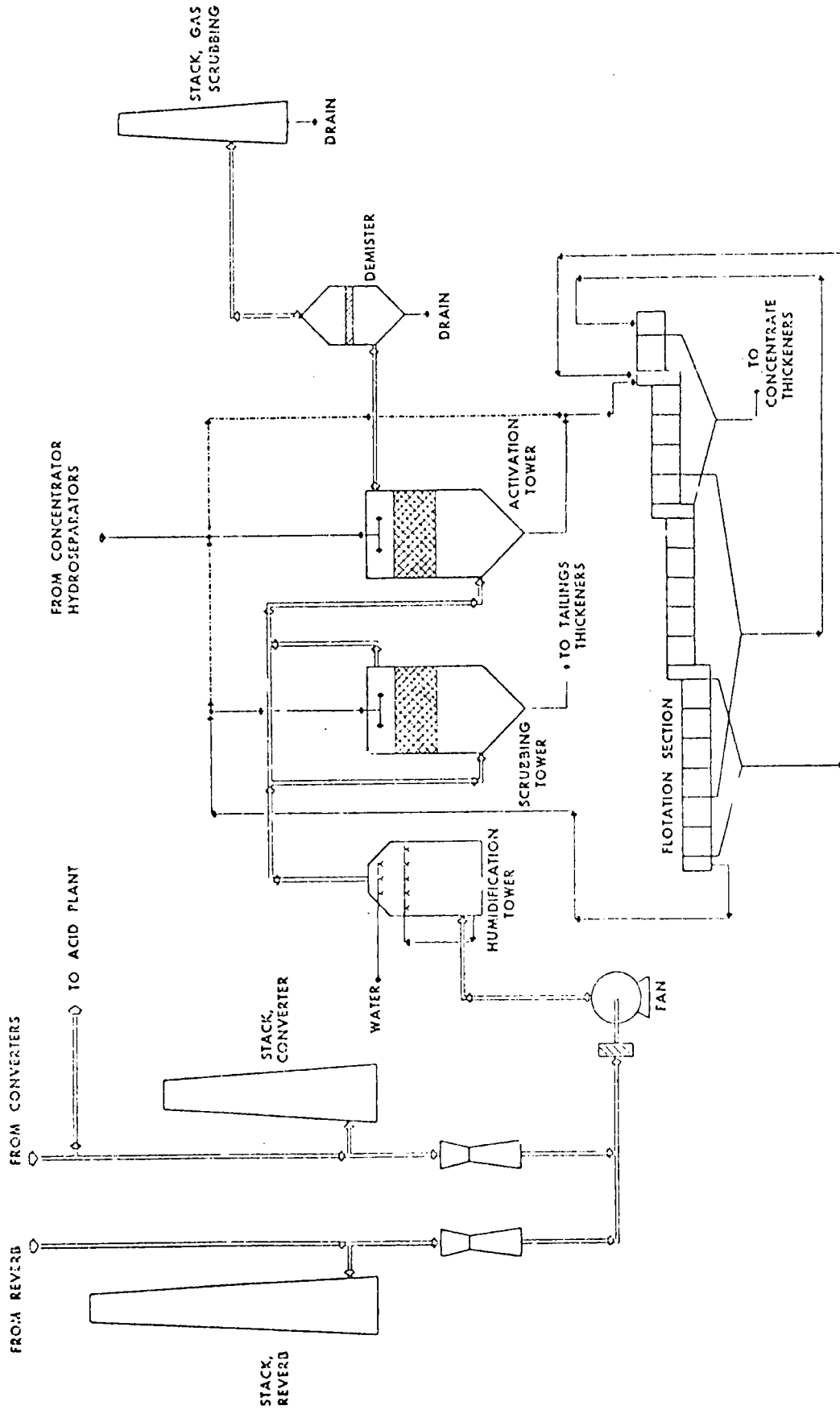


FIGURE 18 PALABORA GAS SCRUBBING PLANT SIMPLIFIED FLOW DIAGRAM (21)

Scale which develops in the tower packing is removed by partial dissolution in sulphurous acid. Exit gases from the activation tower pass through a demister vessel before being released to the atmosphere via a 70 m high rubber lined stack. Pulp flow is countercurrent to gas flow, and passes first through the activation tower, then the flotation section and then the scrubbing tower, before being returned to the concentrator tailings thickeners. Various sections of the plant can be by-passed if necessary.

Environmental regulations at the Palabora smelter require that 70% of the sulphur entering the smelter is recovered. Total sulphur capture achieved is 72%, including 51.5% as acid, 19.5% in mill tailings using the scrubbing system, and 1% in slag.

7.3.2.4 Sodium Carbonate Process

In this process, a sodium carbonate solution is used to absorb the SO_2 from the flue gases following removal of the flyash in a separate scrubber (22). The spent liquor is pumped to settling ponds, where the water is allowed to evaporate. There is no attempt made to regenerate the scrubbing agent or recover a by-product.

The process in its present form is only practical in arid locations, where the natural evaporation rate exceeds the combined rate of spent-liquor production and rainfall. The only operational sodium carbonate scrubbers are at Nevada Power's Reid Gardner units No. 1, 2 and 3, with a capacity of 120 MW each. They are located near Moapa, Nevada, about 50 miles north Las Vegas. The units were designed and built by ADL/Combustion Equipment Associate.

This process has not been applied to the treatment of weak gas streams from copper or nickel smelters.

7.3.2.5 Aqueous Carbonate Process

The most obvious difference between the aqueous carbonate and the sodium carbonate process is that the former is a regenerative process, whereas the latter is a throwaway type (22). In the aqueous carbonate system, the flue gas from the flyash scrubber and an aqueous solution of sodium carbonate are fed to a spray drier which acts as an SO_2 scrubbing vessel. The

exit stream consists of scrubbed flue gas and a dry mixture of sodium carbonate, sodium sulphite and sodium sulphate. The dry salt mixture is blown into a molten salt pool with petroleum coke or coal. The carbon reduces the sodium sulphite-sulphate to sodium sulphide, producing a CO_2 exit stream. The sulphide-rich liquid stream is then reacted with CO_2 to produce Na_2CO_3 and H_2S , the former being used to make up fresh scrubber solution and the latter being piped to a Claus plant, where it is oxidized to elemental sulphur.

There is no commercial aqueous carbonate unit in North America, but one is scheduled to begin in April 1982 at the Niagara Mohawk Power Co-op's Charles R. Huntely No. 6 generating station in Tonawanda, New York. The scrubbing and reversion process for this 100-MW-capacity unit has been developed by Atomics International Limited, a division of the Rockwell International Corporation, and will produce elemental sulphur. The company also has a throwaway modification of this process designed for use with low-sulphur coals in semi-arid locations. In North Dakota, where a 440-MW unit of this type is being planned, there is insufficient rainfall to cause pond overflow.

The aqueous carbonate process has not found application in the metallurgical industry.

7.3.2.6 Double Alkali Process

There are several technologies which go under the designation of the double alkali process (22). One is the so-called "concentrated double alkali process" of the FMC Corporation, which is installed at various small industrial steam plants throughout the United States. Sodium sulphite is the scrubbing medium: it is converted to sodium bisulphite by reaction with the SO_2 . It is then reacted with slaked lime to produce calcium sulphite, which is centrifuged to a firm cake at 60-70% solids. The crystal form of the calcium sulphite is different from that formed in the lime/limestone process, for there is no problem with dewatering.

Another form of the double alkali process was pioneered by General Motors. Their process is known as the "sodium-lime double alkali process using the dilute mode". It uses lime to regenerate the scrubbing material and thus also produces a waste calcium sulphite cake.

A third double alkali process employs sodium hydroxide solution as the scrubbing medium. It is converted to Na_2SO_3 , NaHSO_3 and Na_2SO_4 in the scrubber. The scrubbing solution is regenerated by reacting the sodium salts with $\text{Ca}(\text{OH})_2$, producing a waste calcium sulphite-sulphate cake. The system has been evaluated for a 20-MW unit at Guld Power's Scholz station near Tallahassee, Florida, but as far as is known the process has not been installed.

A double alkali system has been installed at the Afton copper smelter in Kamloops, B.C. to treat off-gases from the TBRC which smelts concentrates unusually high in copper content and correspondingly low in sulphur content. The scrubbing system consists of three wet scrubbers designed to remove residual dust, low vapour point particulate (As_2O_3), gaseous SO_2 and elemental mercury (23, 24). The SO_2 scrubbing and liquor regeneration system is a dual alkali process, since an alkaline solution (Na_2SO_3) is used to scrub SO_2 from the process gas and subsequently a second alkali ($\text{Ca}(\text{OH})_2$) is used to regenerate spent scrubbing liquor. In the first venturi scrubber, most of the residual particulate (including As_2O_3), SO_3 and H_2SO_3 mist is removed by a circulating solution of scrubbing liquor. A second low-intensity tray tower SO_2 scrubber is then used to remove SO_2 by absorption in sodium sulphite (Na_2SO_3) solution to form sodium bisulphite. Scrubbed process gas either passes through the mercury scrubber or is directed to the stack, depending on which stage in the TBRC processing cycle is in progress. Sodium bisulphite solution is regenerated by reacting it with slaked lime to form calcium sulfite ($\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$) which fixes the sulphur in a disposable form. Steady-state conditions have not yet been achieved in the scrubber. Corrosion of materials is a problem, a common feature in double alkali scrubbing systems, due to the higher than expected concentration of SO_3 in the system.

A double alkali scrubbing system is suitable for installation when the $\text{O}_2 : \text{SO}_2$ ratio in the gases is less than 15 : 1. Above this ratio a lime scrubbing system is preferred. The $\text{O}_2 : \text{SO}_2$ ratio affects the oxidation rate of SO_3^- to SO_4^- , which in turn increases the potential for scaling (24).

7.3.2.7 Chiyoda Thoroughbred 101

SO_2 is absorbed in a dilute aqueous solution of sulphuric acid containing ferric sulphate catalyst (22). The resulting H_2SO_3 is oxidized in the scrubber loop to H_2SO_4 , which is ultimately reacted with limestone to give $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The process is a practical method for the production of by-product

gypsum. At the Hokuriku Power Company's electric power station in Japan, two units produce 3,800 tons of gypsum per month. An experimental unit, installed on a 20-MW flue gas stream at Gulf Power's Scholz Station in Florida, was in operation from March 1975 to March 1977.

The process has not found application in the metallurgical industry.

8 MARKETS, USE, OR DISPOSAL OF SULPHUR FIXATION PRODUCTS

8.1 General Considerations

As well as other factors, the air pollution control regulations in force at any particular smelter location will determine the degree of SO_2 capture and fixation. The choice of by-product produced, i.e. elemental sulphur, liquid SO_2 , or sulphuric acid, will largely be determined by the markets available for the particular by-product and the economics of production. Sulphur is the common element in each material and so to a degree all by-products are in competition with each other, as well as with sulphur from other sources, for various end uses.

Clearly, marketing and sale of by-product to offset at least part of the control costs is desirable. Production in excess of local demand will necessitate disposal of by-product in some environmentally acceptable manner. However, certain cases may arise, depending on location, available markets, and price competition from alternative sources of sulphur, where compliance with the regulations will result in a net loss to the smelter on by-product sales. However, the alternative of making and disposing of an inert waste material may result in a greater loss. In particular, if SO_2 is recovered from thermal power plants burning sulphur-containing fossil fuels, it would have a profound impact on the sale of sulphur fixation by-products from copper smelters, particularly in the U.S.A. As environmental control legislation becomes more stringent, by-product production and sale from both of these sources will increase and will be in competition with each other, and with Frasch sulphur, the largest source of supply of sulphur. Because thermal power plants are usually situated closer to industrial users, often in densely populated areas, this source of sulphur may have a competitive advantage over the smelters which are generally in remote locations. Transportation costs are an important factor in determining the economics, competitiveness and marketability of by-products. It is also likely that neutralization of the SO_2 in utilities gas streams by lime/limestone scrubbing to produce a discardable

material will be a preferred approach from technical and economic considerations because of the relatively low concentration of SO_2 in the gases.

Compliance with more stringent environmental controls may provide an overabundance of supply of sulphur, particularly in the form of by-product acid, at least on a regional basis, if not internationally. This will satisfy the needs of consumers, both in terms of amounts and price levels. However, it will create problems for both primary and by-product producers. The metallurgical industry affected by environmental legislation requires the development of technologies that will permit it to cover the capital and operating costs of by-product sulphur recovery at cost levels that will be competitive with other sources. Because the price of copper is fixed in the international market the cost of sulphur recovery cannot be passed on to the consumer initially, but must be absorbed by the smelter or passed back to the mine. Eventually this cost may be passed on to the consumer in the form of higher metal price when all smelters control SO_2 . Quite apart from economic considerations, if tighter environmental controls lead to an oversupply of sulphur containing by-products, this will create disposal problems. However, this situation could be offset to some extent if higher energy costs (in converting water to steam) result in reduced supplies of elemental (Frasch) sulphur.

8.2 Elemental Sulphur

The technological difficulties in making elemental sulphur from the SO_2 contained in metallurgical gases and the high cost of production (due to the high cost of reductants) mitigate against production of elemental S at smelters. In addition, sulphur produced from metallurgical gases often contains undesirable impurities such as As, Se and Hg which must be removed by special processes before it is generally acceptable in quality and competitive with sulphur from other sources (2).

Nearly 85% of the sulphur produced is consumed in the form of sulphuric acid (which in itself is an intermediate product) and so in reviewing the potential supply and demand situation, this close relationship necessitates simultaneous consideration of both materials (14). For several years a situation existed where there was more by-product sulphur (in all forms) produced by the coal, petroleum, natural gas and metallurgical industries than could be used for industrial or agricultural purposes (5). However, a recent study (25) indicates that the market surplus of sulphur will disappear and that supply and

demand will be roughly in balance, with increasing prices. From the smelters' point of view, the decision whether or not to make by-product sulphur must be based on long-term market predictions. Since elemental sulphur would be a by-product of a metallurgical process, it would not be feasible to cut back sulphur production at times of low demand.

Tables 17 - 22 give various production statistics for elemental sulphur in the western world (25). A cumulative annual growth rate in production of 3.1% is forecast from 1980 - 84, and 2.7% for the period 1985 - 90. Consumption figures over the same periods are forecast to be nearly 4% and 3.3% respectively. It is evident from Table 18 that the major sources of sulphur are Frasch sulphur, which is mined, and sulphur produced from natural gas and at oil refineries. Sulphur produced from metallurgical gases, including pyritic smelting, is not significant according to these estimates. Table 23 gives typical end-use pattern of elemental sulphur in the U.S.A. in 1977 (26).

From the point of view of shipment or storage, elemental sulphur is the most desirable product since it can be economically transported much greater distances than either sulphuric acid or liquid SO_2 , per unit of contained sulphur. The material possesses good storage characteristics and so it can be easily stockpiled when no market is available. If needed at a later time, it can be recovered easily and shipped without any unusual precautions. Elemental sulphur is inexpensive to convert to sulphuric acid at destinations. The important factor will be the final cost of acid at the point of consumption.

In summary, reduction of SO_2 contained in copper and nickel smelter gases to produce elemental sulphur is technically complex and is not an economic alternative at present.

8.3 Liquid SO_2

The demand for liquid SO_2 is very limited, even in the U.S.A. The current U.S. liquid SO_2 capacity is approximately 177,000 tpa (14). The single largest use for SO_2 is in the production of sodium hydrosulphite which is used as a bleaching agent in the production of textiles, paper, and clay. The use of SO_2 in pulp and paper manufacture is decreasing due to sulphite process changes

TABLE 17 WESTERN WORLD BRIMSTONE PRODUCTION FORECAST 1975 - 1990 (25)

		('000 tonnes)							
		1975	1976	1977	1978	1979	1980	1985	1990
Western World									
Total		24,427	23,602	24,183	24,172	25,229	27,004	31,614	36,218
West Europe		2,732	2,826	3,292	3,271	3,494	3,547	3,751	4,293
Africa		31	35	36	38	44	51	88	120
Asia		2,072	2,115	2,328	2,399	2,701	3,264	5,350	6,865
Oceania		10	11	7	10	10	10	15	25
North America		16,972	15,987	16,201	16,061	16,355	16,990	18,750	20,915
Central America		2,393	2,396	2,074	2,136	2,355	2,850	3,280	3,530
South America		217	232	245	257	270	292	380	470

TABLE 18 BRIMSTONE PRODUCTION BY TYPE (23)

		('000 tonnes)							
		1975	1976	1977	1978	1979	1980	1985	1990
Frasch Sulphur		10,049	9,026	8,246	3,160	8,460	9,600	10,400	12,150
Recovered Sulphur		14,217	14,417	15,777	15,847	16,599	17,229	21,034	23,873
Natural Gas		10,537	10,190	11,018	10,895	11,073	11,150	12,738	12,563
Oil Refinery		3,476	3,996	4,600	4,824	5,293	5,774	7,321	8,933
Coke Oven Gas		35	37	31	30	25	15	5	5
Pyritic Smelting		82	88	28	-	-	-	130	280
Power Plants		2	2	2	18	28	40	40	42
Tar Sands etc.		85	104	98	120	180	250	700	1050
Coal Gasification		-	-	-	-	-	-	100	1000
Native Refined		161	159	160	165	170	175	180	195
Total		24,427	23,602	24,183	24,172	25,229	27,004	31,614	36,218

TABLE 19 WESTERN WORLD PYRITE PRODUCTION FORECAST 1975 - 1990 (25)

('000 tonnes S)								
	1975	1976	1977	1978	1979	1980	1985	1990
Western World								
Total	4,940	4,619	4,336	4,415	4,565	4,685	5,120	5,745
West Europe	3,266	2,908	2,742	2,700	2,700	2,750	3,090	3,575
Africa	424	376	447	550	645	695	770	850
Asia	598	611	529	550	550	550	570	590
Oceania	106	108	104	110	110	110	110	130
North America	541	611	509	500	500	500	480	500
Central America	-	-	-	-	-	-	-	-
South America	5	5	5	5	60	80	100	100

TABLE 20 WESTERN WORLD SULPHUR-IN-OTHER-FORMS PRODUCTION FORECAST 1975 - 1990 (25)

('000 tonnes S)								
	1975	1976	1977	1978	1979	1980	1985	1990
Western World								
Total	5,208	5,802	5,999	5,950	6,205	6,465	7,815	8,875
West Europe	1,579	1,639	1,735	1,725	1,750	1,800	1,920	2,015
Africa	217	246	244	245	260	285	335	395
Asia	1,311	1,380	1,472	1,465	1,480	1,505	685	800
Oceania	117	143	150	150	150	155	185	225
North America	1,841	2,213	2,208	2,170	2,365	2,510	3,365	3,865
Central America	76	113	116	120	120	125	180	250
South America	67	68	74	75	80	85	145	325

TABLE 21 WESTERN WORLD: SULPHUR-IN-ALL-FORMS SUPPLY FORECAST 1975 - 1990 (25)

('000 tonnes)

	1975	1976	1977	1978	1979	1980	1985	1990
Western World								
Total	34,574	34,023	34,538	34,537	35,999	38,154	44,549	50,838
West Europe	7,577	7,373	7,769	7,696	7,944	8,097	8,761	9,883
Africa	682	657	727	833	949	1,031	1,193	1,365
Asia	3,981	4,106	4,349	4,414	4,731	5,319	7,605	9,255
Oceania	233	262	261	270	270	275	310	380
North America	19,354	18,811	18,918	18,731	19,220	20,000	22,595	25,280
Central America	2,757	2,814	2,514	2,593	2,885	3,432	4,085	4,675

TABLE 22 WESTERN WORLD: BRIMSTONE SUPPLY/DEMAND BALANCE (25)

	1975	1976	1977	1978	1979	1980	1985	1990
('000 tonnes)								
Frasch Sulphur	10,049	9,026	8,246	8,160	8,460	9,600	10,400	12,150
Recovered Sulphur	14,217	14,417	15,771	15,847	16,599	17,229	21,034	23,873
Native Sulphur	161	159	160	165	170	175	180	195
Brimstone Production	24,427	23,602	24,183	24,172	25,229	27,004	31,614	36,213
Imports	1,588	1,985	2,633	2,570	2,220	2,320	4,070	5,070
Vat Breaking	-	-	70	380	530	1,250	1,720	2,790
NET SUPPLY	26,015	25,587	26,886	27,122	27,979	30,574	37,404	44,068
Consumption	20,719	21,277	24,340	25,687	27,079	28,956	34,695	40,928
Exports	181	139	380	400	430	460	505	700
Stock Additions								
- Iran	-	-	-	-	100	120	250	400
- Iraq	345	165	55	-	-	-	-	-
- Saudi Arabia	-	-	-	-	-	90	500	500
- Canada	2,857	2,281	1,560	1,300	850	850	800	550
NET DEMAND	24,102	23,862	26,335	26,987	28,459	30,476	36,750	43,078
Market Surplus (deficit)	1,913	1,725	551	135	(480)	98	654	990

TABLE 23 END-USE PATTERN OF ELEMENTAL SULPHUR, U.S. 1977 (26)

<u>Use</u>	<u>1,000 tonnes</u>	<u>%</u>
Sulphuric acid	9,598	84.5
Organic chemicals (paints, explosives, industrial organic chemicals)	275	2.4
Agricultural chemicals	257	2.3
Industrial inorganic chemicals	220	1.9
Pulp and paper products	147	1.3
Petroleum refining and petroleum and coal products	111	1.0
Synthetic rubber, cellulosic fibers and other plastic products	65	0.6
Food	5	
Unidentified	<u>678</u>	<u>6.0</u>
Total	<u>11,356</u>	<u>100.0</u>

Source: USBM.

and more stringent controls on SO_2 emissions. Other uses for liquid SO_2 , including refining and food processing, are expected to offset the lower demand in pulp and paper. The result will be that liquid SO_2 demand is expected to increase at an annual rate of approximately 4 to 5% during the next 5 years.

Owing to the relatively high price per unit weight of liquid SO_2 , (because of the specialized markets served), unlike sulphuric acid, it can be shipped long distances to serve various markets. However, liquid SO_2 is still expensive to transport because it requires special-pressure tank cars which must return empty to the supply source. Furthermore, the market is scattered and the quantities involved are too small to justify the use of unit trains to increase economic rail distance or special-pressure tanker ships for bulk ocean shipments. Conditions favourable for marketing liquid SO_2 are therefore limited. Due to the stable markets, the supply/demand situation for U.S. liquid SO_2 is in balance. An increase or decrease in production of 10,000 to 20,000 tpa, representing 6 to 12 percent of estimated 1975 consumption, would significantly disrupt the market for this chemical.

Since the liquid SO_2 market in the U.S. is very small and is already in balance, the possibility of a copper or nickel smelter installing a system to produce liquid SO_2 exclusively for sale is not likely. However, consideration could be given to using liquid SO_2 to smooth out the feed to an acid plant to compensate for the smelter off-gas fluctuations. This technique can also be used to reduce the size and cost of acid plants installed at the smelters.

Ideally, the production of liquid SO_2 requires a very highly concentrated gas stream, such as that produced from the Inco oxygen flash furnace or the Kivcet process (around 80% SO_2). Currently the number of smelters employing these processes are very few and so the potential for producing liquid SO_2 is very limited.

8.4 Sulphuric Acid

Sulphuric acid is the most common by-product recovered from metallurgical gases and its production is the accepted control approach for concentrated gas streams at copper and nickel smelters.

As previously mentioned, nearly 85% of the sulphur consumed is in the form of sulphuric acid which has been established in industry as the lowest cost and most versatile of the mineral acids and for which there is no satisfactory substitute for most applications. Sulphuric acid is widely sold in the form of various solutions of H_2SO_4 in water, or of SO_3 in H_2SO_4 called oleums. Commercial grades of by-product sulphuric acid produced by the contact process are generally in the range 93 to 98% acid. Acid strength varies very widely, depending on end use.

For a smelter which produces by-product sulphuric acid from concentrated gas streams, the options for disposal of acid are (26):

- sale as sulphuric acid
- neutralization and discard as gypsum
- manufacture of chemicals
 - phosphoric acid
 - phosphate fertilizers
 - potassium sulphate
- miscellaneous uses

Table 24 shows the end-use pattern for sulphuric acid in the U.S.A. in 1977 (26).

8.4.1 Sale as Sulphuric Acid

The price obtainable for acid in any given location is generally that of acid from the cheapest source, usually the cost of buying sulphur and making acid locally (2). Because smelters are generally situated in remote locations, they are at a disadvantage. The high cost of transporting acid to market, generally in industrialized centres, means that sales of acid may often be at a net loss to the smelter. Sulphuric acid is expensive to transport because it is shipped in special tank cars which return empty to the source of supply. The movement of sulphur to market for conversion to acid is more favourable because of its lower transportation cost per unit of contained sulphur. In addition, conversion of elemental sulphur to acid is relatively inexpensive

TABLE 24 END-USE PATTERN FOR SULPHURIC ACID, U.S. 1977 (26)

(1,000 tonnes 100% H ₂ SO ₄)		
<u>Use</u>	<u>Amount</u>	<u>%</u>
Phosphate Fertilizers	20,278	59.0
Chemical Manufacture -		
Inorganic chemicals including pigments	2,635)	7.7)
Ammonium sulphate and other farm chemicals	988)	2.9)
Organic chemicals including drugs	987)	2.9)
Rubber and Plastics	669)	2.0)
Cellulose fibers (rayon)	538)	1.6)
Soaps and detergents	453)	1.3)
Water treatment chemical (aluminum)	270)	0.8)
Explosives	62)	0.1)
Other chemical Products	<u>900</u>)	<u>2.5)</u>
Petroleum Refining	2,351	6.8
Leaching Ore (copper, uranium)	2,099	6.1
Pulp and Paper	608	1.8
Steel Pickling	398	1.2
Storage Batteries	135	0.4
Metal Processing	47	0.1
Unidentified	<u>951</u>	<u>2.8</u>
Total	<u>34,369</u>	<u>100.0</u>

Source: USBM

and the heat generated when sulphur is burned results in a by-product steam credit. Consequently, by-product acid produced at smelters is generally consumed close to its point of manufacture. The exception would be where the scale of movement to distant markets results in low freight rates, and/or where smelters are willing to subsidize freight to relieve a more expensive neutralization and disposal problem (26).

Many existing conventional sulphur burning plants are old and will ultimately need replacing or may be shut down if smelter acid is available. Others may need installation of control systems to reduce tail gas emissions. These circumstances will result in a competitive advantage to producers of by-product smelter acid if its costs of production are less than the costs of building and operating new sulphur burning acid plants.

At times, sulphuric acid enters world markets but generally this has been to meet a temporary imbalance caused by supply/demand patterns for end-use products such as phosphate fertilizers, or by changing processes for acid manufacture (e.g. from pyrite roasting to use of elemental sulphur)(26).

Because of the large quantities involved, the bulk of by-product acid produced at smelters must be sold through long-term contracts at prices considerably lower than the spot price for tank-car lots. Metallurgical plants, in order to ensure continuous operation, must have long-term contracts for the disposal of the acid and consequently are committed to the lower price (2). Occasions may arise where a smelter must temporarily reduce metal production because of a decrease in the market for acid. The buyer of by-product acid, whether for consumption or re-sale, is motivated by the cost advantage he may enjoy compared with captive main product manufacture and he does not expect from the by-product acid producer, the safeguards that he would demand from the sulphuric acid merchant. By analogy, the producer accepts that the potential realizations from a direct sale are lower than would be obtained from selling the acid in the merchant market, but that this is compensated by fewer, if any, commitments. The by-product acid producer, as a rule, sells on an ex-plant basis.

Sulphuric acid quality is particularly important from a marketing point of view and additional gas-cleaning steps may be required at the smelter to remove volatile elements such as As, Se, Hg, etc., ahead of the acid plant. Selenium can cause discolouration of the acid and most consumers (i.e. for agricultural end-use) insist on a mercury content of less than 0.5 ppm. Table 25 shows the typical analysis for commercial sulphuric acid (2). To be a marketable by-product, sulphuric acid from metallurgical plants will have to meet the specification given and ideally come close to the typical analysis. Failure to meet the most rigid specification will mean that certain markets may not be available for by-product smelter acid.

8.4.2 Neutralization and Discard as Gypsum

Failure to use internally or sell all, or part, of sulphuric acid production will necessitate its neutralization with limestone to form gypsum, a solid, disposable, inert material. This is an expensive proposition, primarily because of the cost of limestone and its freight charges, depending on the remoteness of the source of supply relative to the smelter location. Storage of large quantities of acid does not present an economic or practical alternative.

Limestone is usually the cheapest chemical for the neutralization of acid, but to achieve complete reaction, some hydrated lime might be required, or alternatively excessive grinding of the limestone is necessary, but the latter imposes economic limits because the cost of grinding increases rapidly with decreasing particle size (14). Using lime only would permit smaller reactors with less retention time owing to the higher reactivity of lime. However, lime is more expensive than limestone. If high quality limestone is utilized, the gypsum produced should be of salable quality, but its marketability will depend on alternative sources, in particular, gypsum which is mined. Uncalcined gypsum is used in the manufacture of Portland cement, plaster board and for agricultural purposes. Limestones containing impurities, particularly magnesium, react more slowly than high purity calcium carbonate. If appreciable amounts of magnesium are present in the limestone used for neutralizing the acid, leaching of the magnesium salts from the disposed waste could become a problem.

TABLE 25 SPECIFICATION AND TYPICAL ANALYSIS OF SULPHURIC ACID (2)

ELEMENT	SPECIFICATION ppm	TYPICAL ANALYSIS ppm
Cl		< 0.10
NO ₃		< 0.20
N ₂		< 0.10
SO ₂	50 max.	40
As		< 0.05
Fe	50 max.	30
Cu		0.20
Mn		0.25
Cr		0.40
Ni		0.50
Pb		< 0.10
Hg		< 0.50
Strength (% H ₂ SO ₄)	93.2 min.	93.50
Colour (APHA)	40 max.	30
Non-volatiles (%)		0.01

The most important factor in considering neutralization facilities is the disposal method for the calcium sulphate waste produced. Transport problems, effect on water hardness, effect of dissolved salts on ground water, effect on tailings pond, dusting problems, water requirements, piping scaling, and dry material stability must all be considered.

There are two types of neutralization processes for sulphuric acid disposal. In the 'wet' process, neutralization reaction takes place in dilute acid-water solution and produces a calcium sulphate slurry for disposal. The neutralization reaction in the 'dry' process takes place directly between concentrated sulphuric acid and limestone, producing a plastic mass that eventually turns into a dry solid for disposal.

The neutralization of one tonne of sulphuric acid consumes 1.14 tonnes of limestone and produces 1.71 tonnes of gypsum (26).

8.4.2.1 Dry Process

Figure 19 illustrates the simplified flowsheet for acid neutralization using the 'dry' process (14). Crushed mine limestone is ground to 80% - 100 mesh in a closed circuit, air swept ball mill and fed to a pug mill or blunger, at a controlled rate. Acid is also fed to the pug mill through a flowmeter at a controlled rate. The reaction in the pug mill is exothermic so fresh water is added to control the temperature. This water also controls the output product consistency.

The reacted mass from the pug mill is discharged onto a slow moving conveyor which allows aging to complete the reaction. The conveyor carries the almost dry solid continuous mass to a cutter which breaks the mass into granular fragments to facilitate handling. The cut mass goes to a mobile haulage station for final dry disposal. Gases from the pug mill, containing mainly CO_2 , are scrubbed before being discharged to atmosphere.

The 'dry' process produces principally calcium anhydrite, CaSO_4 , and hemihydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. The reaction heat is sufficient to heat the end-products beyond the temperature where gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) dehydrates. The reaction products will hydrate, at least partially, to gypsum or to hemi-

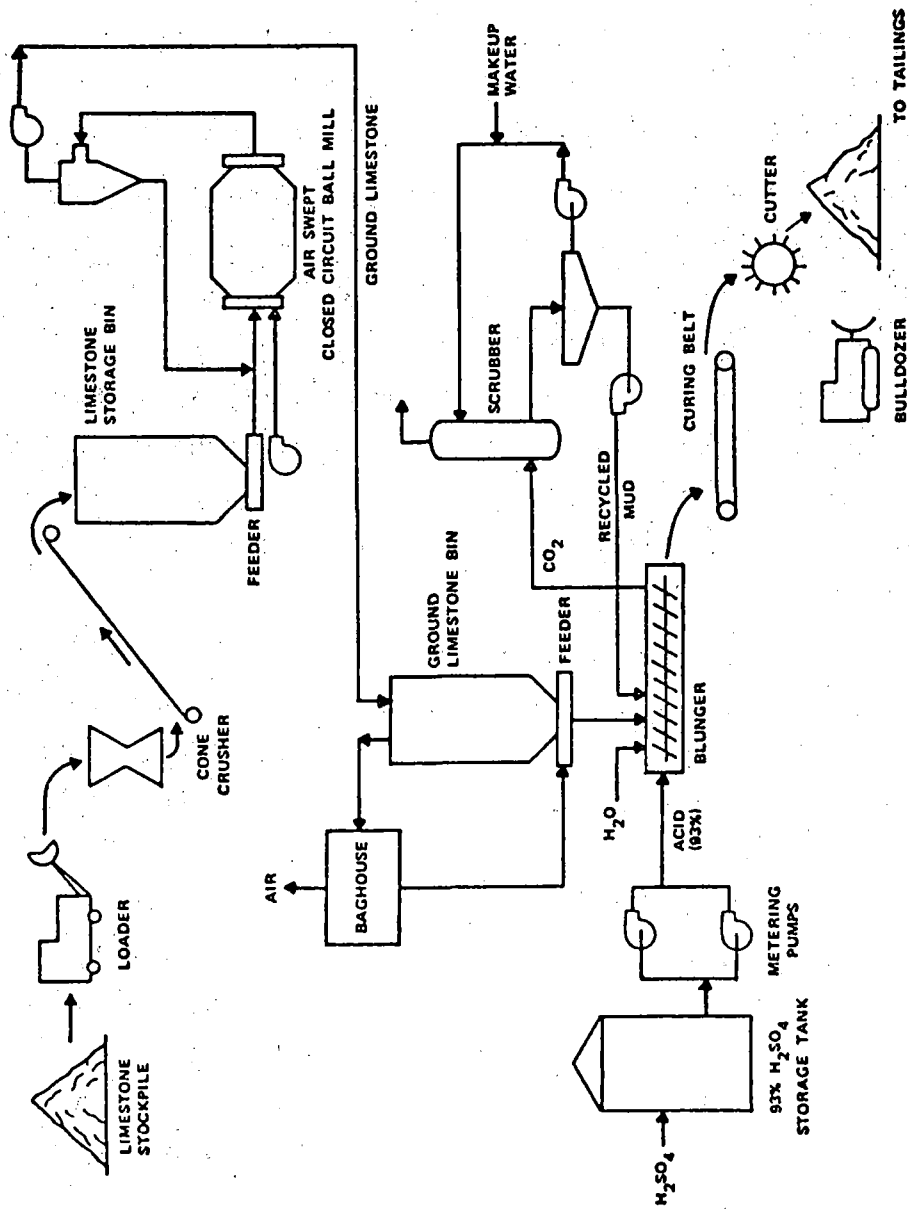


FIGURE 19 SULPHURIC ACID NEUTRALIZATION - DRY PROCESS (14)

hydrate upon exposure to atmospheric moisture.

8.4.2.2 Wet Process

A simplified flowsheet for the 'wet' process is shown in Figure 20 (14). Crushed limestone is ground to a slurry (80% - 100 mesh) in a wet ball mill, the slurry being pumped to a neutralizing reactor station which comprises two or more reactors operating in series.

Acid is pumped to the first reactor at a controlled rate to maintain proper sulphate concentration (0.2 to 0.5%) in the outlet of the second or last reactor. A constant recycle of slurry (about 50%) is maintained to control scaling and to promote gypsum crystal growth.

Reactor temperature is controlled to 71°C by adding fresh water and evaporative cooled reclaim water, recycled from the disposal pond. The neutralization reaction is quite exothermic and thus requires cooling or large water excess to control the temperature. The reactor system is designed to provide two hours retention time.

Waste gypsum slurry is discharged to the tailings pond by gravity flow. The tailings pond provides area for cooling by surface evaporation and for ponding of water. In the design, it is assumed that the tailings will retain 40% moisture, and the remaining water is recycled to the reactor system.

8.5 Manufacture of Chemicals

As shown in Tables 23 and 24, nearly 90% of total sulphur consumption is in the manufacture of sulphuric acid, some 60% of which is used in the manufacture of phosphate fertilizers. Although these figures are for the U.S.A. they are reported to be representative of the world situation (26). Approximately 20% of sulphuric acid is used in the manufacture of various chemicals.

Depending on the location of existing copper and nickel smelters relative to phosphate rock deposits, the manufacture of phosphoric acid, phosphate fertilizers or chemicals at the smelter site may represent a viable alternative to the sale or neutralization of sulphuric acid. Stringent environmental regulations may determine that new smelters are located near available

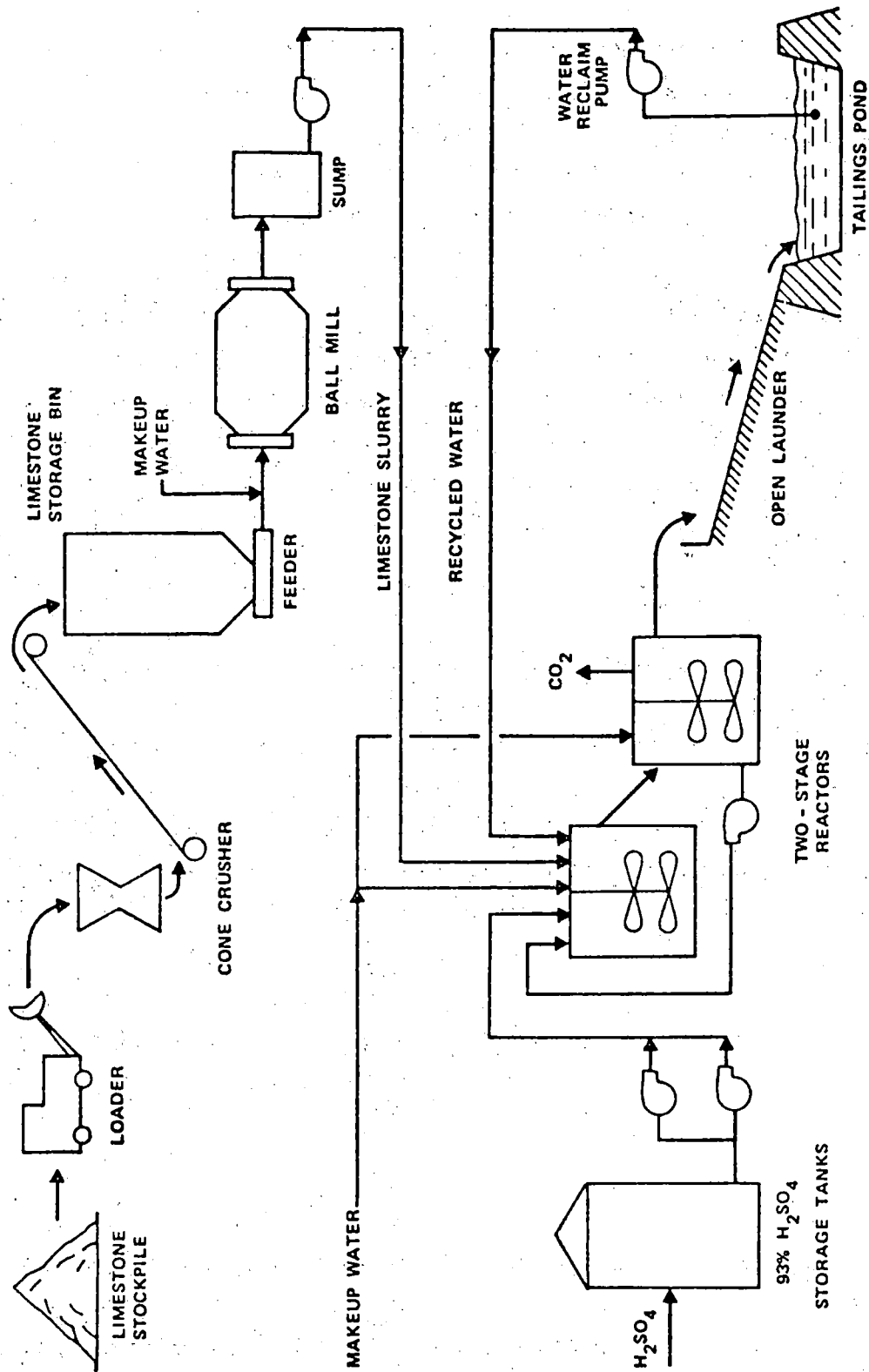


FIGURE 20 SULPHURIC ACID NEUTRALIZATION - WET PROCESS (14)

markets for acid, or where the acid can be used locally for manufacture of fertilizers or chemicals. In such a case, concentrates would have to be transported from the mine site to the smelter. The smelter may become a custom smelter for treating several different concentrates. Other factors to consider are end-product market location and local power costs when evaluating smelter location under these circumstances.

Other uses of sulphuric acid, e.g. in petroleum refining, leaching of copper and uranium ores, the pulp and paper industry, are relatively minor uses in terms of global statistics. However, the use to which sulphuric acid could be put will vary with each smelter location, necessitating an evaluation of all factors, including the creation of new acid outlets, in each case.

8.5.1 Phosphoric Acid

An average of one tonne of sulphuric acid consumes 1.22 tonnes of phosphate rock to produce 0.34 tonnes of 100% P_2O_5 in phosphoric acid (26). The fertilizer industry consumes phosphoric acid in the form of 54% P_2O_5 in the manufacture of phosphate fertilizers. Phosphate rock is transported large distances to make phosphoric acid, e.g. in North America, from Florida to Saskatchewan by ship and rail, and from the western U.S. to Alberta by rail. East coast U.S. phosphate rock is shipped to Japan. Phosphoric acid is a widely traded commodity. It is estimated that 6 million tonnes of the latter will be transported by ocean freight in 1980 (26). Subject to favourable economics, particularly in regard to freight costs, and markets being available, the production of sulphuric acid at a smelter and its subsequent use to produce phosphoric acid at site may be a viable proposition.

8.5.2 Ammonium Phosphate Fertilizers

The largest outlet for phosphoric acid is in the manufacture of ammonium phosphate fertilizers. The production of sulphuric acid from smelter gases, its reaction with phosphate rock to produce phosphoric acid for subsequent conversion to phosphate fertilizers at, or near the smelter site may be a viable proposition.

There are a whole series of ammonium phosphate fertilizers and various fertilizer blends incorporating ammonium phosphates, urea, ammonium nitrate, potash and ammonium sulphate. The types of fertilizer products and their composition will depend on market opportunities which can only be determined by a detailed market study. A common fertilizer is diammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$ or 18-46-0. Production of one tonne of fertilizer requires 0.87 tonne of phosphoric acid and 0.23 tonne of ammonia (26).

From the smelter's point of view, the least desirable option to dispose of sulphuric acid is likely to be the manufacture of ammonium phosphates. The fact that fertilizers are used, in temperate zones at least, only a few months a year necessitates a large inventory of product and hence a large working capital requirement. The need for fertilizers in the developing countries is immense and so at certain smelter locations this constraint may be less onerous. Ammonia is a high cost item compared to the value of the sulphuric acid whose disposal was sought in the first place. If sulphuric acid or phosphoric acid could be sold, their sale would be at a constant rate throughout the year, thereby minimizing working capital requirements. The customer would then absorb the costs of working capital for fertilizer production.

8.5.3 Potassium Sulphate

For some crops requiring a fair amount of potassium (tobacco, citrus fruits, sugarbeet, potato) a fertilizer containing chloride is undesirable. This creates a demand for potassium sulphate, a chemical whose manufacture consumes a considerable quantity of sulphuric acid. In 1976, world trade in sulphates of potash (i.e. potassium sulphate and potassium magnesium sulphate) reached 716,000 tonnes of K_2O equivalent (26). Although the market for potassium sulphate is quite specific, on a world scale it is reasonably large. The sulphate forms of potash account for some 6% of total world potash trade.

The production of one tonne of potassium sulphate consumes 0.91 tonne of potash (KCl) and 0.61 tonne of sulphuric acid. In addition, a by-product credit of 1.27 tonnes of hydrochloric acid is produced (as 33% HCl),

but for which a market has to be found (26). The economics of this alternative will depend largely on the cost of potash which may be as high as 90% of the total operating cost.

Potassium sulphate is formed by the following reaction:



Two processes are generally used for the production of potassium sulphate - the Mannheim process and the newer Climax process. In the Mannheim process, a high purity product is produced by mixing potash and sulphuric acid prior to their reaction in a continuous muffle furnace. Dry potassium sulphate is produced and a steam-hydrochloric acid gas which is scrubbed with water to form aqueous hydrochloric acid. In the newer Climax process a fluid bed reactor replaces the Mannheim muffle furnace which results in fewer corrosion problems.

8.5.4 Miscellaneous Chemicals

The manufacture of aluminium fluoride, an essential chemical in the manufacture of aluminium metal, may have merit. Production involves the digestion of fluorspar with sulphuric acid. The resulting hydrofluoric acid is reacted with alumina to form aluminium fluoride. The economics of this option will depend on access to aluminium production facilities and the location of the source of fluorspar (26).

A significant end-use for sulphuric acid in much of the world is the leaching of low-grade copper and uranium ores (26). The sulphuric acid, in dilute solution, is pumped through ore still in place, crushed ore placed on prepared drainage pads, flotation mill tailings, or old mine workings. The copper or uranium values are leached from the ore and recovered from solution by solvent extraction, ion exchange or cementation with iron. Generally oxide ores are treated in this manner. Acid consumption depends on a number of factors including the mineralization of the ore. Based on U.S. experience, sulphuric acid consumption varies from nil to 5 kg per kg of copper extracted (26). This option would prove attractive where the smelter and acid plant are located at a mine site which has leaching operations. Part of the acid

production would be used internally, obviating the need to look for outside markets for all the acid while possibly incurring high transport costs and being forced to accept a low price. All the acid production, particularly from a large smelter, is unlikely to be used for leaching purposes. Leaching also creates an environmental problem in that liquid effluents, containing sulphate ions, have to be disposed of.

9 IMPOSITION OF MORE STRINGENT EMISSION CONTROLS

9.1 Deficiencies of Traditional Smelting Processes

Multihearth roasting, sintering and blast furnace smelting are now virtually obsolete in the copper and nickel smelting industries because they are energy-inefficient processes when viewed in the overall smelting context and also because they are in the main, environmentally unacceptable processes. Compared with the modern smelting processes, these processes produce gas streams low in SO_2 content. Fugitive emissions are also more difficult to control than in the newer processes.

For many years the matte smelting reverberatory furnace has been the mainstay of the copper and nickel smelting industries, and there are still many furnaces of this type in existence. The principal disadvantages of this process are that it is energy inefficient - it uses large amounts of expensive hydrocarbon fuels to melt the charge - and it produces a large off-gas volume (due to dilution and the large amount of air required to burn the fuel) of high heat content, generally of a strength too low in SO_2 to make its capture and fixation an economic proposition. Melting in the reverberatory furnace produces a 'natural' matte grade because little of the iron sulphide is oxidized. As a result, little of the sulphur in the charge (except for some 10 - 15% oxidation in the furnace freeboard) enters the gas phase, thereby limiting the SO_2 content of the latter. The use of oxy-fuel roof burners, as practised at the El Teniente copper smelter in Chile and on Inco's Copper Cliff nickel reverberatory furnaces, allows the SO_2 content in the off-gases to be increased to about 7% SO_2 . This is sufficiently high to allow direct processing of the gases in a sulphuric acid plant, although an acid plant has not been installed at either smelter. Because a low or 'natural' matte grade is produced, most of the sulphide oxidation (ferrous sulphide followed by cuprous sulphide) takes place in the converters, a batch process with cyclic operation which produces intermittent gas flows of variable volumetric flow rate and strength. Because the converter is rotated in and out of the stack or blowing position, engineering design of converter hoods to minimize ingress of dilution air is made difficult. Converter gas strengths are therefore diluted, generally by a minimum of 75 - 100% for tight-fitting hoods and up to 400% when the hood is in a state of disrepair. This increases the size and cost of a sulphuric acid plant, the accepted control approach in the industry.

High gas volumes in the primary smelting furnace generally result in large quantities of flue dust carryover in the gases although this is also a function of exit gas velocity.

Electric furnace matte smelting also produces a 'natural' matte grade since only melting of the charge (calcine or concentrate), takes place. However, because hydrocarbon fuels are not burnt to effect melting, gas volumes are generally low compared with those in reverberatory furnaces. However, the SO_2 content is also low because there is little oxidation (except for some 10 - 15% desulphurization in the furnace freeboard) and enrichment of matte grade. In certain copper smelting applications, an off-gas containing up to 5% SO_2 can be generated if the concentrate demonstrates pyrophoric properties and air is ingressed into the furnace to complete the oxidation of sulphur. Electric furnaces smelting nickel concentrates are sometimes operated under non-oxidizing conditions in which case the off-gas only contains about 0.5% SO_2 .

Fugitive emissions, the most significant sources being from matte tapping and its transport in ladles by overhead crane in the converter aisle and during rotation of converters from the blowing position, are more of a problem in smelters which produce a low grade of matte in the primary smelting furnace because of the large number of crane movements.

9.2 Changes in Smelting Technology

The deficiencies in traditional smelting processes, i.e. their inability to utilize efficiently the inherent energy in the concentrate at the smelting stage and the production of uneconomic gas strengths, has led to the development of various commercially available alternative smelting technologies to overcome these shortcomings.

The concept of 'flash' smelting was developed, which essentially combines roasting and melting (i.e. smelting) of concentrate in the furnace freeboard. Part of the inherent energy content of the concentrate is released in the exothermic oxidation of ferrous sulphide, thereby helping to sustain the smelting reactions. This results in enrichment of the matte grade above its 'natural' grade (produced if only melting, as opposed to smelting, took place). The degree of matte grade enrichment is controlled by the reaction

air :concentrate ratio and is also dependent on concentrate composition. Enrichment of the matte grade coincidentally results in an off-gas sufficiently high in SO_2 to make its recovery as sulphuric acid, the accepted control approach in the industry, both technically and economically feasible using the contact process. The two flash smelting variants (Outokumpu and Inco) both utilize the 'flash' smelting concept in various ways. The Kivcet process also operates on the 'flash' smelting principle. Both the Inco and Kivcet processes are oxygen flash smelting processes.

In the Noranda process, upgrading of the 'natural' matte grade is brought about by oxidation of the matte by blowing with oxygen-enriched air through submerged tuyeres. The Noranda process is capable of producing blister copper directly from concentrate, depending on concentrate composition (i.e. impurity content), but for impurity reasons the process currently produces a high-grade matte (70 - 75% Cu) at the Horne and Garfield smelters.

In the Mitsubishi continuous smelting process, upgrading of the 'natural' matte is achieved by top-blowing the molten bath with oxygen-enriched air in the smelting furnace to produce a matte (65% Cu)-slag emulsion which is oxidized to blister copper in the converting furnace.

Matte grade, the degree of oxygen enrichment of reaction air, and the SO_2 contained in off-gases are all interrelated. The matte grade selected is governed by such factors as concentrate composition and impurity content and the capacity of a furnace to dissipate the heat of reaction in the gases. The general tendency in modern smelters is to aim for a high matte grade (65% Cu in Outokumpu flash smelting, 70 - 75% Cu in the Noranda process) in the primary smelting furnace in order to produce a continuous gas flow of constant volume and relatively high strength (10 - 15% SO_2) as a base load for conversion to sulphuric acid. The exceptions are in the Inco and Kivcet processes, both of which, as a consequence of utilizing the oxygen flash smelting principle, produce a matte grade in the range of 45 - 50% Cu at the autogenous point for the grade of concentrate currently treated. An off-gas of low volume containing around 80% SO_2 is produced. The matte grade at the autogenous point is governed by concentrate composition and the ability of the system to dissipate heat, particularly to the gases. This is limited when using technically pure oxygen because of the virtual absence of nitrogen. Increasing the matte grade by diluting technical oxygen with air in order to dissipate the additional heat liberated by the smelting reactions in the gases would detract from the cost

advantages of using oxygen. The SO_2 content of the gases would also be diluted by the addition of nitrogen contained in air. The presence of nickel in the copper matte at Inco's Copper Cliff smelter also places an upper limit on matte grade in order to optimize nickel recovery to matte. By producing a high-grade matte in the primary smelting process, the amount of oxidation in the converters is reduced, thereby minimizing the problems associated with a batch unit operation which produces an intermittent gas flow of variable volume and strength. As a consequence of the lower matte grade produced in the Inco and Kivcet processes, the volume of gas from the converters is somewhat greater than when the other processes mentioned are employed. In addition, the overall smelter gas volume may be slightly greater because of the difficulty in controlling the amount of dilution air ingressed through converter hoods.

Smelting to high-grade mattes, regardless of process, requires a slag treatment stage, either in a separate electric furnace or by milling and flotation, in order to maintain metal losses at an acceptably low level. Integral slag cleaning is carried out in the Furukawa flash furnace using electrodes in the settler, the matte grade being in the medium range (50% Cu).

In all the processes, oxygen enrichment of the reaction air further increases the gas strength, simultaneously reducing gas volume, through partial replacement of the nitrogen content. By utilizing the inherent energy in the concentrate combined with oxygen enrichment, the modern processes are energy efficient to the extent that the use of hydrocarbon fuel is reduced and even dispensed with at the autogenous point.

The difference between the primary smelting processes can be considered in engineering terms - furnace design including method of charging concentrate, and in metallurgical terms - degree of oxygen enrichment, grade of matte or blister copper produced, process continuity, and the point in the overall smelting process at which the inherent energy is released.

The Noranda process, while producing a high-grade matte (75% Cu), has a gas off-take (i.e. hood arrangement) similar to that of the Peirce-Smith converter, and so is prone to ingress of dilution air, a factor which unless controlled, increases the size and cost of an acid plant. However, when operating in the blister mode, converters are not required and under this condition the Noranda process may offer the lowest total smelter gas volume of all processes.

Smelting concentrates to produce a higher matte grade reduces the number and frequency of matte taps and ladles of matte transferred by crane in the converter aisle. As a result, fugitive emissions are somewhat reduced. The Mitsubishi continuous smelting process would appear to offer an improved solution in reducing, or even eliminating, fugitive emissions. By locating the three furnaces (smelting, converting and slag cleaning) at different elevations, matte and slag are able to cascade among the furnaces along enclosed heated launders for further processing, thus eliminating the conventional converter aisle. A matte containing about 65% Cu is produced for converting in an enclosed stationary furnace using oxygen-enriched, top-blown air lances, as opposed to tuyeres as in the rotary Peirce-Smith converter. The Mitsubishi process can be considered more sophisticated than others and demands close attention to engineering and operating details.

The Hoboken syphon converter has been installed in some copper smelters as a replacement for the Peirce-Smith converter. As previously described, the former is better able to contain SO_2 emissions because of a specially designed flue system enabling control of draught. However, the required differences in operating technique from Peirce-Smith converting have not always been fulfilled, and together with more sophisticated engineering design, the syphon converter, particularly the larger vessel, has not yet achieved wide acceptance in the industry.

Combinations of various unit operations are possible. One that is being studied by several U.S. copper smelters is a flash furnace and Mitsubishi type converter as a replacement for the traditional reverberatory furnace - Peirce-Smith converter combination.

In special applications the TBRC can be considered. One such application is at Afton Mines where the vessel is used to smelt high-grade chalcocitic concentrate containing little sulphur and also significant quantities of native copper. Another application is the treatment of concentrates containing deleterious impurities as practised at Boliden.

Several other processes, such as cyclone smelting, oxygen sprinkle smelting, Amax dead roast, Q-S oxygen process, Worcra continuous smelting process, are under various stages of development. These processes aim at being energy efficient and the production of high strength gas streams suitable for recovering SO_2 as sulphuric acid. These processes are not yet commercially proven.

In nickel smelting, the processes generally employed are the reverberatory furnace, Outokumpu flash smelting and the electric furnace. The reverberatory furnaces at Inco's Copper Cliff smelter treat calcine produced in multiple hearth roasters, while the electric furnace smelters, being more modern plants, smelt calcine produced in fluid bed roasters as at Inco's Thompson smelter and Falconbridge's plant near Sudbury. Characteristics of the gas streams are similar to those in the corresponding copper smelting processes assuming a similar level of sulphur input to the furnaces. A special application of the electric furnace is used in South Africa for smelting refractory concentrates which are comparatively low in nickel and platinum group metals. These concentrates are correspondingly low in sulphur and therefore the gases contain a maximum of about 0.5% SO_2 . The electric furnace is readily able to achieve the high slag temperatures required in smelting these concentrates.

Inco is currently carrying out testwork on a fluid bed roaster and electric furnace at the Thompson smelter, aimed at producing a sulphur deficient matte which would undergo only an iron removal (finishing) blow in the converters. Roasting conditions will be controlled so as to eliminate about 80% of the sulphur contained in concentrate, simultaneously producing a continuous source of high-strength SO_2 gas suitable for the manufacture of sulphuric acid, thereby reducing emissions to the atmosphere.

At the Copper Cliff smelter, Inco has successfully smelted nickel concentrates using oxygen flash smelting techniques to produce a relatively high-grade matte containing 32% Ni and a slag assaying 0.47% Ni. Oxygen consumed varied between 25 and 30% of the weight of dry concentrate. Pilot plant testwork has also been undertaken to examine the technical feasibility of a continuous nickel smelting process. A pyrrhotite separation process aimed at reducing SO_2 emissions by 25% at Inco's Sudbury operations will be installed in the concentrator and is scheduled for commissioning in mid-1983. This will further reduce the sulphur input to the smelter.

9.3 Engineering Requirements

Imposition of additional environmental regulations will necessitate changes being made to smelters utilizing outdated technology. Experience at Japanese smelters, where modern smelting technology (generally flash smelting) is employed, indicates that greater than 90% total sulphur containment can be achieved. Some plants claim 99% sulphur capture and fixation using double absorption acid plants and tail gas scrubbing (1).

Old smelters are typically equipped with the technology of the time, those still in existence generally being reverberatory furnaces, and converters with hood designs which allow in-leakage of large volumes of air used as a means of cooling high-temperature off-gases. These plants were designed to meet the accepted air pollution standards, if any, of the time. Under these conditions there was little incentive for sulphur containment which means that these smelters require considerable engineering modifications, process changes and capital expenditure if they are to meet current and proposed air pollution legislation. These older smelters can be remodelled for improved sulphur containment but the possibilities, while varying from one smelter to another, are invariably limited. Fluid bed roasters can be installed ahead of reverberatory or electric furnaces, and converters can be equipped with tight-fitting, water-cooled hoods provided there is sufficient room for the extra equipment needed. However, only partial sulphur containment can be achieved by these changes, and often the gases obtained by rehabilitating old smelters are far from ideal for processing to sulphuric acid, so that the acid plants become large and costly to build and operate (2).

More fundamental remodelling such as replacement of unit operations, e.g. reverberatory by flash smelting, may require extensive modifications to smelter buildings and auxiliary facilities such as storage and conveying systems, electric power, water and steam systems. In addition, the addition of an acid plant, and in some cases an oxygen plant, will be necessary. Considerable disruption to production will occur during such extensive rehabilitation. Costs of this work will be very high and in some cases almost

as costly as a completely new smelter. Certain design features may of necessity be complicated and far from ideal when an old smelter is extensively remodelled or processes are replaced and this may lead to operating difficulties later on.

Even for an extensively remodelled old smelter, it is still difficult to achieve a high degree of sulphur containment within present-day economic limits. This is because a substantial proportion of the sulphur is contained in the converter gases of variable volumetric flow rate and SO_2 content.

10 CAPITAL COSTS

10.1 Alternative Smelting Technologies

As mentioned previously, each smelter is unique in terms of its location, smelting and sulphur containment (if any) technologies employed, and requirements for compliance with environmental legislation. The latter also varies according to location. These factors mean that it is difficult to quantify costs, other than in very general terms, for modifications and additions to an existing smelter. Each smelter must be assessed on an individual basis, taking into account the measures that are technically and economically feasible for sulphur containment.

The capital expenditure required to achieve a significant degree (90% and greater) of sulphur containment from older smelters will be large. Investment will be required for sulphur fixation facilities (usually sulphuric acid plants) and for rehabilitating and modernizing the metallurgical plant itself. These expenditures will frequently be incurred without any increase in metal production and therefore may be accompanied by no financial return on the investment. The expenditures must be amortized over a period of 10 to 20 years and therefore require corresponding ore reserves or supplies of concentrate to ensure economic operation of the smelter over this period. The remaining life of an orebody can therefore place a constraint on the availability of capital required for sulphur containment facilities (2).

In the case of new smelters, the requirement for sulphur containment alters the criteria for optimum economic location. For the reasons already put forward in Section 8, it is likely that any new smelter would be located in an acid-consuming area with concentrates being transported to the smelter site.

Average order-of-magnitude costs (mid-1980 Canadian dollars, $\pm 30\%$ accuracy) are shown in Figure 21 for four copper smelters of varying capacity based on a greenfield site (27). The smelters include sulphuric acid and oxygen plants as appropriate to the technology employed. The costs represent the mean of four processes (Inco and Outokumpu flash smelting,

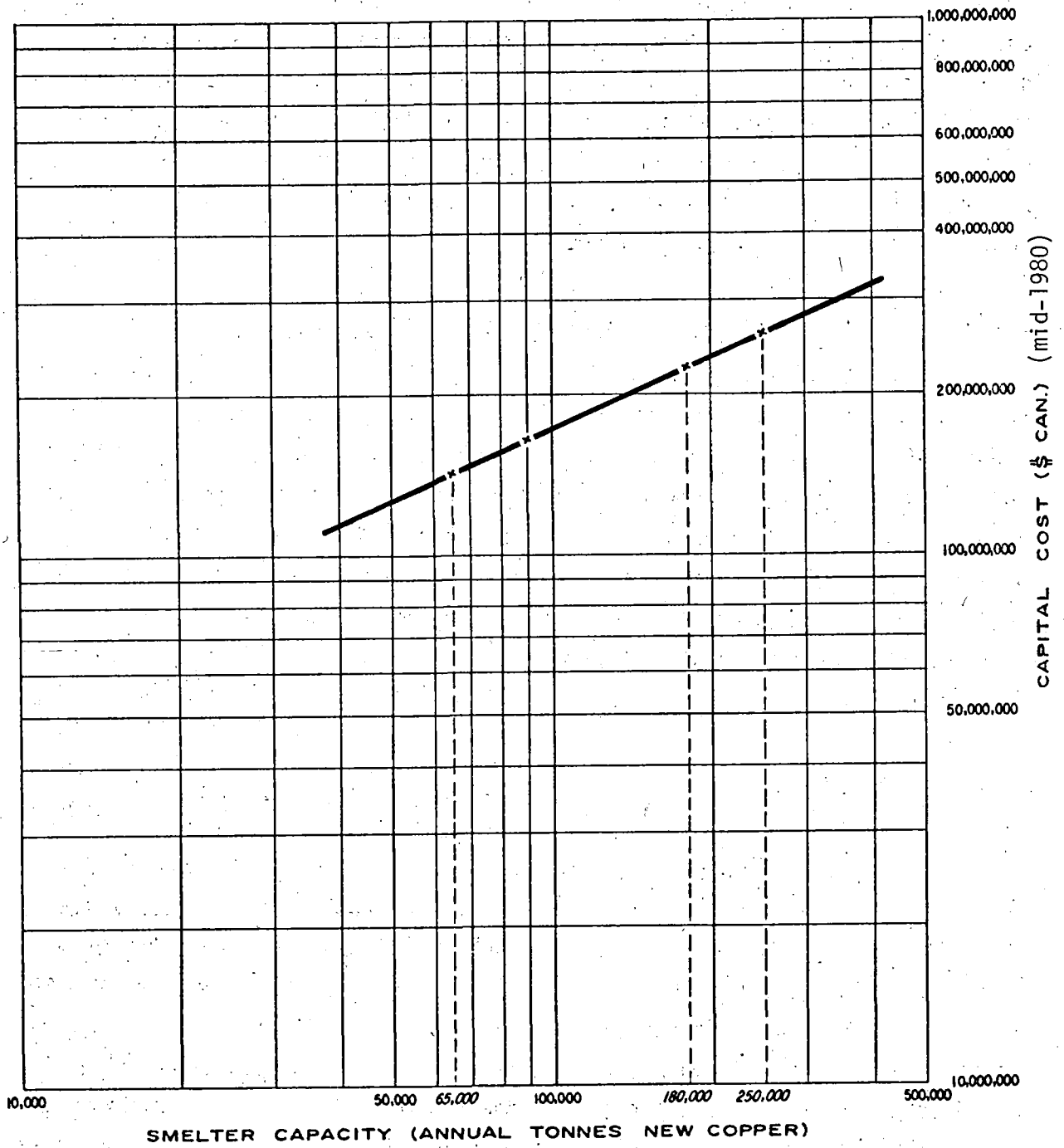


FIGURE 21 COPPER SMELTER - AVERAGE TOTAL INSTALLED COST (GREENFIELD SITE) (27)

Noranda process, and roast-electric smelting), with each process varying $\pm 25\%$ from the mean line. The costs also represent the 'total installed cost', but exclude those items which vary with location, i.e. freight, duties and taxes, construction indirects, site preparation and initial stores inventory, which in total could account for an additional 20 - 30% of the cost given on the graph. These costs could also be considered representative for nickel smelters employing Outokumpu flash smelting or roast-electric smelting technology.

10.2 Sulphur Containment Plants - Concentrated Gas Streams

Order-of-magnitude capital costs are given in this section for various sulphur containment plants, i.e. sulphuric acid plants, liquid SO_2 and elemental sulphur production facilities. These costs do not include the cost of adapting the metallurgical plant to the sulphur fixation technology. Extensive smelter modifications, such as process changes and installation of hot gas cleaning facilities will vary in each case and could well exceed the cost of the sulphur fixation plant. An allowance is included to cover a proportion of the auxiliary equipment and services which can reasonably be assigned to the sulphur product recovery plant.

10.2.1 Sulphuric Acid Plant

Sulphuric acid plant costs vary according to the maximum volumetric gas flow rate which determines the size of blower and other equipment, and with the gas strength. Smelter gases should not be below about 4% SO_2 if an acid plant is to operate autothermally. Below this concentration, acid plant costs increase dramatically and could be as much as 50 - 80% higher than the lowest concentration curve shown on Figure 22, which gives typical total installed costs for double absorption acid plants varying with gas flow and SO_2 concentration (27). Where a manufacturer's price is available for an acid plant package (i.e. equipment F.O.B., engineering and licence fee) the total installed cost can be calculated by applying a factor of about 3.1 which will allow for civil works, interconnecting services, acid tanks, oil storage, effluent disposal, spares, freight and erection. The costs in

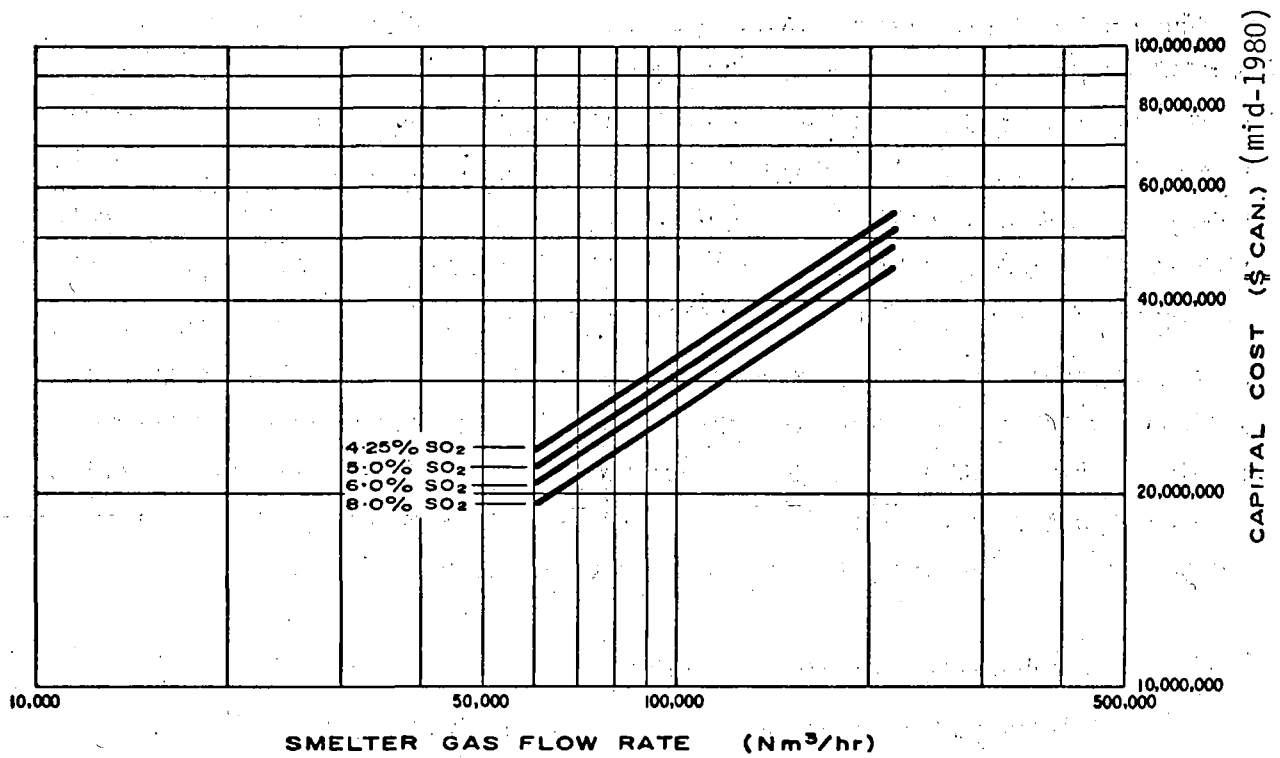


FIGURE 22 DOUBLE ABSORPTION ACID PLANTS - TOTAL INSTALLED COST (27)

Figure 22 are on the basis of Canadian dollars, at mid-1980 prices. Import duties are excluded.

The cost of an acid plant also varies according to whether the plant uses single or double absorption technology, and according to whether the plant treats a continuous gas stream only, variable gas stream only, or a combination of the two. A double contact acid plant (which has a lower strength tail gas emission) is between 10 - 15% more expensive than a single contact plant (2, 19). Indications are that the additional acid recovered, or sulphur fixed, in a double absorption plant does not offset the additional capital and operating costs, particularly in areas where energy costs are high (2). Table 26 gives typical order-of-magnitude double absorption acid plant costs (mid-1979 Canadian dollars) and shows the dependence of cost on the characteristics of the gas streams referred to above (2).

Acid plant capacity also varies according to the size of the smelter and the amount of input sulphur required to be recovered. The largest plants at copper smelters exceed 2000 tpd for a single stream installation. From a smelter of economic size, acid production is commonly 500 - 1000 tpd, depending on the number of gas streams processed.

10.2.2 Sulphuric Acid Neutralization

If environmental regulations and other factors determine that production of sulphuric acid from smelter gases should be the control approach, the acid may be used on site, or sold into various markets. If no markets exist, or if market saturation occurs, all or part of the acid must be neutralized with lime/limestone to form gypsum, a stable material which can be discarded. Table 27 gives order-of-magnitude costs for neutralizing and impounding 540 and 1100 tpd of sulphuric acid at the smelter site (2).

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

Basis for Estimates	Continuous Gas Only	Variable Gas Only	Continuous Gas Base Load with Variable Gases	Continuous Gas Base Load
Production: t/day 100% H ₂ SO ₄	540	540	540	1,100
Gases:				
Continuous smelter gas, i.e. from roaster, flash furnace, % SO ₂	12	-	12	12
Variable gas, i.e. from converters, % SO ₂	-	5-8	5-8	5-8
CAPITAL COST (\$, June 1979 cost level)				
Double catalysis sulphuric acid plant ¹	13,200,000	21,665,000	16,443,000	24,848,000
Contingency @ 25%	3,288,000	5,416,000	4,110,000	6,212,000
Auxiliary equipment and services	1,649,000	2,708,000	2,055,000	3,106,000
TOTAL CAPITAL COST	18,137,000	29,789,000	22,608,000	34,166,000

1 Includes engineering and construction overhead costs.

TABLE 27 COST OF NEUTRALIZING SULPHURIC ACID FROM A DOUBLE CATALYSIS ACID PLANT WITH LIMESTONE AT THE SMELTER SITE (2)

Basis for Estimates

Acid plant production to be neutralized

t/yr 100% H ₂ SO ₄	190,000	380,000
t/day 100% H ₂ SO ₄	540	1,100

CAPITAL COST (\$, June 1979 cost level)

Neutralization plant ¹	5,818,000	9,272,000
Contingency @ 25%	1,454,000	2,318,000
	<hr/> 7,272,000	<hr/> 11,590,000
Auxiliary equipment and services including gypsum impounding	1,257,000	2,000,000
TOTAL CAPITAL COST	<hr/> 8,529,000	<hr/> 13,590,000

1 Includes engineering and construction overhead costs.

10.2.3 Elemental Sulphur Plant

As previously mentioned, the production of elemental sulphur from smelter gases is both technically and economically less attractive than is the production of sulphuric acid, the accepted control approach in the industry. The production of elemental sulphur requires a continuous flow of relatively strong SO_2 gas with a very low oxygen content as feed material. This can be produced by some smelting units such as flash furnaces, but converter gases of variable flow and SO_2 content would have to be processed to sulphuric acid. Table 28 gives an order-of-magnitude cost (mid-1979 Canadian dollars) estimate for a sulphur recovery plant of 270 tpd elemental sulphur capacity (2). This corresponds to a production of about 820 tpd of sulphuric acid from the same gases and represents a reasonably large smelting installation. Because few elemental sulphur plants treating smelter gases have been built, there is a lack of reliable cost data.

10.2.4 Liquid SO_2 Plant

As in the case of the elemental sulphur plant, few plants have been built which recover the SO_2 contained in smelter gases in the form of liquid SO_2 . The plant at Copper Cliff treats gases containing approximately 80% SO_2 from an oxygen flash furnace of Inco design. Table 29 gives an order-of-magnitude cost estimate (mid-1979 Canadian dollars) based on producing 160 tpd of liquid SO_2 from roaster or flash furnace gases containing 12% SO_2 (2). As in the case of elemental sulphur production, only a continuous stream of comparatively rich smelter gas is suitable for processing to liquid SO_2 . Variable flow and lower-grade converter gases would have to be processed to sulphuric acid to achieve a high overall sulphur fixation rate.

10.2.5 Combined Sulphur Fixation Plants

As previously mentioned, only high-strength, continuous flow smelter gases are suitable for producing liquid SO_2 or elemental sulphur. In the case where the highest degree of sulphur fixation is required, the variable, lower-strength converter gases must be processed separately to sulphuric acid. This additional processing increases the capital costs for sulphur recovery by the

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

Basis for Estimates	
Production:	270 t/day elemental sulphur, corresponding to 89 000 t 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 ₂ S 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 (\$, June 1979 cost level)	
Elemental sulphur plant ¹	\$21 275 000
Additional smelter auxiliary facilities ²	5 936 000
Subtotal	27 211 000
Contingency @ 25% ³	6 803 000
	34 014 000
Sulphur plant tail gas stack	3 321 000
Contingency @ 25% ⁴	830 000
	4 151 000
Total cost for sulphur recovery	38 165 000

- 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 discharge of incinerated sulphur plant tail gas.

TABLE 29 COST OF RECOVERING LIQUID SULPHUR DIOXIDE FROM SMELTER GASES (2)

Basis for Estimates

Production: 160 t/day liquid SO₂, corresponding to 56,000 t annually (assuming 350 operating days)

Gas processed: Smelter gases with 12% SO₂, cleaned in hot electrostatic precipitator

	Chemical Absorption Process (Asarco's Dimethyl Aniline Process)	Physical Recovery Process (Compression & Refrigeration)
Liquid SO ₂ plant ¹	7,103,000	6,314,000
Contingency @ 25%	1,778,000	1,578,000
TOTAL CAPITAL COST	8,881,000	7,892,000

¹ Includes engineering and construction overhead costs.

cost of the acid plant required. These total costs, based on the previous plant costs shown in Tables 26 to 29, are shown in Table 30 (2). It should be noted, however, that the costs are not directly comparable since in the elemental sulphur case approximately 65% more sulphur is fixed than in the case when making liquid SO_2 .

In cases where the smelter produces both continuous high-strength gases and variable lower-strength gases (which is normally the case in copper and nickel smelters), the processing of all gases to sulphuric acid requires the lowest capital expenditure and is technically less complex. In most cases the acid produced can be neutralized and disposed of as gypsum slurry at almost the same or lower capital cost per tonne of sulphur fixed, than following either of the two approaches outlined in Table 30.

10.2.6 Capital Cost Summary

Table 31 summarizes total estimated capital costs for the various sulphur containment processes previously mentioned (2). A 25% contingency and an allowance for auxiliary equipment and services is included. In addition, capital charges, amortized at 10% per annum over 15 years, are shown in dollars per tonne of sulphur fixed as acid, liquid SO_2 , or elemental sulphur.

10.3 Sulphur Containment Plants - Weak Gas Streams

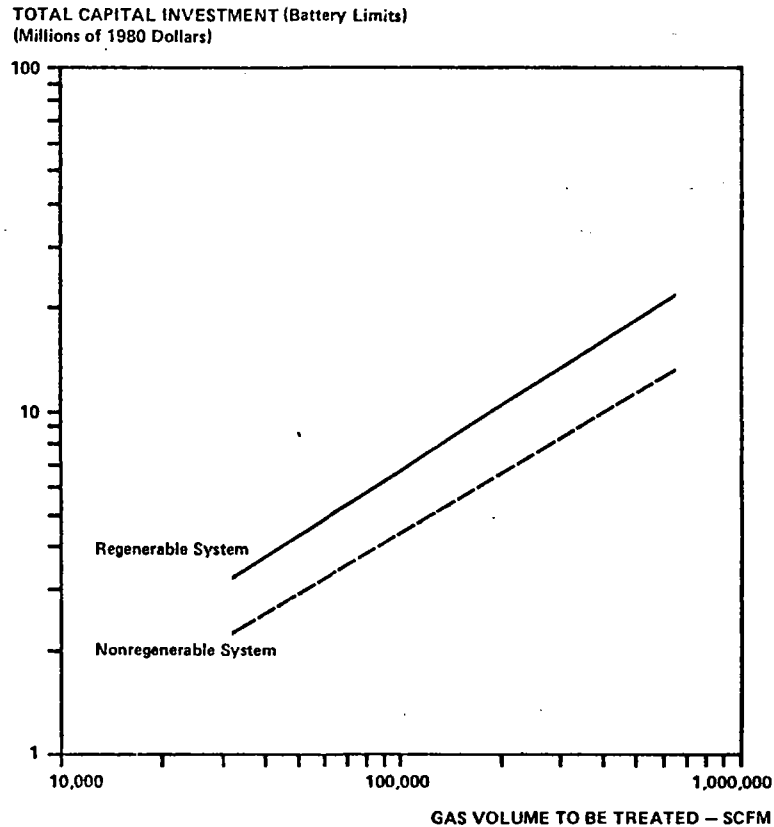
SO_2 can be removed from weak gas streams using either regenerable absorption systems or nonregenerable absorption (scrubbing) systems. Typical estimated capital costs (1980 U.S. dollars) for gas cooling, conditioning (humidifying) and residual particulate removal prior to the SO_2 absorption stage (which is common to both systems) are shown in Figure 23 for both systems as a function of volumetric gas flow rate (28). The amount of cooling and conditioning depends upon the characteristics of the gas stream and the limitations of the SO_2 removal system. Conditioning requirements for scrubbing systems are supplied by providing gas cooling and humidification only. Regenerable systems may require additional cooling and an increased degree of particulate removal. Costs for disposal of sludge

TABLE 30 TOTAL COST FOR SULPHUR RECOVERY FROM SMELTERS WITH VARIABLE LOW-STRENGTH GAS FLOW (2)

\$, June 1979 Cost Level		
	<u>Chemical Absorption</u>	<u>Physical Recovery</u>
(1) <u>Liquid SO₂ Plant</u>		
160 t/day liquid SO ₂ from continuous gases	8,881,000	7,892,000
	<u>Double Catalysis</u>	<u>Double Catalysis</u>
Sulphuric acid plant 540 t/day H ₂ SO ₄ from variable gases	29,789,000	29,789,000
TOTAL CAPITAL COST	38,670,000	37,681,000
(2) <u>Elemental Sulphur Plant</u>		
270 t/day elemental sulphur from continuous gases	38,165,000	
Sulphuric acid plant 540 t/day H ₂ SO ₄ from variable gases	29,789,000	
	67,954,000	
<u>Sulphuric Acid Plant</u>		
t/day H ₂ SO ₄ from continuous and variable gases	540	
Acid Plant	22,608,000	
Neutralization Plant	8,529,000	
	31,137,000	

TABLE 31 TOTAL ESTIMATED CAPITAL COSTS FOR VARIOUS SULPHUR CONTAINMENT PROCESSES (2)

		\$, June 1979 Cost Level Double Catalysis Capital Charges	
		<u>Capital Cost</u>	<u>\$/t fixed S</u>
<u>Sulphuric Acid Plants</u>			
540 t/day H ₂ SO ₄			
Continuous gases only		18,137,000	38
Variable gases only		29,789,000	63
Combined continuous & variable gases		22,608,000	48
1,100 t/day H ₂ SO ₄			
Combined continuous & variable gases		34,166,000	36
Neutralization of sulphuric acid			
540 t/day H ₂ SO ₄		8,529,000	18
1,100 t/day H ₂ SO ₄		13,590,000	14
		<u>Chemical Absorption</u>	<u>Physical Recovery</u>
		<u>Capital Cost</u>	<u>Capital Charges</u>
<u>Liquid SO₂ Plant</u>			
160 t/day liquid SO ₂	8,881,000	41	7,892,000 36
<u>Elemental Sulphur Plant</u>			
270 t/day elemental sulphur		-	38,165,000 56



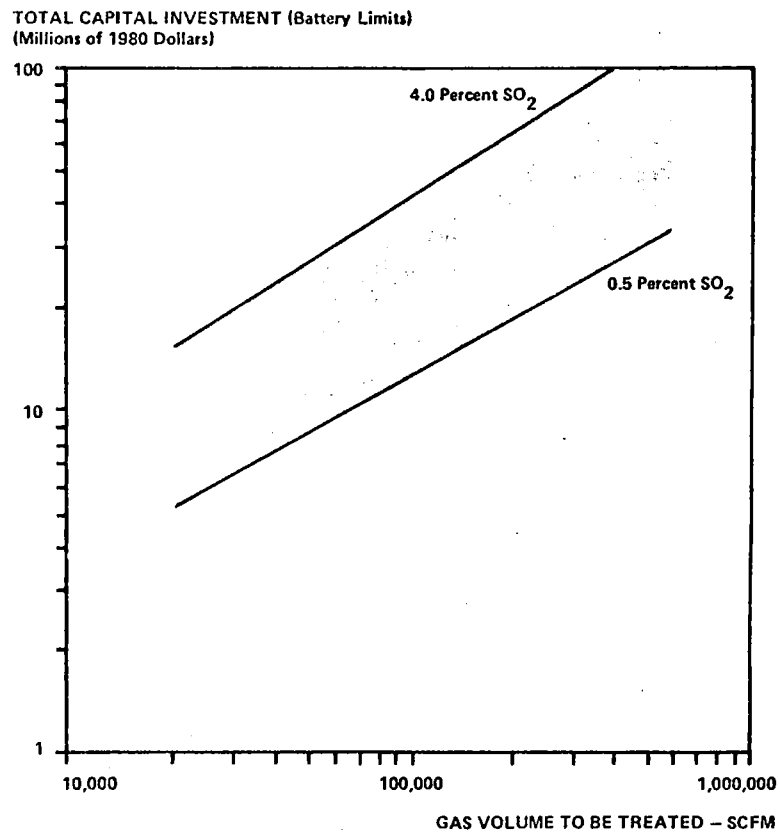
- 1) Regenerable systems include: Sodium Scrubbing (Wellman-Lord Process); Dimethylaniline (DMA)/Xylidine Process; and Sodium Citrate Process.
 2) Nonregenerable systems include: Lime and Limestone scrubbing; and Sodium Scrubbing (Double-Alkali Process).

FIGURE 23 TOTAL CAPITAL INVESTMENTS FOR SO_2 GAS COOLING AND CONDITIONING FOR BOTH REGENERABLE AND NONREGENERABLE (SCRUBBING) SYSTEMS (28)

produced in the nonregenerable system are included. The regenerable step, or disposal step if the system is nonregenerable, is specific to the SO_2 removal process employed.

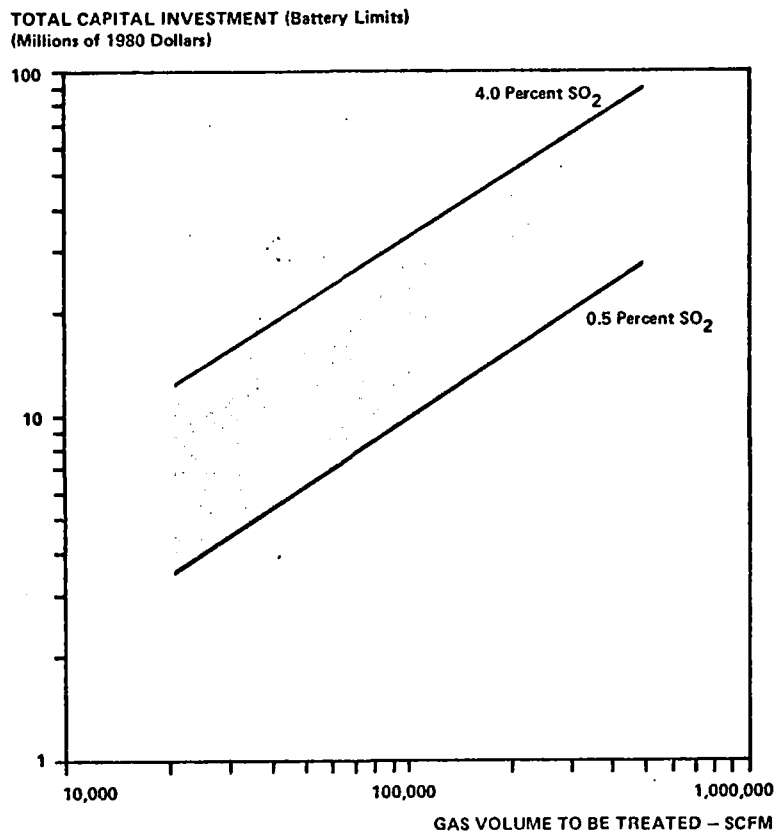
Figures 24 and 25 show estimated capital costs for regenerable and nonregenerable absorption systems, respectively, as a function of volumetric gas flow rate and SO_2 concentration (28). The shaded areas represent the range of possible costs depending on the SO_2 concentration in the gas and the type of SO_2 removal process.

To obtain the total capital costs for the respective SO_2 removal systems, the costs for gas cooling and conditioning, shown in Figure 23, must be added to the costs given in Figures 24 and 25.



NOTE: 1) Gas Cooling and Conditioning not included.
2) Regenerable systems include: Sodium Scrubbing (Wellman-Lord Process);
Dimethylaniline (DMA)/Xylidine Process; and Sodium Citrate Process.

FIGURE 24 TOTAL CAPITAL INVESTMENTS FOR SO_2 REMOVAL USING
REGENERABLE SYSTEMS (28)



NOTE: 1) Gas Cooling and Conditioning not included.
2) Nonregenerable systems include: Lime and Limestone scrubbing; and Sodium Scrubbing (Double-Alkali Process).

FIGURE 25 TOTAL CAPITAL INVESTMENTS FOR SO_2 REMOVAL USING NONREGENERABLE (SCRUBBING) SYSTEMS (28)

11 PRODUCTION COSTS

11.1 Alternative Smelting Technologies

Smelter production costs vary very widely according to location because of the different unit costs of fuel, power and labour, and cost of refractories delivered to site. Operating costs will also vary according to the smelting technology used. U.S. smelters typically would incur direct operating costs (excluding depreciation and capital charges) in the range 16-20 U.S. c/lb Cu (mid-1979). However, a greenfield smelter would incur much higher costs due to capital charges and depreciation on new plant.

Nickel smelters would incur direct operating costs of about U.S. \$2.00 - 2.50 per lb of contained nickel as refined product. The final smelter product, Bessemer matte, still contains some 21% S which has to be fixed. In order to put operating costs on a comparable basis it is therefore more meaningful to compare the costs of producing anode copper with refined nickel, both of which are essentially sulphur-free.

The direct smelter operating costs, which would include the costs of fixing sulphur, allow the costs of the latter (given in later sections) to be put in perspective.

11.2 Sulphur Containment Plants - Concentrated Gas Streams

Production cost estimates are based on typical Canadian unit costs prevailing in mid-1979. At any particular smelter location these unit costs will vary. The estimates assume that SO_2 in smelter gases is delivered free of charge to the sulphur fixation plant and therefore show only the cost of operating the sulphur recovery plant. The costs would increase if a value were applied to the sulphur contained in feed gases. The significant cost items are power, fuel and plant maintenance.

11.2.1 Sulphuric Acid Plant

The production cost of fixing sulphur as sulphuric acid in a double absorption plant is given in Table 32 (2). The estimates are based on treating continuous gas only, variable gas only and a combination of the two. The

TABLE 32 PRODUCTION COST OF FIXING SULPHUR AS SULPHURIC ACID FROM SMELTER GASES USING DOUBLE CATALYSIS ACID PLANT (2)

Basis for Estimates	Continuous Gas Only	Variable Gas Only	Continuous Gas Base Load with Variable Gases	
Production: t/day 100% H ₂ SO ₄	540	540	540	1,100
Gases:				
Continuous smelter gas, i.e., from roaster, flash furnace, % SO ₂	12	-	12	12
Variable gas, i.e., from converters, % SO ₂	-	5-8	5-8	5-8
PRODUCTION COST (\$/t H ₂ SO ₄)				
Operating Cost				
Supervision	0.53	0.53	0.53	0.26
Operating labour	1.04	1.04	1.04	0.58
Utilities ¹	1.73	3.09	2.17	2.13
Operating supplies ²	0.28	0.28	0.28	0.28
Maintenance ³	3.14	5.16	3.91	2.93
Indirect costs ⁴	0.69	0.69	0.69	0.37
Subtotal	7.41	10.79	8.62	6.55
Contingency @ 10%	0.74	1.08	0.86	0.66
Total operating cost	8.15	11.87	9.48	7.21
Capital Charges:				
Amortization & Interest @ 15 years and 10%/yr	12.51	20.56	15.60	11.79
Total Production Cost	20.66	32.43	25.08	19.00

1 Includes natural gas, water and electric power

2 Includes limestone for weak acid neutralization and other operating supplies.

3 @ 3.3%/yr of total capital cost.

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

costs per tonne of acid using a single absorption plant would be about 8% lower than the costs given in Table 32 (2). Where waste heat steam is available from the smelting process, savings can be made in the power required for acid production by using direct steam turbine drive on the acid plant blowers.

11.2.2 Sulphuric Acid Neutralization and Gypsum Impounding

For those smelters where it is not practical or economic to market sulphuric acid because of remote location or market saturation, it is necessary to neutralize the acid with lime/limestone to produce gypsum which can be impounded as a waste product. These production costs are shown in Table 33 on the basis of dollars per tonne of acid neutralized for the cases previously described, i.e. 540 and 1100 tpd of acid (2). The major factor affecting the cost of acid neutralization, exclusive of waste disposal, is the cost of mining, crushing, grinding and transporting limestone to the plant site. This cost will vary considerably with distance from the quarry to the smelter.

11.2.3 Elemental Sulphur Plant

The production cost for recovering elemental sulphur from SO_2 contained in smelter gases is shown in Table 34 (2). The significant item is the cost of natural gas used as reductant.

11.2.4 Liquid SO_2 Plant

The production cost for recovering liquid SO_2 from smelter gas is given in Table 35 (2).

11.2.5 Production Cost Summary

Production costs, including operating costs and capital charges, for the three methods of sulphur recovery are given in Table 36 (2). The costs are shown on the basis of dollars per tonne of sulphur fixed in order to facilitate a true comparison.

TABLE 33 PRODUCTION COST OF NEUTRALIZING SULPHURIC ACID FROM A DOUBLE CATALYSIS ACID PLANT WITH LIMESTONE AT THE SMELTER SITE (2)

Basis for Estimates

Acid plant production to be neutralized

t/yr 100% H ₂ SO ₄	190,000	380,000
t/day 100% H ₂ SO ₄	540	1,100

PRODUCTION COST (\$/t H₂SO₄ neutralized)

Operating Cost

Supervision	normally part of acid plant supervision	
Operating labour	0.77	0.39
Utilities ¹	0.67	0.67
Operating supplies (incl. limestone) ²	19.06	19.03
Maintenance ³	0.99	0.79
Indirect costs ⁴	0.64	0.32
Subtotal	22.13	21.20
Contingency @ 10%	2.21	2.12
Total operating cost	24.34	23.32

Capital Charges

Amortization & interest @ 15 years and 10%/yr	5.89	4.68
Total Production Cost	30.23	28.00

1 Includes natural gas, water and electric power

2 Includes limestone (49% CaO) for acid neutralization and other operating supplies.

3 @ 2.2%/yr of the total capital cost.

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

TABLE 34 PRODUCTION COST OF RECOVERING ELEMENTAL SULPHUR FROM SMELTER GASES (2)

Basis for Estimates

Production:	270 t/day elemental sulphur, corresponding to 89,000 t 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 ₂ S 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

PRODUCTION COST

	\$/t recovered sulphur
Operating Cost	
Supervision	1.51
Operating labour	5.93
Utilities ¹	39.48
Operating supplies ²	3.25
Maintenance ³	13.96
Indirect costs ⁴	<u>2.26</u>
Subtotal	66.75
Contingency @ 10%	<u>6.68</u>
Total Operating Cost	73.43
Capital Charges	
Amortization & interest @ 15 years and 10%/yr	<u>55.86</u>
Total Production Cost	<u>129.29</u>

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

2 Includes chemicals, catalyst replacement and other operating supplies.

3 At following annual percentages of total capital cost:

3.5%/yr for sulphur plant and additional smelter auxiliary facilities;
1.5%/yr for tail gas stack.

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

TABLE 35 PRODUCTION COST OF RECOVERING LIQUID SULPHUR DIOXIDE FROM SMELTER GASES (2)

Basis for Estimates	
Production:	160 t/day liquid SO ₂ , corresponding to 56,000 t annually (assuming 350 operating days)
Gas processed:	Smelter gases with 12% SO ₂ , cleaned in hot electrostatic precipitator
PRODUCTION COST	Chemical Absorption Process (Asarco's Dimethyl Aniline Process)
	Physical Recovery Process (Compression & Refrigeration)
	<u>\$/t SO₂</u>
Operating Cost Supervision	0.75
Operating labour	3.45
Utilities ¹	9.85
Operating supplies ²	3.83
Maintenance ³	7.13
Indirect costs ⁴	1.36
Royalties ⁵	0.63
Subtotal	<u>27.00</u>
Contingency @ 10%	<u>2.70</u>
Total Operating Cost	<u>29.70</u>
Capital Charges, Amortization & interest @ 15 years and 10%/yr.	<u>20.43</u>
TOTAL PRODUCTION COST	<u>50.13</u>

1 Includes steam, water and electric power.

2 Includes chemicals and other operating supplies.

3 @ 4.6%/yr of total capital cost.

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

5 Royalties payable for proprietary process.

TABLE 36 TOTAL PRODUCTION COSTS FOR SULPHUR BY-PRODUCTS FROM SMELTER GASES (2).

		\$ /tonne Sulphur Fixed	
<u>Sulphuric Acid Plants</u>			
Nominal Production t/day H ₂ SO ₄	540	1,100	
	<u>Double Catalysis</u>	<u>Double Catalysis</u>	
From			
continuous gas flow	63	-	
variable gas flow	99	-	
continuous & variable gas flows	77	58	
Sulphuric acid neutralization	92	86	
<u>Liquid SO₂ Plant</u>			
Nominal production t/day SO ₂		160	
	<u>Chemical Absorption</u>	<u>Physical Recovery</u>	
continuous gas flow	100	85	
<u>Elemental Sulphur Plant</u>			
Nominal production t/day sulphur		270	
continuous gas flow		129	

Copper and nickel smelters produce a mixture of continuous and variable gas streams. The cost of sulphur fixation from all major smelter gas streams is summarized in Table 37 in terms of dollars per tonne of sulphur fixed (2).

In the case where acid cannot be sold, the costs of acid neutralization and gypsum impounding must be added to the costs shown in Table 37. The operating costs for total fixation of the sulphur in smelter gases then become those shown in Table 38 (2).

11.2.6 Sulphur Containment Plants - Weak Gas Streams

Figure 26 gives estimated total annual operating costs (1980 U.S. dollars) for the gas cooling and conditioning stages for both regenerable and scrubbing systems as a function of volumetric gas flow rate (28). The operating costs in Figure 26 correspond to the capital costs shown in Figure 23.

Figures 27 and 28 show estimated annual operating costs for regenerable and nonregenerable absorption systems, respectively, as a function of volumetric gas flow rate and SO_2 concentration (28). The shaded areas represent the range of possible costs depending on the SO_2 concentration in the gas and the type of SO_2 removal process. In regenerable systems, the products produced (elemental sulphur, liquid SO_2 or sulphuric acid) have commercial value and may provide a source of revenue that would affect the costs associated with the control systems. However, because the factors associated with marketing these products are highly variable, the credits for these products or the costs associated with neutralization or disposal are not included in the cost curves for regenerable systems shown in Figures 24 and 27.

To obtain the total operating costs for the respective SO_2 removal systems, the costs for gas cooling and conditioning, shown in Figure 26, must be added to the costs given in Figures 27 and 28.

11.2.7 Cost of Sulphur Containment per Pound of Metal Recovered

In both copper and nickel concentrates, the ratio of sulphur to metal varies widely according to mineralization. For this reason, and because

TABLE 37 PRODUCTION COST OF SULPHUR FIXATION FROM ALL MAIN SMELTER GAS STREAMS (2)

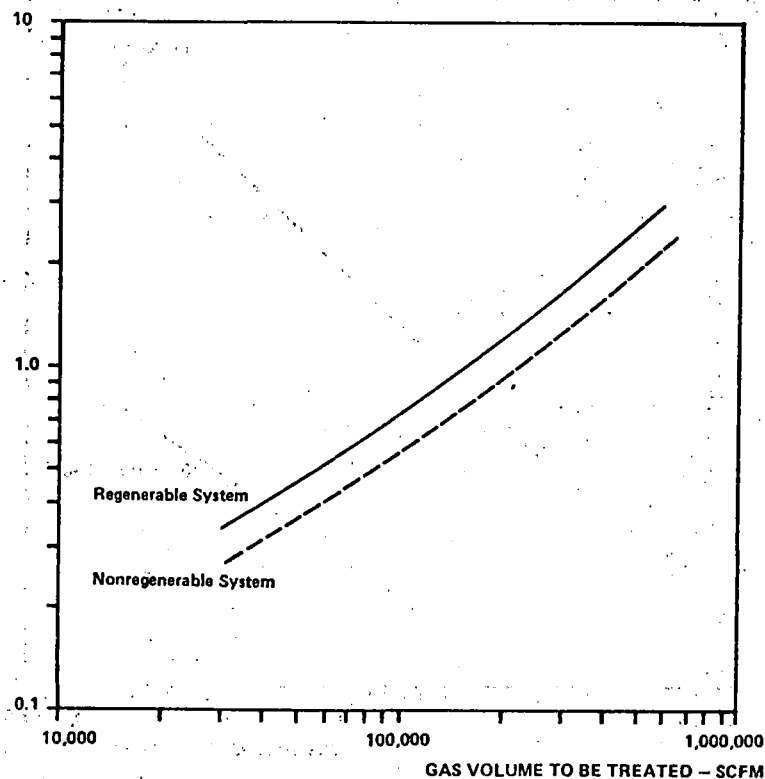
	\$/tonne Sulphur Fixed
<u>All Gases to Sulphuric Acid</u>	<u>Double Catalysis</u>
(1) 540 t/day H_2SO_4	77
(2) 1,100 t/day H_2SO_4	58
<u>Liquid SO_2 and Sulphuric Acid</u>	
(1) 160 t/day liquid SO_2	85 to 100
(2) 540 t/day H_2SO_4	99
Sulphur Recovery Cost Range	95 to 99
<u>Elemental Sulphur & Sulphuric Acid</u>	
(1) 270 t/day elemental sulphur	129
(2) 540 t/day H_2SO_4	99
Average Sulphur Recovery Cost	117

TABLE 38 PRODUCTION COST OF SULPHUR FIXATION WITH NEUTRALIZATION AND GYPSUM IMPOUNDING (2)

	\$/tonne Sulphur Fixed
	<u>Double Catalysis</u>
<u>All Gases to Sulphuric Acid & Acid Neutralization</u>	
(1) 540 t/day H_2SO_4	169
(2) 1,100 t/day H_2SO_4	144
<u>Liquid SO_2, Acid Production & Acid Neutralization</u>	
(1) 160 t/day SO_2 540 t/day H_2SO_4 to neutralization	158 to 163
<u>Elemental Sulphur, Acid Production & Acid Neutralization</u>	
(1) 270 t/day elemental sulphur 540 t/day H_2SO_4 to neutralization	155

Note: Liquid SO_2 and elemental sulphur are produced from high-grade continuous gas streams. Lower-grade variable converter gases are processed to sulphuric acid.

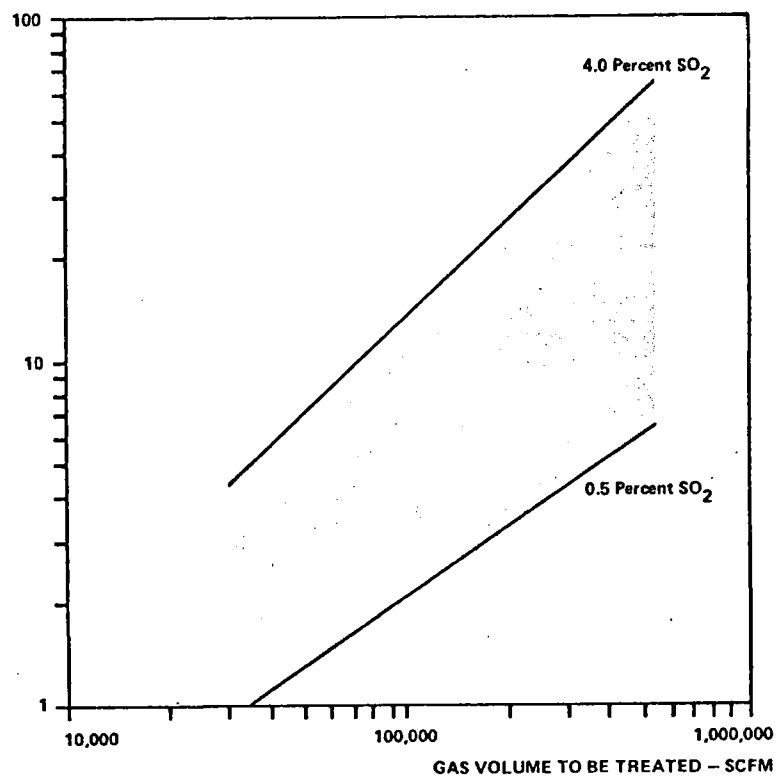
TOTAL OPERATING COST (Battery Limits)
(Millions of 1980 Dollars)



- 1) Regenerable systems include: Sodium Scrubbing (Wellman-Lord Process); Dimethylaniline (DMA)/Xylidine Process; and Sodium Citrate Process.
 2) Nonregenerable systems include: Lime and Limestone scrubbing; and Sodium Scrubbing (Double-Alkali Process).

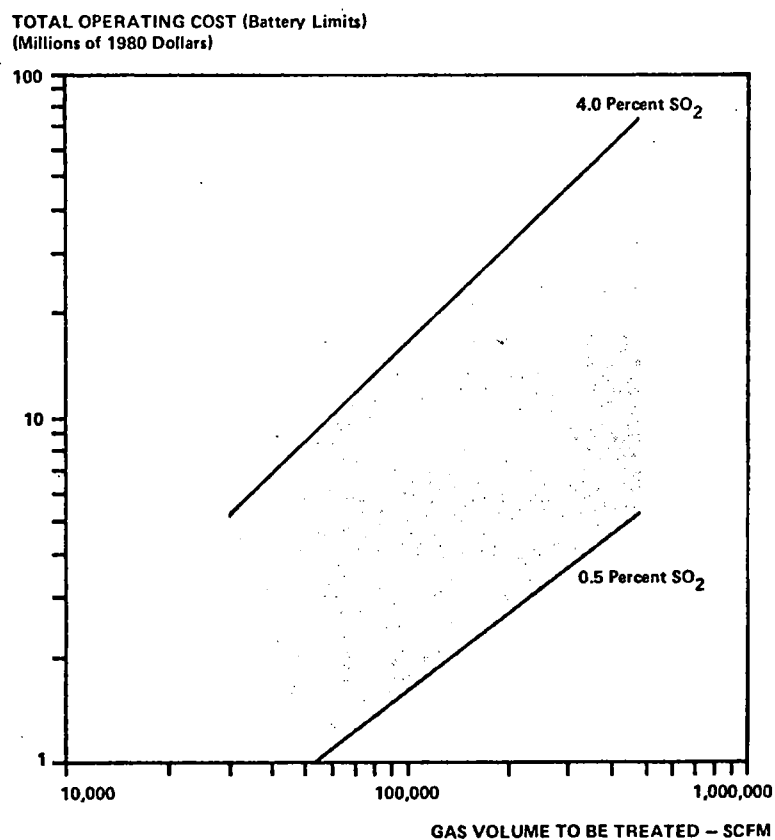
FIGURE 26 TOTAL OPERATING COSTS FOR SO₂ GAS COOLING AND CONDITIONING FOR BOTH REGENERABLE AND NONREGENERABLE (SCRUBBING) SYSTEMS (28)

TOTAL OPERATING COST (Battery Limits)
(Millions of 1980 Dollars)



NOTE: 1) Gas Cooling and Conditioning not included.
2) Regenerable systems include: Sodium Scrubbing (Wellman-Lord Process);
Dimethylaniline (DMA)/Xylidine Process; and Sodium Citrate Process.

FIGURE 27 TOTAL OPERATING COSTS FOR SO₂ REMOVAL USING
REGENERABLE SYSTEMS (28)



NOTE: 1) Gas Cooling and Conditioning not included.
2) Nonregenerable systems include: Lime and Limestone scrubbing; and Sodium Scrubbing (Double-Alkali Process).

FIGURE 28 TOTAL OPERATING COSTS FOR SO₂ REMOVAL USING NONREGENERABLE (SCRUBBING) SYSTEMS (28)

unit costs vary according to smelter location, the range in costs of sulphur containment per pound of metal recovered, both for copper and nickel concentrates, will be different and will vary widely. Other variables affecting production costs are the type of smelting and sulphur containment processes used.

Table 39 shows a typical range of order-of-magnitude costs (Canadian currency, mid-1979) for containing sulphur as sulphuric acid (both for single and double absorption plants) per pound of metal produced for various gas streams and levels of sulphur fixation (2). The costs are based on those given in previous tables for sulphuric acid production and neutralization and include amortization and direct operating costs. No allowance for credit from acid sales is included. A common basis of 360 tpd of sulphur in concentrates is assumed. The degree of sulphur fixation includes sulphur contained in slag and other solid products leaving the smelter as well as in the acid.

A tentative analysis (29) was made in 1978 to assess the pollution control costs incurred by the U.S. copper industry compared with similar costs incurred by overseas copper producers. Meaningful comparisons are difficult to make because of the wide variety of circumstances. In 1978 it was estimated that U.S. copper smelters incurred additional direct operating costs of some 4 U.S. c/lb Cu in attempting to meet the EPA SO₂ and particulate emission standards. This cost increases to 9 c/lb Cu when depreciation, interest charges and sundry overheads are included. These costs exceed those of any other major producing country. It was further reported that only 50% of western world copper producers, including the U.S.A. and Japan, incur atmospheric pollution control costs exceeding 4 c/lb Cu. All of these are major industrial nations of which only Canada and Germany export copper to the U.S.A. In contrast, 40% of western world copper producers incur no significant atmospheric pollution control costs. Canadian smelters were reported to be incurring total costs of 5 - 7 c/lb, smelters in European and other developed countries in the range of 2 - 4 c/lb, while most smelters in countries such as Chile, Peru, Zambia and Zaire, where minimal or no atmospheric pollution control measures are adopted, incurred costs in aggregate of less than 1 c/lb.

TABLE 39 PRODUCTION COST OF SULPHUR FIXATION PER POUND OF METAL PRODUCED,
COPPER AND NICKEL (2)

	Single Catalysis Acid Plant ¹						Double Catalysis ²	
	Continuous Gases only		Variable Gases only		Continuous & Variable Gases		Continuous & Variable Gases	
Sulphur fixation, %	50		45		95		97	
Production cost \$/tonne S	59		92		54		58	
Neutralization cost \$/tonne S	92		92		86		86	
Sulphur/Metal Ratio in Concentrate ³	Low	High	Low	High	Low	High	Low	High
Sulphur Fixation Costs								
Copper, ¢/lb Cu	1.07	2.14	1.50	3.01	1.86	3.73	2.05	4.10
Nickel, ¢/lb Ni	2.95	6.43	4.14	9.02	5.12	11.18	5.64	12.31
Neutralization - total cost of making acid and neutralizing it								
Copper, ¢/lb Cu	2.75	5.50	3.02	6.03	4.67	9.64	5.07	10.14
Nickel, ¢/lb Ni	7.57	16.51	8.29	18.09	13.25	28.91	13.94	30.42

1 Tail gas emission 1500 - 1700 ppm SO₂

2 Tail gas emission 500 - 650 ppm SO₂

3 Copper conc. 20 - 35% Cu, 26 - 33% S, S/Cu 0.8 - 1.6

Nickel conc. 6 - 12% Ni, 26 - 29%, S/Ni 2.2 - 4.8

It has recently been reported that it is costing the U.S. copper industry from 10 to 15 c/lb of copper to meet the current EPA SO₂ emission regulations (30).

Uncorroborated estimates (8) have been made (1977) of the costs of air and water pollution control at non-ferrous smelters in Japan. Based on operating costs for pollution control representing about 10% of the metal (Pb - Zn) sales price at one smelter and 10 to 20% of total costs at two others, the cost of pollution control at Japanese smelters was thought to represent from 10 to 20% of total production costs, including administration. At the same time, it was estimated that operating costs in the range 4 - 6 U.S. c/lb Cu were being incurred by Mitsubishi's Onahama smelter for the MgO system that concentrates SO₂ in the reverberatory furnace off-gas.

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