Volume 2-Chapter 4

SMELTING AND REFINING

Minnesota Environmental Quality Board
Regional Copper-Nickel Study
Authors: Michael J. Pojar*
Peter J. Kreisman

Prepared under the direction of:
David L. Veith
Peter J. Kreisman
Robert H. Poppe

*Please contact Peter J. Kreisman regarding questions or comments on this chapter of the report.

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A NOTE ABOUT UNITS

This report, which in total covers some 36 chapters in 5 volumes, is both international and interdisciplinary in scope. As a result, the problem of an appropriate and consistent choice of units of measure for use throughout the entire report proved insurmountable. Instead, most sections use the system of units judged most common in the science or profession under discussion. However, interdisciplinary tie-ins complicated this simple objective, and resulted in the use of a mix of units in many sections. A few specific comments will hopefully aid the reader in coping with the resulting melange (which is a reflection of the international multiplicity of measurement systems):

1) Where reasonable, an effort has been made to use the metric system (meters, kilograms, kilowatt-hours, etc.) of units which is widely used in the physical and biological sciences, and is slowly becoming accepted in the United States.

2) In several areas, notably engineering disucssions, the use of many English units (feet, pounds, BTU's, etc.) is retained in the belief that this will better serve most readers.

3) Notable among the units used to promote the metric system is the metric ton, which consists of 2205 pounds and is abbreviated as mt. The mertric ton (1000 kilograms) is roughly 10% larger (10.25%) than the common or short ton (st) of 2000 pounds. The metric ton is quite comparable to the long ton (2240 pounds) commonly used in the iron ore industry. (Strictly speaking, pounds and kilograms are totally different animals, but since this report is not concerned with mining in outer space away from the earth's surface, the distinction is purely academic and of no practical importance here).

4) The hectare is a unit of area in the metric system which will be encountered throughout this report. It represents the area of a square, 100 meters on a side (10000 m^2), and is roughly equivalent to 2½ acres (actually 2.4710 acres). Thus, one square mile, which consists of 640 acres, contains some 259 hectares.

The attached table includes conversion factors for some common units used in this report. Hopefully, with these aids and a bit of patience, the reader will succeed in mastering the transitions between measurement systems that a full reading of this report requires. Be comforted by the fact that measurements of time are the same in all systems, and that all economic units are expressed in terms of United States dollars, eliminating the need to convert from British Pounds, Rands, Yen, Kawachas, Rubles, and so forth!

Conversions for Common Metric Units Used in the Copper-Nickel Reports

1 meter = 3.28 feet = 1.094 yards

1 centimeter = 0.3937 inches

1 kilometer = 0.621 miles

1 hectare = 10,000 sq. meters = 2.471 acres

1 sq. meter = 10.764 sq. feet = 1.196 sq. yards

1 sq. kilometer = 100 hectares = 0.386 sq. miles

1 gram = 0.037 oz. (avoir.) = 0.0322 Troy oz.

1 kilogram = 2.205 pounds

1 metric ton = 1000 kilograms = 0.984 long tons = 1.1025 short tons

1 m^3 = 1.308 yd^3 = 35.315 ft^3

1 liter = 0.264 U.S. gallons

1 liter/minute = 0.264 U.S. gallons/minute = 0.00117 acre-feet/day

1 kilometer/hour = 0.621 miles/hour

degrees Celsius = (5/9)(degrees Fahrenheit -32)

Volume 2-Chapter 4 SMELTING AND REFINING

4.1 INTRODUCTION AND SUMMARY OF FINDINGS

The copper-nickel ores of northeastern Minnesota occur as sulfides. Preceding chapters of Volume 1 discussed various sulfide ore treatment processes which produce one or more concentrates enriched in the metals of economic interest, copper, nickel cobalt and precious metals. These enriched products are produced by mechanical concentration processes. Some type of treatment beyond this physical concentration is necessary in order to recover the copper and nickel in a metallic form which is usable in the manufacturing sector of the Minerals Industry. This treatment is provided by the smelting and refining operations.

Briefly, in the smelting phase the concentrate is melted and the liquid is moved through a series of steps which remove the bulk of the iron, silica, and sulfur in the concentrate, and separate the majority of the copper from the nickel to produce a blister or anode copper, and a nickel-copper matte. These two products then move to a refinery stage for purification. Here the smelting products are either dissolved in an aqueous solution and the metals recovered by chemical or electrolytic precipitation or purification occurs by direct transfer of the metal from the impure anode form through an electrolytic solution to the purified cathode. In this process, trace metallic impurities and remaining sulfur are removed. It is here that cobalt and the precious metals are also separated from the copper and nickel. The final outputs of copper, nickel cobalt, and precious metals are suitable for sale directly to manufacturers.

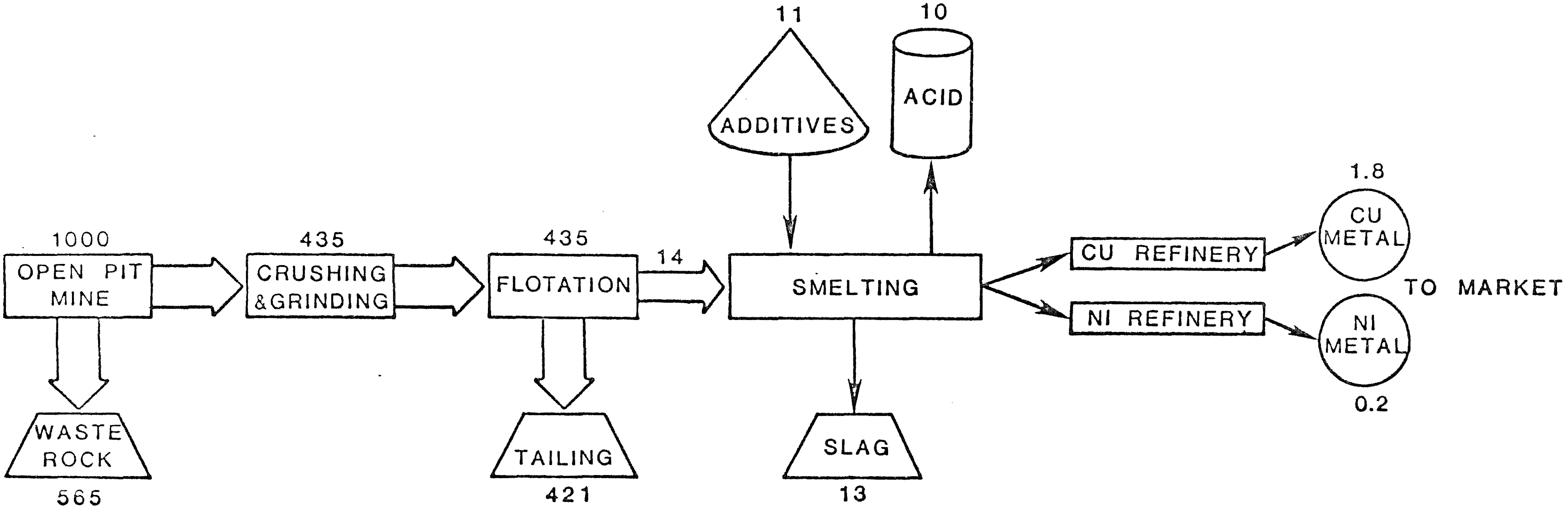
The nature of the concentrate as feed to a smelter will determine the type of metallurgy to be used and ultimately where the principal separation of the nickel from the copper will occur. If a bulk copper-nickel sulfide concentrate is produced as feed to the smelter (Figure 1), then separation of the nickel from the copper will most probably occur as a result of either: 1) treating the copper-nickel matte produced during smelting by some type of mineral processing technique (i.e. flotation); or 2) removing the nickel from the copper during converting following smelting. If selective or differential flotation is used as a means of producing a copper concentrate and a nickel-copper concentrate (Figure 2), then the major separation occurs prior to smelting and the copper concentrate is treated using conventional or standard pyrometallurgical techniques. The nickel-copper concentrate may be treated by a combination pyrometallurgical/hydrometallurgical scheme. Preliminary data indicates that the copper-nickel concentrate resulting from bulk flotation techniques will range from 10.3 to 22.3% Cu and 1.8 to 3.3% Ni. A model based on bench and pilot plant tests shows a concentrate that averages approximately 13.8% Cu and 2.65% Ni, indicating the expectation of a Cu/Ni ratio of approximately 6 or 7 to 1. The nickel-rich nickel-copper concentrate resulting from selective flotation techniques will range from 4 to 7% Cu and 4 to 6.5% Ni and might average 5.5% Cu and 5.25% Ni for a Cu/Ni ratio of approximately 1/1. Table 1 shows the typical range of analyses for Minnesota concentrates produced by the various concentrating techniques considered to date. See Volume 2-Chapter 3 on processing for a discussion of this.

Figures 1 & 2, Table 1

For copper and copper-nickel concentrates, the copper is considered to be the principal metal, and nickel, cobalt, and the precious metals are considered to be minor elements which will generally follow the copper through the system

FIGURE 1

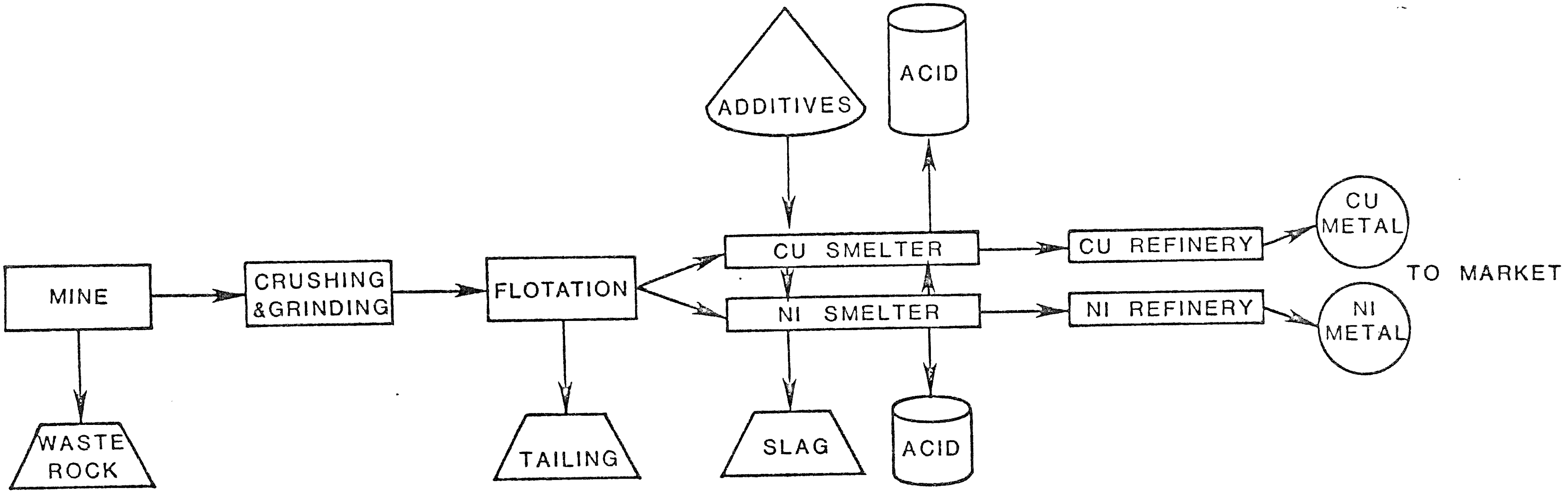
INTEGRATED MINNESOTA CU-NI OPERATION UTILIZING BULK FLOTATION PROCESS*



*THE NUMBERS MODEL THE FATE OF 1000 UNITS OF MATERIAL REMOVED FROM AN OPEN PIT MINE.

FIGURE 2

INTEGRATED MINNESOTA CU-NI OPERATION UTILIZING SELECTIVE FLOTATION PROCESS*



* NO SPECIFIC MATERIAL DISTRIBUTION HAS BEEN MODELED FOR THIS CASE.

Table 1. Minnesota Cu-Ni concentrate analyses.[a]

	BULK FLOTATION	SELECTIVE FLOTATION	
COMPONENT	Cu-Ni Concentrate	Ni-Cu Concentrate	Cu Concentrate
Cu	10-22%	3-8%	11-24%
Ni	3 -3%	2-10%	0.2-0.8%
Fe	21-42%	18-30%	36-42%
S	19-33%	9-20%	32-34%
CO	0.1-0.2%	0.1-0.4%	0.04-0.05%
Si_2	3-23%	b	b
Al_2O_3	1-7%	b	b
CaO	1-3%	b	b

[a] Percent composition by weight (see Vol. 3-Chap. 3 for further discussion).

[b] No data is available for selective flotation. It is estimated that these values are in the same range as the bulk Cu-Ni concentrates.

until a specific separation of elements is made. For nickel and nickel-copper concentrates, the nickel is now considered to be the principal metal, and copper joins the other metals being considered as minor elements which will now generally follow the nickel through the system until a specific separation is made. Those metals or elements which are considered to be minor or trace elements will tend to complicate whatever metallurgy is chosen to selectively recover the principal metal or element in the concentrate feed.

Regardless of the type of concentrate produced, some type of pyrometallurgical treatment will likely be used prior to final separation of the principal elements. This is due to the fact that pyrometallurgy is in a more advanced stage of development than its counterpart, hydrometallurgy. As a consequence, the various principles involved are reasonably well-proven on a production scale, and more likely to be viewed favorably by a company responsible for safeguarding an investment of hundreds of millions of dollars. This, then, means that the principal elements will be smelted by injecting concentrate, flux, fuel, and possibly oxygen into a smelting furnace to form a matte composed of simple sulfides, an iron-siliceous slag which is either directly discarded or treated for removal of excess metals and then discarded, and a gas stream which will be treated for removal of SO_2, particulates, and heat prior to release to the atmosphere.

Table 2 shows the typical range of analyses by elements and compounds for mattes and slags resulting from a smelting operation. The table also indicates the probable chemistry of the major constituents for both matte and slag. Several complex reactions take place spontaneously and simultaneously during major smelting operations which makes predictions concerning the chemistry of constituents (i.e. the exact chemical formulas of the compounds which make up the matte and slag) difficult, if not impossible. The sulfur is eliminated principally as sulfur dioxide gas (SO_2).

Table 2

A special comment is in order here concerning sulfur emissions from a smelter, since this problem is uppermost in the minds of many when mention is made of the possibility of the development of a smelting industry in Minnesota. It is true that the non-ferrous minerals smelting industry is a major national source of anthropogenic air pollutants. The major pollutant emitted by this industry to receive regulatory scrutiny since the enactment of federal and state clean air legislation is sulfur dioxide. Sulfur dioxide is produced in pyrometallurgical smelting operations by the burning or oxidation of sulfides originating in the concentrate feed. Figure 3 is an example of the complex distribution of this sulfur among the various smelter outputs. The particular values shown here represent a facility utilizing the best state-of-the-art control technology, which is discussed later in this chapter. As previously mentioned, a Minnesota Cu-Ni concentrate can contain between 19% and 33% S. If uncontrolled, this would result in the discharge of between 240 and 420 x 10^3 mt of SO_2 each year from a large smelter (100,000 mtpy total metal production).

Figure 3

Such uncontrolled operations were standard practice in the U.S. and are still operated today in many developing and developed nations having large base metals smelting industries. However, since the enactment of clean air laws in the United States, Japan and other countries, considerable advancement has been made in the control and treatment of air pollutants, specifically SO_2. Sulfur

Table 2. Range of matte and slag analyses (weight %).

	TYPICAL COPPER INDUSTRY VALUES		PROBABLE MINNESOTA CU-NI VALUES		
COMPONENT	Smelter Matte	Discard Slag	Smelter Matte	Converter Ni-Cu Matte	Discard Slag
Cu	30-60%	0-1%	45-47%	45-47%	0.1-0.3%
Ni	1-3	0-0	7-10	38-40	0.05-0.2
Fe(as FeO, Fe_3O_4)	20-40	30-45	18-22	0.3-0.5	30-70
S	20-30	0-2	22-27	10-13	0.4-0.7
SiO_2	0-1	30-40	-	-	32-35
Al_2O_3	0-1	0-10	-	-	4-6
CaO	0-1	0-10	-	-	4-6
Cu_2S	37-75	0-1	52-55	52-55	0.1-0.4
Ni_3S_2	1-4	0-1	10-14	49-52	0.07-0.3
FeS	20-40	0-1			
Fe_3O_4	2-10	6-15	25-31	0.4-0.7	42-52
FeO	8-9	33-43			
SiO_2	0-1	30-40	-	-	32-35
Al_2O_3	0-1	0-10	-	-	4-6
CaO	0-1	0-10	-	-	4-6

Probable Chemistry of the Major Constituents Which Make Up the Matte:

Cu_2S, Cu_2O, Cu
Ni_3S_2, NiO
FeS
Fe_3O_4
FeO

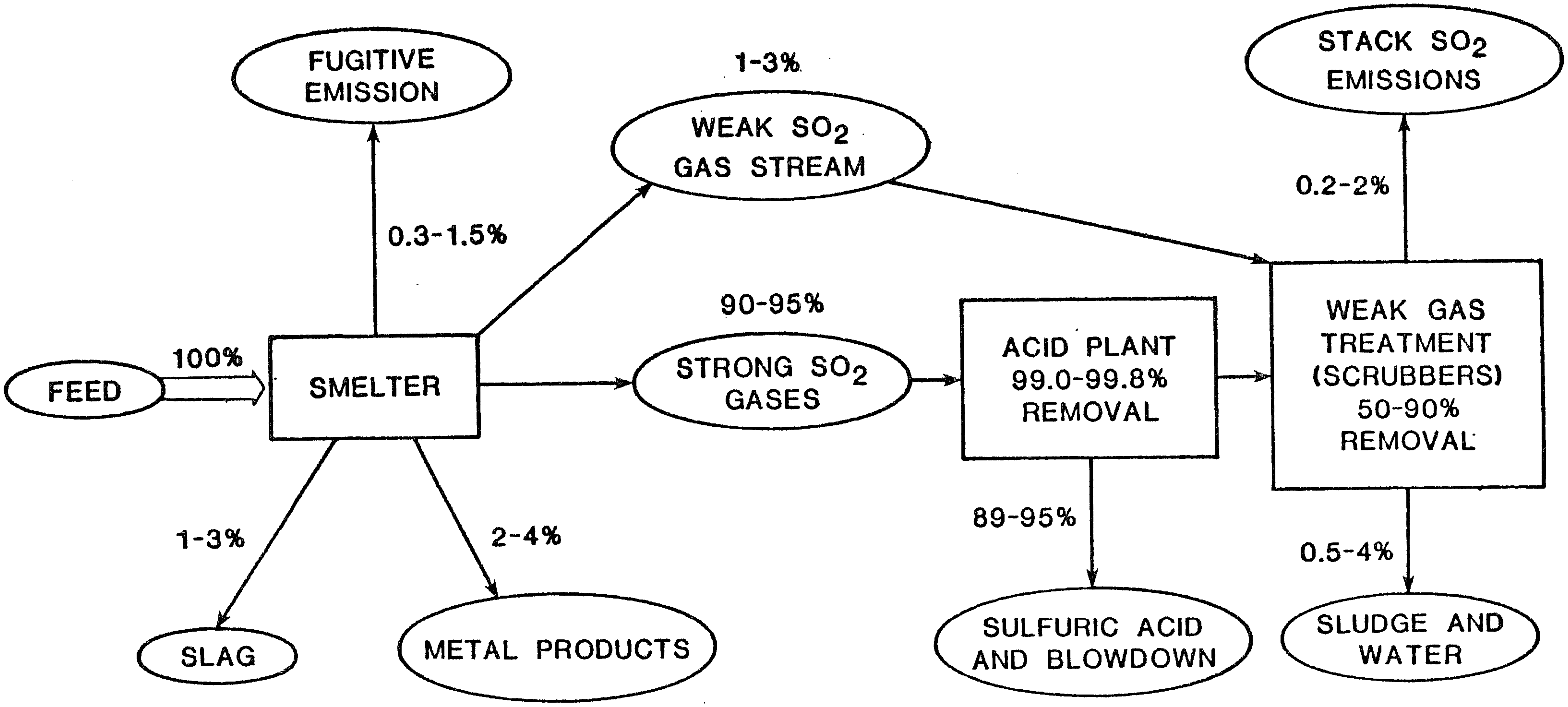
Probable Chemistry of the Major Constituents Which Make Up the Slag:

$3CaO\ Al_2O_3\ 2SiO_2$
$2FeO\ SiO_2$
Cu_2O, Cu
NiO
Fe_3O_4
FeO

FIGURE 3

SULFUR DISTRIBUTION* RANGE FOR A FLASH SMELTER WITH SECONDARY HOODING AND WEAK GAS TREATMENT

* SULFUR LOSSES VIA STACK AND FUGITIVE PARTICULATES ARE NEGLECTED SINCE THEY SHOULD BE ON THE ORDER OF, OR LESS THAN 0.5% OF INPUT SULFUR. NORMAL OPERATING CONDITIONS ARE ASSUMED.



dioxide pollution control development and application is most advanced in Japan and has concentrated on three factors.

1) Increasing SO_2 off-gas concentrations by reducing infiltration of dilution air and by reducing the content of gases such as nitrogen and hydrocarbons in combustion air.

2) Increasing the efficiency of gas collection devices to reduce fugitive SO_2 losses.

3) Improving the performance of high concentration and low concentration SO_2 treatment systems, especially those which produce a marketable byproduct.

The result of these developments and future advances will enable a modern smelter to control from 95 to 99+% of potential SO_2 air pollution emissions under normal operating conditions. In other words, instead of between 230 and 400×10^3 mtpy of SO_2 emission, the emissions would be significantly reduced down to between 1 and 20×10^3 mtpy.

Mention must also be made of the lack of good information available on fugitive dust control and the efficiency of such efforts. Fugitives leak out from wherever there is a weak point in the gas and/or dust collection systems. They are minor when compared to the amounts collect in modern smelter applications, but they are nontheless important and represent a major health hazard potential. As will be pointed out later in this chapter, efforts are being made to monitor and control fugitive emissions to a much greater degree than has been the rule in existing smelter/refinery operations.

Returning to consideration of the metals of principal economic interest, the main route of copper and other metal losses from smelters is through the slags which are discarded from one or two of the following units:

1) a smelting furnace

2) an electric settling furnace, in which smelting furnace (particularly flash furnace) slags and/or converter slags have been settled to recover their copper

3) a slag flotation plant in which most of the copper has been recovered by flotation from solidified, finely ground converter slag

The copper concentration in discarded slags typically varies from 0.2 to 1% depending upon the particular type of operation and initial chemistry of the concentrate.

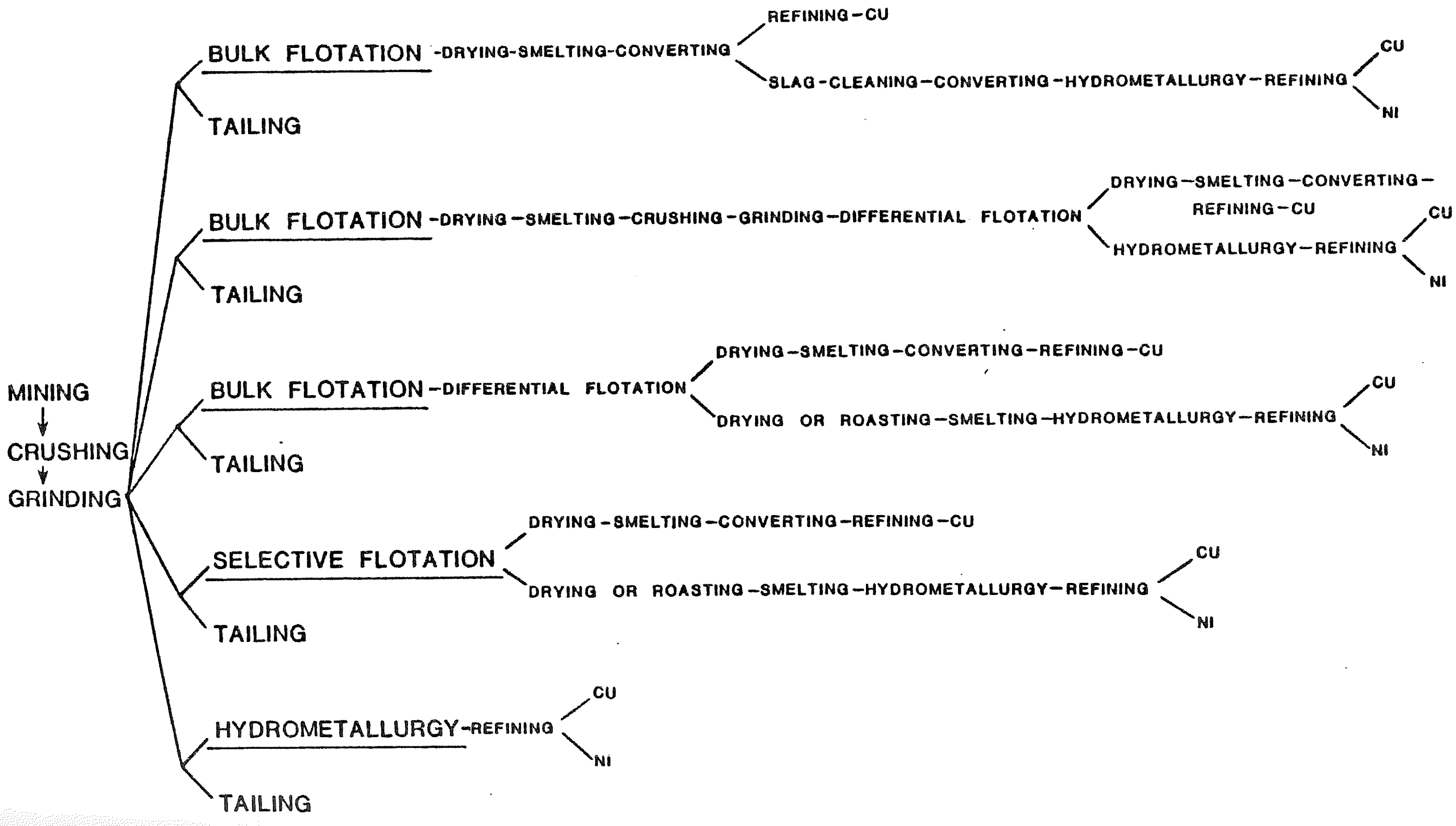
Figure 4 illustrates in generalized form the potential pyrometallurgical and/or hydrometallurgical process flowsheets which could be applicable to the treatment of Minnesota ores. The figure includes systems currently being developed as well as established systems.

Figure 4

As Figure 4 indicates, after the ore is mined, crushed, and ground to the proper size, a number of alternative processes may follow which, depending upon the chemistry of the concentrate coming from the milling or processing operation, will consequently recover the copper, nickel, and other byproducts. A bulk flotation concentrate may be further treated by various techniques which are either purely pyrometallurgical, purely hydrometallurgical, or most pro-

FIGURE 4

GENERALIZED FLOWSHEET SHOWING SOME OF THE POTENTIAL PROCESSES FOR THE TREATMENT OF DULUTH GABBRO ORES AND CONCENTRATES



bably, a combination pyro-hydro-metallurgical operation. Differentially prepared concentrates offer the metallurgist still additional process options.

Currently, sulfides are not principally treated by hydrometallurgical methods since they are not easily leached. Consequently, the vast majority of the extraction is by pyrometallurgical techniques starting with copper, copper-nickel, nickel-copper, or nickel concentrates.

More specifically, it is highly unlikely that copper-nickel sulfide ores will be mined, ground, and treated directly by a wet process technique (leaching) which usually involves the dissolution of a particular component, and its subsequent recovery from the solution. Further, it is highly unlikely that copper-nickel concentrates will be directly processed via a hydrometallurgical technique. The probability of selectively dissolving valuable elements directly from ores or concentrates after suitable comminution and/or flotation to expose the valuable minerals by aqueous and chemical (i.e. water, sulfuric acid, hydrochloric acid, etc.) attack is small. On the other hand, hydrometallurgical attack subsequent to major pyrometallurgical treatment is seen as a likely means of treating intermediate smelting products before final treatment in a refinery.

As pointed out in the nickel refinery discussions of this chapter, hard data on this topic is very difficult to obtain-particularly that which can be applied to Minnesota Cu-Ni resource treatment. Much of the reported data was adjusted based on certain assumptions. These assumptions, the rational employed, and the assumed acuracies are all stated in the text.

Land requirements for an on-site smelter/refinery complex for modeling purposes are estimated to be 175 acres with an additional 70 acres as nearby undisturbed watershed, which has access limited due to the presence of the smelter/refnery, but is not used otherwise. Factors affecting these requirements are the production capacity, equipment selection, the extent to which the metals are refined on site, and the degree of emission control incorporated into the facility.

Siting flexibility is much greater for a smelter/refinery complex than for a processing facility as the unit value of the material being treated by the smelter (concentrate) is much greater than for the processing plant (ore). Remote location from the mine and processing however, does add cost to the overall system (see Chapter 5) due to additional transportation needs, and due to additional facility needs since formerly shared facilities, such as electrical substations, security fences and staff support facilities, now need to be installed at both sites.

Natural gas and electricity are the main forms of energy used in the non-ferrous metals industry today. In the Study models the energy requirements were derived from a variety of sources and with certain assumptions due to lack of sufficient data. However, the model value of 4.1×10^4 BTU/lb of metal produced appears within reason when compared to published industrial information. In summary, the energy requirements for a flash smelter/refinery installation producing 100,000 mtpy of copper-nickel metal from concentrate produced by the model processing facilities, are as follows:

	ENERGY CONSUMPTION, 10^9 BTU/yr				
	Smelter	Cu Refinery	Ni Refinery	Total	Distribution By Fuel Type, %
Natural Gas			222	222	2
Coal	1060			1060	12
LPG			92	92	1
Miscellaneous thermal		331	1300	1631	18

Electricity	4053	567	1470	6090	67
Total	5113	898	3084	9095	100
Distrib. by operation, %	56	10	34	100	

The model indicates that all forms of fossil fuel are likely to be imported to the site of the smelter/refinery is located in Minnesota. Electricity would likely be purchased from local public utilities; however, if a sufficient supply (580 X 10^6 ku H/yr with a peak load requirement of about 83 mw) is not available, either the supply from the public utilities must be expanded or private industry must consider building its own facilities.

Smelter/refinery operations require <u>water</u> in the two basic areas of process or contact water and cooling or non-contact water. Process water is subject to contamination (both quality and thermal) due to contact with products throughout the complex. Non contact cooling water, however is subject only to thermal impact and minor concentration changes of naturally occurring constituents due to evaporation in subsequent cooling treatment.

Two systems are modeled to illustrate extremes for smelter/refinery water treatment facilities: The once-through system where only fresh water is introduced and no internal recycle is practiced; and the maximum reuse system which fully utilizes cooling towers and ponds and internal recycling. In either case some discharge is necessary to prevent undesired buildup of chemicals.

In summary the models indicate that for a smelter/refinery complex producing 100,000 mtpy of metal, between 0.2 and 0.6 X 10^9 gpy of water will be consumed and must be replaced with fresh water if a water treatment plant is utilized to treat discharge waters to a quality suitable for reuse. If no such water treatment is available, 1.7 to 24.7 X 10^9 gpy of fresh water is required.

Modeled operative manpower requirements for an on site smelter/refinery complex are expected to total 621, with a possible range of 580 to 785 workers. Manpower will be split into administrative (20%) and hourly (80%); with 35% to the smelter, 15% to the copper refinery, and 50% to the nickel refinery.

Offsite operations necessarily require repeating some facilities already provided in the mining and processing which would normally be shared by the smelting/refining operation. Such offsite considerations would then require a 4 to 5% increase in the total number of employees to man the duplicated facilities.

Relatively small amounts of pollutants are generated by a modern smelter under normal operating conditions. However, under upset conditions (including start-up, shutdown, and equipment failure) major quantities of pollutants can be generated, indeed, major from the standpoint of both quantity and quality, based on allowable emissions for such a facility.

Unfortunately, operating data is not available to accurately predict either the frequency of upsets or the impact of such occurrencs in a modern smelter/refinery complex. Other than catastropic failure which is the least likely but potentially most serious upset, breadkown of the sulfuric acid plant would result in the greatest environmental hazard due to the high concentrations of both SO_2 and votabile elements in the process gases. Proper design can minimize these potentially hazardous occurances as can efficient operation and a regular schedule of preventative maintenance.

It is clear that of the elements of concern, sulfur is likely to be emitted in the largest quantities and in the form of SO_2. Other emission possibilities include metallic dust and vapors, particularly Cu and Ni. From the standpoint of employee safety as well as the controlling of accidental discharges to the environment each individual facility in the smelting/refining complex must be examined in detail and all possible safegards installed to prevent such occurances.

In short, all major and minor smelter/refinery upsets must be anticipated so that they may be handled in the most environmentally sound manner, from the drawing boards to actual execution, to provide the best possible work environment and the least possible pollution potential to the ambient environment of northern Minnesota.

General predictions were made of the distribution of all major and minor elements in the smelting/refining process of Minnesota copper-nickel concentrate based on all available data. Input data for the concentration of elements present in the system generally resulted from detailed mineralogic studies of laboratory and pilot plant concentrates produced at the University of Minnesota's MRRC.

Impurities in the concentrate are eliminated in the smelting process either by volatilization or by slagging, the paths of major constituents were well defined, but the paths of minor or <u>trace elements</u> elude definite analytical prediction and could only be estimated based on other smelter performance information and educated guesses by experts in the field.

A study of the movement of the trace elements was conducted and the result was a list of all trace metals in either Priority 1 or Priority 2 categories, depending on their potential impacts on the environment. Priority 1 trace elements are those of concern due to their high toxicity or which may be present in sufficient quantity to pose potential pollution implications; Priority 2 elements are those of traditional concern which do not appear to be present in sufficient quantity to be placed in the Priority 1 category. The major basis for this categorization were the quantity of the element present in the concentrate, the toxicity of the element, and the likelihood of release of the element into the environment.

Priority 1 elements of concern are:

Arsenic-Although a serious health hazard and a difficult control problem in most U.S. smelters, only minor amounts (31 ppm) exists in the projected smelter feed material and for this reason arsenic is not expected to be of major concern.

Cadmium-Also a toxic material and a serious environmental threat, cadmium levels (40 ppm) in anticipated smelter feed material are minor and not expected to pose a problem.

Cobalt-As a major constituent (0.1%) of the anticipated smelter feed material, cobalt will be a recoverable by-product of the smelter/refinery system. Although almost as toxic as cadmium, cobalt emission levels are expected to be below the threshold of concern.

Copper-A major component (13.8%) of the smelter feed, copper in the fumes, dust and acidic wastewaer poses a ptoential environmental threat. It is less toxic than either cobalt or cadmium but more toxic than arsenic.

Nickel-Another major component (2.6%) in the smelter feed materia, nickel in the dust, fume and wastewater products is about as toxic as copper. However, if present in the carbonyl form, $Ni(CO)_4$, nickel is extremely toxic.

Of the above mentioned Priority 1 elements nickel and copper appear to pose the greates actual threat based on the data available. All other elements including the Priority 2 elements listed later in this chapter are not considered significant based on the current understanding of toxicity levels and elemental levels in the smelter feed material. If either of these levels change, or if technological adjustments change elemental levels, further evaluation will be necessary.

Solid wastes resulting from any smelting/refining operation consist primarily of a discard slag and a variety of sludges, as described in sectio 4.8 of this chapter. These products are relatively predictable, depending on the equipment selection, and must be either recycled to the system or discarded in an appropriate and safe manner.

Slag is the principal solid waste product of smelting operation, and is produced regardless of smelter loction in a fairly predictable amount and quality, depending on the smelter feed and on the selected process. An operation producing 100,000 mtpy metal from Minnesota Cu-Ni concentrates would produce between 0.55 and 0.65 X 10^6 mtpy of slag containing 30-45% Fe and 30-40% SiO_2 combined in solid solution and therefore relatively inert from the weathering viewpoint.

Typically slag is open dumped on piles near the smelter in either a hot liquid form or granulated from (achieved by quenching with water). Dump areas resulting from 25 to 30 years operation at the production rate of 100,000 mtpy metal would occupy roughly 25 acres in a pile 200 to 300 ft high.

Sludges generated in a typical smelting/refining operation result from SO_2 removal procedures such as gas scrubbing with chemical solutions and consist mainly of sulfates of Ca, Mg and Na. These products are water soluble, and unless totally recycled to the smelter may cause problems in a permanent disposal situation. Additionally trace amounts of potentially hazardous constituents are found in sludge materials. These residuals may include hearing metals such as As, Cd, Pb, Zn, Ca, Cr, Sb, Ni and Hg.

A 100,000 mtpy smelter/refinery might generate 24,000 to 36,000mtpy of SO_2 removal wastes which in a fully integrated operation, could be directed to the processing tailing basin (along with 300-800 times as much processing tailing material) and be lost in the system. Normally though, a significant portion of the sludge would be separated out at the site and immediately returned to the smelter for use as a flux thus reducing futher the minor amount to be directed to the tailing basin.

If not combined with the processing tailing, sludges resulting from a 100,000 mtpy operation can be settled in a lagoon of 7 to 17 acres in size, with the settled solids periodically dredged, chemically fixed to prevent leaching and disposed of in land-fill disposal sites.

4.2 SMELTING PRINCIPLES

Pyrometallurgy traditionally involves three sequential operations, drying or roasting, smelting, and converting. Each step performs a specific function.

4.2.1 Drying

Concentrates as produced by the mill generally have a 10-15% moisture content if filtered, or 35-50% if thickened, which is too high to be successfully smelted using present-day pyrometallurgical processes. The principal purpose of dryers, then, is to dry the furnace charge and simultaneously heat it to 200-500°C prior to smelting. Water is removed to a level which will allow further treatment, typically 0-0.2% moisture content for flash furnaces.

4.2.2 Roasting

Where concentrates are excessively rich in sulfur content, in excess of 30%, the drying stage is replaced by a roasting stage. In roasting, the concentrate is dried and heated (500-700°C) until the sulfur begins to combine with oxygen to form sulfur dioxide gas, which is removed in a gaseous stream usually containing 2-16% SO_2 by volume. In this way the sulfur content of the concentrate is lowered to a level of 25-30%, adequate for smelting. The roaster product is known as calcine.

4.2.3 Smelting

Concentrate drying or roasting is followed by smelting in which dried concentrate is subjected to intense heat. It melts, forming a liquid sulfide, or matte, phase containing the bulk of the copper, nickel, cobalt, and precious metals, and a liquid slag phase, containing the bulk of the iron and silica. The actual chemistry of the smelting reaction is quite complex, and depends on many variables including the concentration and initial chemistries of all the feed materials, including any air or other gas streams present. The matte contains the copper and nickel, probably principally in the form of Cu_2S and Ni_3S_2, along with residual iron, principally as FeS. As much of the iron, as well as excess sulfur, are removed during smelting as possible without causing excessive copper and nickel losses to the slag. The iron leaves in the slag principally as silicate complexes such as $2FeO\ SiO_2$, in combination with the silica added for this purpose. Lime and alumina in the flux result in the formation of silicate complexes such as $3CaO\ Al_2O_3\ 2SiO_2$ which improves the immiscibility properties of the slag and matte phases. Excess sulfur is oxidized and evolves as SO_2 gas. Smelting is generally accomplished by melting the entire furnace charge at approximately 1100 to 1300°C, usually with a lime and silica flux. The silica, alumina, iron oxides, lime, and other minor oxides form molten slag, while the copper, nickel, sulfur, unoxidized iron, and precious metals form the matte. The slag is lighter than, and almost immiscible with the matte. It thus floats in a layer above the matte and is easily tapped off separately.

The affinities that particular compounds or elements have for each other in a mixture are related to their concentrations in the original mixture. Iron as a sulfide demonstrates the greatest affinity for oxygen. However, as the oxygen combines with the iron to form an oxide compound (slag), thereby decreasing the iron sulfide concentration in the remaining melt, the affinities of the other metallic sulfides, such as cobalt, nickel, and copper sulfide, for available oxygen now become more important. That is, cobalt, nickel and copper sulfides begin to react more strongly, and in the order listed, to form their respective oxides. The separation of metals or elements, consequently is never complete in such a 2-phase, matte-slag system, simply because the various affinities and reactivities of one element for another are constantly changing as reactions proceed.

An important objective of matte smelting is to produce a discardable slag which is as low as possible in copper and nickel content. This is accomplished by keeping the slag near silica saturation, which is 35-40% silica in the FeO-Fe_2O_3-SiO_2 system, to promote matte-slag immiscibility. The objective is also furthered by keeping the furnace sufficiently hot so that the slag is molten and fluid, and by avoiding excessively oxidizing conditions caused by an oxidizing flame or an overoxidized calcine. This last is necessary to minimize the formation, in the presence of excess oxygen, of solid magnetite, Fe_3O_4, which creates viscous conditions and consequently hinders the separation of matte from slag. Table 2, given earlier, shows the typical range of analyses for mattes and slags produced from smelting operations.

In the treatment of concentrates where nickel is found in appreciable quantities, such as in the copper-nickel concentrates produced from Minnesota copper-nickel ores, the matte produced as a result of smelting must be further treated to separate that excess nickel which has followed the path of copper. The majority of the nickel present must be removed before a traditional blister copper is formed and subsequently treated in a copper refinery. One technique used to affect the separation of the nickel from the copper is a modified converting process (refer to section 4.2.4 on converting) where selective fluxing, blowing, slagging, and skimming produce a blister copper and a converter nickel-copper matte (column 4 of Table 2).

The principal reactions which take place during smelting may be explained in terms of the differences in the thermodynamic properties of the metallic compounds. Thermodynamics provides the basis for predicting whether a reaction will take place or not. The speed with which a reaction takes place is a consequence of its chemical kinetics. At elevated temperatures most thermodynamically possible reactions take place and will occur as rapidly as the reactants are brought into intimate contact with each other (Boldt 1967).

Figure 5 illustrates in graphical form the relative affinities that the metals copper, nickel, iron, and cobalt have for sulfur and oxygen. At smelting temperatures iron sulfide is thermodynamically only slightly more stable, or less likely to decompose into its constituent elements, than is nickel sulfide. Nickel and cobalt sulfides, on the other hand, have nearly equal stabilities, while the stability of copper sulfide is considerably greater than that of iron sulfide. Generally speaking, all the sulfides of the above mentioned metals are in the same stability range (Boldt 1967).

Figure 5

In the presence of oxygen, each of the above sulfides is unstable with respect to its corresponding oxide. Iron has the greatest affinity for oxygen, followed successively by cobalt, nickel, and copper. This thermodynamic relationship between sulfides and oxides provides one key to separating the iron from the nickel, copper, and, to a lesser extent, cobalt values. If a mixture of the sulfides of the four metals is brought to equilibrium with a supply of oxygen insufficient to completely oxidize the mixture, the available oxygen will combine preferentially with the metals in the order of their oxygen affinities (Boldt 1967).

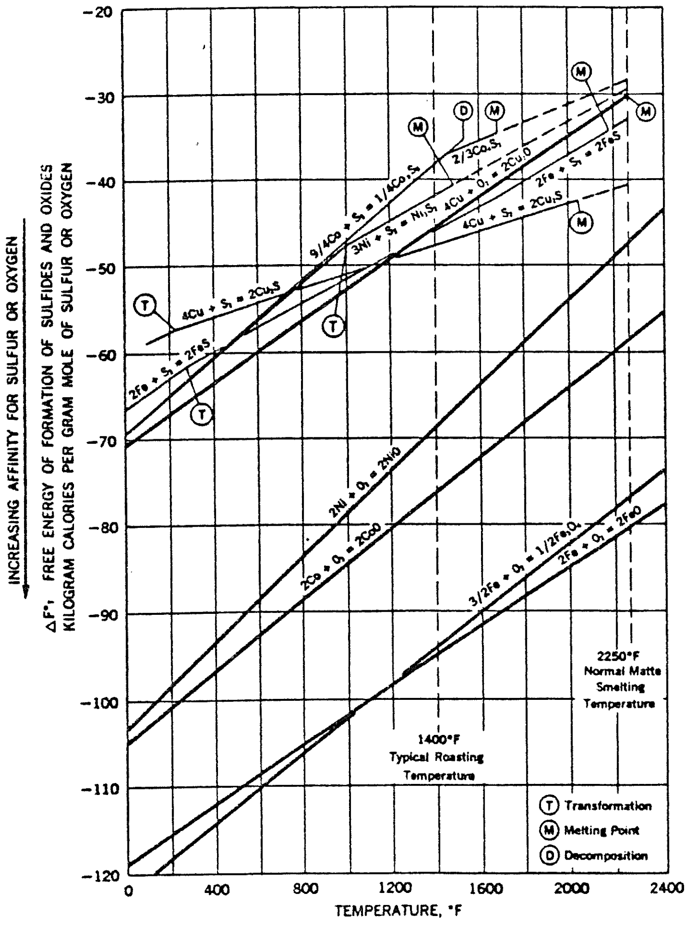
The addition of silica to the smelter feed promotes the formation of separate matte and slag phases. Silica is added both directly and in the form of recycled converter slag to achieve these conditions. Lime and alumina are also added since they tend to stabilize the slag structure and are beneficial in concentrations up to 10% in the slag. This mixture of metal sulfides, iron oxide, gangue, and siliceous flux are melted together in the smelting furnace.

As an example, for an operation producing 100,000 mtpy of metal, where 600,000-700,000 mtpy of bulk copper-nickel concentrate is required as feed, between 125,000-175,000 mtpy of silica and lime are needed as flux. This represents approximately 20-30% of the input feed by weight.

FIGURE 5

DIAGRAM SHOWING THE EFFECT OF TEMPERATURE ON THE SULFER AND OXYGEN AFFINITIES OF THE PRINCIPAL METALS ENCOUNTERED IN SMELTING

(SOURCE: BOLDT, 1967)



Oxide Reactions:

$2Fe + O_2 = 2FeO$

$3/2Fe + O_2 = 1/2\ Fe_3O_4$

$2Co + O_2 = 2CoO$

$2Ni + O_2 = 2NiO$

$4Cu + O_2 = 2Cu_2O$

Sulfide Reactions:

$4Cu + S_2 = 2Cu_2S$

$2Fe + S_2 = 2FeS$

$3Ni + S_2 = Ni_3S_2$

$9/4Co + S_2 = 1/4Co_9S_8$

$= 2/3Co_4S_3$

The iron oxide, concentrate gangue, and silica flux immediately begin to form a floating layer of slag which is normally discarded, leaving the matte as a homogenous solution of copper, nickel, cobalt, iron, and sulfur, with small amounts of other base elements, precious metals, and oxygen.

There is no distinct trend for copper losses into slags produced from various types of smelting processes. The blast, reverberatory, and electric furnace process slags are often discarded directly from the smelting furnace without further treatment. These slags generally range from 0.2-0.6% Cu and typically average 0.4% Cu. The two most important factors which determine the amount of copper lost are (Biswas 1976):

1) matte grade
2) the quantity of slag discarded per unit of copper produced

Flash furnace slags contain as much as 1% Cu, most of which is in the form of unsettled droplets of matte. These slags are usually transferred to small electric furnaces where they are allowed to settle under quiescent reducing conditions. A small amount of concentrate may be added to the furnace to aid in slag cleaning.

Slag cleaning by processing, using crushing, grinding, and flotation, has been used to treat converter slags in flash smelters for a number of years. More recently, milling has also been used to clean the slag from the Noranda Continuous Process and flash smelting furnaces as an alternative to electric furnace cleaning.

Although all smelter practices are based upon the same thermochemical principles, each has significantly different energy consumption patterns. Several variables are involved which make it difficult to develop energy tabulations even for a single smelting process that could be described as typical or ideal (Kellogg 1976a). Table 3 indicates the order and arrangement of the various smelting furnaces in terms of energy required to treat a unit amount of concentrate, both with and without the energy required for acid plant treatment of SO_2-laden gases.

Table 3

The essential features of a smelting furnace are that heat is supplied by combustion of a fuel (in certain cases the sulfides in the concentrate themselves) and that the flame and combustion products pass directly over and are in direct contact with the material being heated. That is, one chamber serves both as combustion chamber and as working chamber.

The combustion system is essentially a steady state system with two entering streams, fuel and air, and one product stream, flue gas.

The maximum temperature theoretically attainable in burning a fuel-air mixture under given conditions is the temperature of the products of combustion when the combustion is carried out adiabatically. An adiabatic process is one in which the system neither loses heat to, nor gains heat from the surroundings. The adiabatic flame temperature is a theoretical maximum which is normally not attained in actual flames. Actual flame temperatures are generally in the range from 48-75% of the calculated adiabatic flame temperatures. At ordinary metallurgical furnace temperatures, up to 1600°C, combustion reactions such as

$$CO + 1/2O_2 = CO_2$$

and

$$H_2 + 1/2O_2 = H_2O$$

Table 3. Energy use by smelting furnace type (in order of increasing energy required per metric ton of metal produced, 10^6KCAL/mt metal).

	ENERGY USE WITHOUT ACID PLANT TREATMENT		ENERGY USE WITH ACID PLANT TREATMENT		
FURNACE TYPE	Range of Energy Required	Typical Value	Range of Energy Required	Typical Value	Acid Plant Energy (% of total)
INCO	2.4- 2.1	1.8	0.4- 2.8	2.8	36
Mitsubishi	3.1- 3.5	3.3	3.9- 7.5	5.7	42
Noranda	2.3- 6.4	4.1	4.3- 8.1	6.2	35
Outokumpu	3.4- 5.9	4.2	5.1-11.9	7.9	47
Reverberatory	4.0-12.6	7.0	5.1-19.4	9.9	30
Electric	4.9- 9.1	7.2	5.1-28.6	15.4	54

go substantially to completion when the reactants are well mixed in appropriate quantities. At very high temperatures, however, chemical equilibrium is reached with appreciable quantities of carbon monoxide and oxygen or hydrogen and oxygen remaining unreacted. The dissociation reactions are the reverse of the combustion reactions, absorbing rather than evolving heat, and therefore lowering the adiabatic flame temperature. Corrections for dissociation become appreciable at approximately 1600°C and large at temperatures above 2200°C.

A second reason for the fact that actual flame temperatures are below calculated adiabatic temperatures is that actual flames are not adiabatic. Rapid though the combustion may be under favorable conditions, still it is not instantaneous.

The adiabatic flame temperature is not a specific characteristic of the fuel, but depends on the conditions of combustion. In particular, the temperatures of fuel and air fed to combustion and the fuel-air ratio affect the calculation. The theoretical adiabatic flame temperatures for a number of the common fuels are near or a little under 2200°C. There is no over-all correlation between calorific power and flame temperature.

The actual flame temperature has considerable direct and indirect importance as a criterion of fuel utilization. An obvious requirement is that the flame temperature be above the temperature which must be reached in the furnace charge. The rate of transfer of heat from the flame to the furnace contents is directly proportional to the temperature difference between the two, so that high flame temperatures favor rapid heating. On the other hand, higher flame temperatures are accompanied by greater danger of overheating and destroying the furnace refractories and even sometimes locally overheating the furnace charge.

Only under unusual conditions do the interior furnace surfaces, the furnace gases, and the solid or molten charge reach a single uniform temperature which could be defined as the process temperature. In fact, substantial temperature differences within the furnace are necessary to obtain the flows of heat on which furnace processes depend. In spite of these variations and differences in temperature, careful study of any given process usually will disclose a rather definite critical or minimum temperature level which must be met or exceeded in the coolest parts of the furnace interior if the process is to operate smoothly and satisfactorily. For example, in the continuous melting of metals or in the various processes of refining liquid metals, certainly no large portion of the furnace interior and contents can remain below the melting point of the metal. Actually, in such processes involving liquid metals, the critical temperature might well be the pouring or tapping temperature at which the liquid metal is to be withdrawn from the furnace. In processes characterized by the formation of liquid slags, the critical temperature is generally the so-called free-running temperature of the slag, which is the lowest temperature at which a slag is formed fluid enough to discharge freely from the furnace. In still other processes, the critical temperature may be the temperature required to carry out a certain chemical reaction effectively.

The critical temperature has a simple and direct significance in relation to the utilization of heat from the burning of fuel, that is, the critical temperature is the lowest temperature at which the flue gases, the products of combustion, can leave the working chamber of the furnace. A flue gas temperature lower than the critical temperature could only be obtained if some part of the furnace interior walls or charge were below the critical temperature, which would be inconsistant with the concept of critical temperature outlined in the previous paragraph.

A flue gas temperature well above the critical process temperature shows an unnecessary loss of heat into the flue gases. Such a condition might result from poor furnace design, for example, from failure to provide for good heat transfer from combustion gases to furnace charge. Other causes of excessive flue gas temperatures include driving the furnace over capacity, insufficient cold charge, and too high a fuel feed rate.

The sensible heat in the flue gases at the critical process temperature is not available to the process in the furnace. It is at too low a temperature level to be useful. The higher the process temperature, the larger this sensible-heat item will appear in the heat balance, to the point where it frequently becomes by far the largest item for processes at temperatures over 2000°F. Moreover, this is a loss of heat from the furnace which is inherent in the very nature of heating with fuels and therefore should be placed in a different category from heat losses chargeable only to poor furnace management. Recognition of this feature of fuel utilization leads to the important concept of available heat.

The gross available heat may be defined as the total heat input from the combustion of the fuel, less the sensible heat in the products of combustion at the critical process temperature. The total heat input includes sensible heats in fuel and air, as well as heat of combustion. Thus, the gross available heat is the heat given up to the furnace and its contents by the combustion products as they cool to the critical temperature. Available heat may be expressed in various ways according to convenience, for example, BTU/lb of fuel, BTU/hr, percent of total heat input, percent of calorific power of fuel, etc.

From another point of view, the gross available heat is the heat given up by the combustion products in cooling from the adiabatic flame temperature, AFT, to the critical temperature. If it is assumed as an approximation that the specific heat of the combustion products does not vary with temperature, the gross available heat is then proportional to ($T_{AFT} - T_{CRIT}$) and

$$\text{approx. gross available heat (\% of total heat input)} = 100 \frac{T_{AFT} - T_{CRIT}}{T_{AFT}}$$

This rough approximation shows the importance of adiabatic flame temperature in relation to fuel utilization.

Although the gross available heat truly represents the heat quantity available from the combustion process at the critical temperature, it does not represent heat available to the metallurgical process. Some high-temperature heat must be used to keep the furnace hot, that is, to supply the heat loss to the furnace surroundings. Once a furnace is designed and built, the rate of heat loss to the surroundings when the furnace is at a given working temperature is relatively fixed and not under the operator's control. Hence, the net available heat is defined as the heat available to the metallurgical process itself, as the gross available heat less the heat loss to the surroundings with the furnace at working temperature. The net available heat thus is a criterion for comparing the effectiveness of the system of fuel combustion plus furnace in supplying heat to the process, whereas the gross available heat is a criterion for comparing different fuel combustion systems.

For some simple smelting and melting processes that require large quantities of heat, the principal factor determining furnace capacity is the rate at which the fuel and furnace can supply heat. For such processes, the smelting power of the furnace is measured by the net available heat which can be developed in the furnace chamber per unit time. However, other factors like heat transfer rates and chemical reaction rates also limit furnace capacities, so that an increase in rate of production of net available heat does not necessarily lead to an increase in capacity.

Knowledge of the above thermodynamic principles, summarized principally from Schuhman (1952), is necessary in order to understand the implications for energy use implicit in the selection of a smelting process. There are choices in the design of the various furnace types mentioned earlier, and discussed by Kellogg (1976a), which can lead to important energy savings. They are:

1) use of fuel rather than electrical energy where applicable
2) use of oil or coal rather than natural gas where applicable
3) maximum use of oxygen enrichment of combustion process air
4) drying of charge before smelting
5) drying and preheating of charge by partial roasting in a fluid-bed roaster
6) recovery of waste heat from all major hot process gases

It has long been recognized that the nature of the fuel used in smelting has a significant effect on both the fuel rate (kcal/mt) and smelting rate (mt/hr). The difference between oil and gas is mainly due to the lower hydrogen/carbon ratio of the oil. For a given heat release, natural gas combustion produces a larger volume of exhaust gas. Based on gross heating value of the fuel, the ratio of combustion gas volume for gas/oil is 1.57; based on net heating value the same ratio has a value of 1.16. This larger waste gas volume carries away more sensible heat, thus increasing the required fuel input rate. It also reduces the smelting rate because the capability to burn fuel efficiently is limited by the available combustion volume of the furnace. Thus, the use of heavy fuel oil or pulverized coal as opposed to natural gas will result in lower fuel rates and higher smelting capacity.

Enrichment of the combustion air with oxygen has the principal effect of decreasing the flow of nitrogen through the furnace per unit of combusted fuel. This results in:

1) an increased flame temperature, hence an increased rate of heat transfer to the charge

2) an increased residence time of the combustion gases in the furnace (due to their lower volume per unit of fuel) and hence a more complete transfer of their heat to the charge

3) a decreased carry-off of sensible heat in the effluent gases

4) an increase in SO_2 concentration in the effluent gases.

The 79% nitrogen in the air normally used for combustion passes through fuel-fired furnaces without reacting and comprises a major part of the volume of the flue gases. Thus, of the sensible heat tied up in the flue gases at the critical temperatures (the non-available heat), a large part is that required by the nitrogen. Reduction in the quantity of nitrogen passed through the furnace obviously then increases the yield of available heat, other factors remaining unchanged. This reduction in nitrogen throughput is obtained by oxygen enrichment of combustion air, that is, by substituting straight oxygen for part of the combustion air. This also serves to enrich the SO_2 concentration of effluent gases, making treatment for SO_2 removal more efficient and economical. Although the maximum effect is obtained by replacing all the air with oxygen, this extreme is rarely justified. Ordinarily, oxygen enrichment during a high-demand part of a furnace operating cycle, or enrichment to increase the oxygen content from 21% for air up to 25% or 30%, has proved to be more attractive.

As with other means of increasing available heat per unit of fuel, oxygen enrichment also increases flame temperature. In fact, oxygen-fuel combinations are often used to attain extremely high temperatures on a small scale (oxygen-acetylene, oxygen-hydrogen, oxygen-gas) where the cost of oxygen is not a serious part of the total cost. In metallurgical furnaces, the increase in flame temperature with oxygen enrichment can be used to increase the rate of heat transfer from the flame to the charge in the furnace, sometimes greatly speeding up the work of the furnace. On the other hand, the effect on flame temperature may limit the use of oxygen, since the life of the furnace refractories suffers when too high a temperature is reached. This limitation has been observed particularly with furnaces having silica roofs: they fail rapidly at temperatures close to 3000°F.

When a given fuel-air combination is inadequate, either because of poor available heat yield or because of too low a flame temperature, oxygen enrichment is, in theory at least, an alternative to installation of preheating apparatus. Moreover, it is more flexible, will give greater increases in available heat and flame temperature, and is not subject to the often messy maintenance and upkeep problems usually associated with high-temperature heat recovery. Burners using oxygen in place of part of the air can be added to existing furnaces without extensive structural changes. None of these advantages, however, is sufficient to economically justify the use of oxygen if the cost of the oxygen is greater than the over-all savings in cost resulting from its use (Schuhmann 1952).

The problem of optimizing the use of oxygen both economically and in terms of energy consumption is a complex one, depending, for example, on the detailed composition of the smelter feed and the design of the equipment chosen. Some general observations can be made, however. The production of one metric ton of oxygen requires approximately 400 kwh of electrical power (Kellogg 1976b). The electrical power to produce this oxygen would require the consumption of about 1/6 net of coal in a typical large coal-fired power plant. However, taking this into account, the result is still an overall savings. Data on existing flash smelter operations indicate an overall savings of 1/3 net of coal for each metric ton of oxygen used, or a savings of 9 million BTU per metric ton of oxygen. This further means that the coal usage shifts, with the smelter requiring 1/2 net of coal less, and the power station using 1/6 net more for the overall savings of 1/3 net of coal.

The use of oxygen is clearly desirable from the point of view of energy conservation. Not only is the fuel requirement of the smelter itself reduced, but the above savings reflects the fact that the resulting exhaust gases are richer in SO_2, making sulfur removal more efficient, less expensive, and less energy intensive. The question of the economically optimum level of enrichment is, however, not simple. The answer depends on factors such as the cost and availability of electrical power, in comparison with other energy sources such as coal. The overall size of the facility is a factor also, since the unit cost of oxygen decreases dramatically as the capacity of the oxygen plant increases. For plants with capacities ranging from 100 to 1,000 mtpd of oxygen production capacity, the cost of the oxygen ranges from a high of about \$21/mt to a low around \$14/mt (EPA 1975). Thus, each installation must conduct detailed studies to determine their own economically optimum use of oxygen enrichment.

The drying of concentrate prior to smelting requires energy for the evaporation of water, but the water vapor may leave the drier at temperatures as low as 80°C (176°F) so that considerably less fuel is required for drying than for handling the same moisture content in wet-charge smelting. This points out the energy advantage of drying prior to smelting.

Preheating combustion air is an important method of improving the energy efficiency of the smelting process. To carry out the smelting reaction, a certain amount of energy is needed to create the thermal environment required for the smelting reaction to proceed. The smelting reaction itself is exothermic, and thus actually acts as an energy source itself. Additional energy is required to offset losses from the furnace, however, and any energy introduced by preheating the combustion air reduces the need to provide that energy through the combustion of a fuel. This can allow the use of fuels, such as natural gas, with a lower flame temperature without lowering the overall operating temperature. Also, a given fuel generally can be burned in a preheater with greater efficiency than burning the same amount of fuel in a smelting furnace because of the much lower temperature, and thus energy loss, of waste combustion gases in the preheating operation. Finally, for a given fuel, the use of preheating reduces the energy input required from the fuel, and thus the amount of fuel required. This in turn reduces the amount of hot combustion exhaust gases produced and leaving the furnace, cutting this energy loss and reducing the overall energy requirement of the process (Kellogg 1976a).

In summary, preheating the combustion air is a practical means of increasing available heat, and is widely applied in metallurgical furnaces requiring temperatures above 1000°C. Some gaseous fuels also may be preheated. Combustion air or both the air and the gaseous fuel are generally heated with heat recovered from the flue gases, using regenerators or recuperators. The development of several important high-temperature metallurgical processes has been closely tied to combustion procedures involving preheating and heat recovery from flue gases, since such procedures have afforded in many cases the only economical means of supplying high-temperature heat.

The units of heat added to the heat input by preheating, as sensible heat in air, or in both air and fuel, add directly to the available heat. That is, increasing heat input by preheating involves no increase in the quantity or critical temperature of flue gases, so that the added heat is 100% available. Taking an extreme case as an example, firing with cold air and fuel might furnish available heat equivalent to only 5% of the calorific value of the fuel. By using a fraction of the sensible heat in the flue gases to preheat the air, sensible heat in preheated air might easily be brought to 10 or 15% of the calorific power of the fuel. This addition would multiply the available heat per unit of fuel by a factor of 3 or 4, making possible a substantial reduction in fuel consumption or increase in furnace capacity.

Heating the combustion air, or both the air and the gaseous fuel, requires additional equipment which must be built, operated, and maintained. Thus, even if the heat is derived from waste heat which would otherwise pass up the stack with the flue gases, the cost of recovering the heat is not negligible by any means. Accordingly, in determining whether or not to use preheating, the savings in fuel must be balanced against the over-all cost of heat recovery (Schuhmann 1952).

The roasting of a concentrate to remove part of the sulfur before smelting can result in substantial energy savings provided the hot calcine is charged to the smelting furnace without significant loss of sensible heat. By burning part of the sulfur in roasting, the fuel value of this sulfur is used for both drying and preheating of the calcine in the roasting step. The dry, preheated calcine requires considerably less fuel for smelting, thus increasing the capacity of the smelting furnace over that for wet-charge practice. Further, the higher grade matte produced requires less energy in converting.

Recovery of part of the sensible heat from hot smelter gases through use of waste-heat boilers has been standard practice with reverberatory furnaces for many years and has recently been more widely adopted for converters and fluid-bed roasters as well. The iron and sulfur in copper-nickel concentrates are fuels that are burned one way or another in any smelting process, and any process that seeks to minimize use of purchased energy must maximize recovery of heat resulting from combustion of the fuel in concentrates treated. Full use of waste-heat boilers on all major smelter gas streams is one way of accomplishing this goal.

The steam recovered in waste-heat boilers may be used in two quite different ways, for heating or for generation of mechanical and/or electrical energy. The energy credit allowed for steam is different for each. The use of steam for heating is more energy efficient than is its use for power generation. Smelters located adjacent to refineries commonly take advantage of this by using waste-heat steam for heating of refinery electrolyte (Kellogg 1976a).

The smelting system which offers the greatest flexibility in the above areas will offer the smelter designer the greatest degree of potential energy savings.

4.2.4 Converting

Smelting is generally followed by converting. In copper converting where all other metals or elements are assumed to act as minor constituents, the matte from smelting is oxidized using air and removing the iron and sulfur from the matte. The process is almost universally carried out in the horizontal basic refractory lined cylindrical Pierce-Smith Converter (Figure 6). Molten matte is added to the converters at 1100°C and the heat generated in the converter by the oxidation of iron and sulfur is sufficient to make the process autogenous. Copper converting is carried out in 2 sequential stages, both of which involve blowing air into the molten sulfide phase. These are:

1) The FeS elimination slag forming stage

$$2FeS + 3O_2(air) + SiO_2(flux) = 2FeO \quad SiO_2(slag) + 2SO_2$$

2) The blister copper (98.5% - 99.5% Cu) forming stage

$$Cu_2S + O_2(air) = 2Cu \text{ (Blister Copper)} + SO_2$$

Figure 6

The copper making stage does not occur until the matte contains less than 1% Fe. In normal industrial practices, the converter is charged with matte and flux in several steps, each being followed by partial oxidation and slag removal. This results in a gradual accumulation of Cu_2S in the converter and is followed by a final "copper making" blow. The product of the converting process is blister copper, which typically contains from 0.02% to 0.1% S. Significant formation of copper oxide does not occur until the sulfur content is below 0.02% so that oxidation of the copper is not a problem.

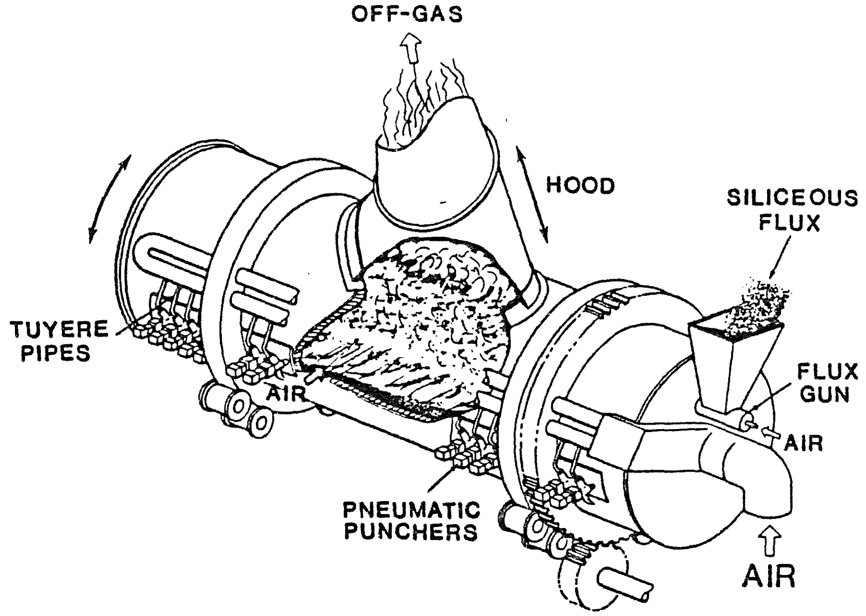
As was stated earlier, the Pierce-Smith converter dominates copper converting today. In recent years, however, two novel types of converter have been developed:

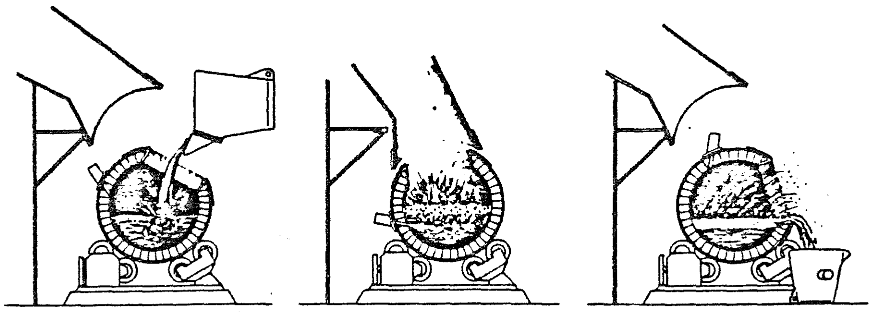
1) The Hoboken or syphon converter which is a Pierce-Smith type of converter with an improved gas-collection system

FIGURE 6

CUTAWAY VIEW OF A HORIZONTAL SIDE-BLOWN PIERCE-SMITH CONVERTER FOR PRODUCING BLISTER COPPER FROM MATTE

(SOURCES: BISWAS 1976, BOLDT, 1967)





CHARGING BLOWING SKIMMING

2) The top-blown rotary converter (TBRC) which blows air or oxygen onto the liquid surface via a water-cooled lance suspended above the converter

The Hoboken converter offers an improved solution to the problem of controlling SO_2 emissions from the converting operation. Exhaust gases are drawn off by means of a "goose neck" or siphon which is an integral part of the converter vessel (Figure 7). Unlike the Pierce-Smith design, the converter mouth does not act as a duct for the exhaust gases, and is therefore much smaller. An exhaust fan in the flue draws off the residual gases introduced through the tuyeres and the SO_2 being generated, and at the same time maintains a zero or negative draft at the converter mouth. This results in 2 immediate advantages in terms of emission controls:

1) Fugitive emissions from the converter mouth are reduced, particularly during charging and pouring operations where a conventional Pierce-Smith converter is rolled out of the hoods.

2) Dilution of converter exhaust gases, which may be 100% or more in Pierce-Smith converters, is greatly reduced, allowing gas with a higher SO_2 concentration to be produced as feed for the sulfuric acid plant. The converter has the further operational advantage of being able to be charged during a blow, since the mouth is unobstructed by hoods or flues.

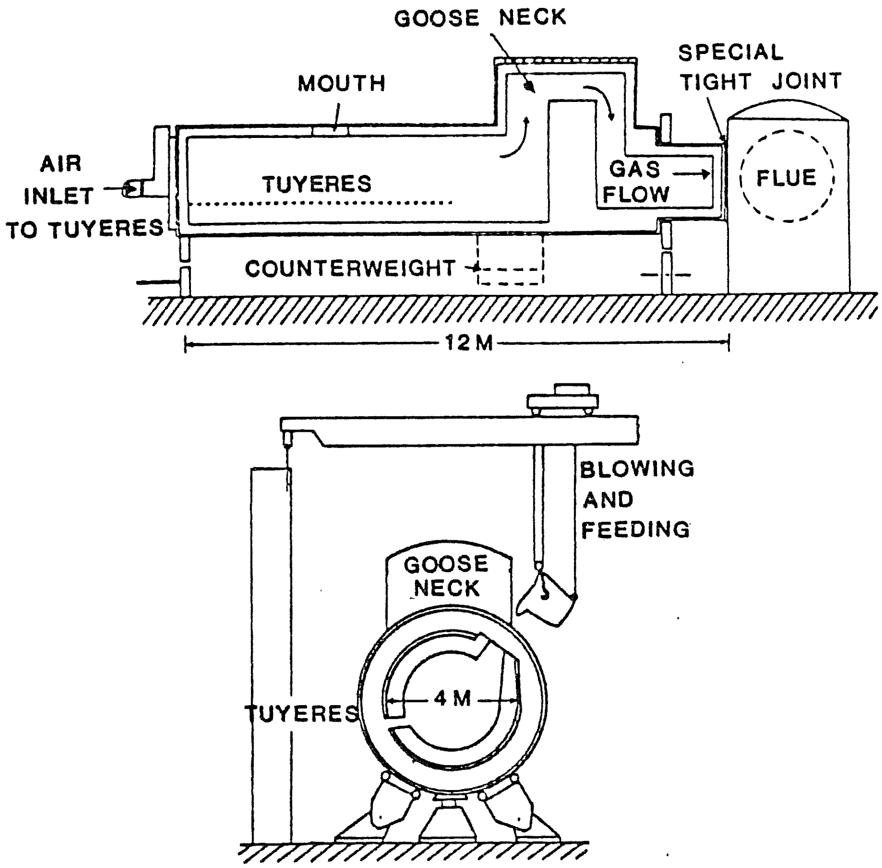
Figure 7

The implications of these advantages can be seen by comparing estimates of the capital costs and fugitive SO_2 control efficiencies of the Pierce-Smith and Hoboken converters (Verney 1978). In terms of estimates of fugitive SO_2 emissions, it must be stated that firm performance values based on complete

FIGURE 7

END AND SIDE VIEW OF THE HOBOKEN OR "SYPHON" CONVERTER

(SOURCE: BISWAS 1976)


LONGITUDINAL SECTION

monitoring data simply do not exist. The scientific quantification of these emissions is in its infancy, and the best values available typically are not well-supported by convincing data but rather often rely on the estimates of experts in the field. As such, the conclusions reached based on these estimates must include a provision for modification as more reliable data is obtained. With this caveat, it is estimated that the fugitive SO_2 emissions from a Hoboken converter may be a fifth of that from a Pierce-Smith. It is true that converter operation is estimated to contribute only 1/3 of the overall plant fugitives (see section 4.7.5), so it is by no means a final solution to the SO_2 problem. However, low level fugitive emissions are particularly influential in affecting ambient air quality, so any technology whose design inherently affords a reduction in these emissions should be carefully considered if an improvement is air quality is desired. The increase in stack emissions caused by decreased fugitive emissions is essentially negligible, due to the high removal efficiency of a sulfuric acid plant, so there is no undesirable tradeoff in this respect.

In terms of costs, the basic converter operation may account for 15% or more of the total capital cost of a smelter (Biswas 1976). Looked at in isolation, the Pierce-Smith converter is less expensive than the Hoboken. However, with present environmental regulations, the various required emission control equipment must be considered "part of the package" and here important cost differences show up. The expensive hooding required to effectively control Pierce-Smith emissions is not needed by the Hoboken. Another savings results from the smaller gas stream requiring treatment for particulate removal with the Hoboken since dilution air is not taken in. These economies are estimated to result in an overall cost savings of about 20% for an installation using Hoboken converters, and this does not even include expected savings in the acid plant (Verney, 1978). Clearly, these features indicate that the Hoboken may be an attractive alternative to the Pierce-Smith Converter. They do have various operating problems associated with them (Billings 1977b), but nevertheless should be given serious consideration.

In the top-blown converter air or oxygen is blown onto the surface of the liquids via a suspended water-cooled lance. The main advantage of lancing from above is that pure oxygen can be used for the converting process which has not been possible with submerged tuyeres (a tube or opening in a metallurgical furnace or vessel through which air is blown as part of the extraction or refining process) due to severe refractory erosion problems. However, normal copper converting is autogenous without oxygen or oxygen enrichment, so that top-blown converters will not be applied extensively to the normal copper converting process.

In nickel converting where all other metals or elements are assumed to act as minor constituents, iron and sulfur are oxidized, eliminating substantially all of the remaining iron sulfide. Nickel, copper, precious metals, and most or all of the sulfur that was combined with them remain in the matte.

The top-blown oxygen converter is also used to convert nickel matte to crude nickel. In this case top-blowing with oxygen generates the high temperatures required to minimize nickel oxide formation.

In copper-nickel converting where both copper and nickel are appreciably concentrated so as to make it desirable to recover both metals, the mere presence of the excess nickel with the copper tends to complicate the eventual separation of the two metals during converting. If during the converting stage some sort of separation is desirable, such as formation of a blister copper and a nickel-copper matte, then the process of converting may be modified and selective fluxing, blowing, slagging, and skimming required to effect proper segregation and separation. The nickel along with some of the copper is preferentially slagged off during the first stage of converting, leaving a blister copper as the converter product. The blister copper is sent to a copper refinery for further treatment. The first stage converter slag containing the nickel and some copper is combined with smelting furnace slag and cleaned in electric arc furnaces to produce a nickel-copper matte alloy product and a discardable waste slag. The nickel-copper matte alloy is further refined during a second stage of converting before being sent to a nickel refinery for final treatment. This process is complex and not well-proven on a large scale.

4.3 SUMMARY OF SMELTING METALLURGY — Technology Options

When designing an integrated smelter system which will effectively dry, smelt, and convert material to a desired chemical and physical form, several options are available. Figure 8 illustrates in a generalized flowsheet the various choices in current and developing technology offered to the smelter designer.

Each system involves the basic sequence of reactions just described, which are carried out by the application of heat supplied partly by the burning of fuel and partly by the exothermic reactions involved. Historically speaking, pyrometallurgy has developed from the concept of "conventional" metallurgy through the current concepts of "flash" metallurgy, to the developing concepts of "continuous" metallurgy. Each band of Figure 8 traces this historical development, with the lowest band representing the oldest technology, the highest band representing the newest technology. Each band is open-ended in the sense that with time, current technology will likely become conventional, and developing technology may become current. Technology is in a constant state of flux, and at any specific time the number of systems commercially available will be less than the total number which are possible in theory.

Figure 8

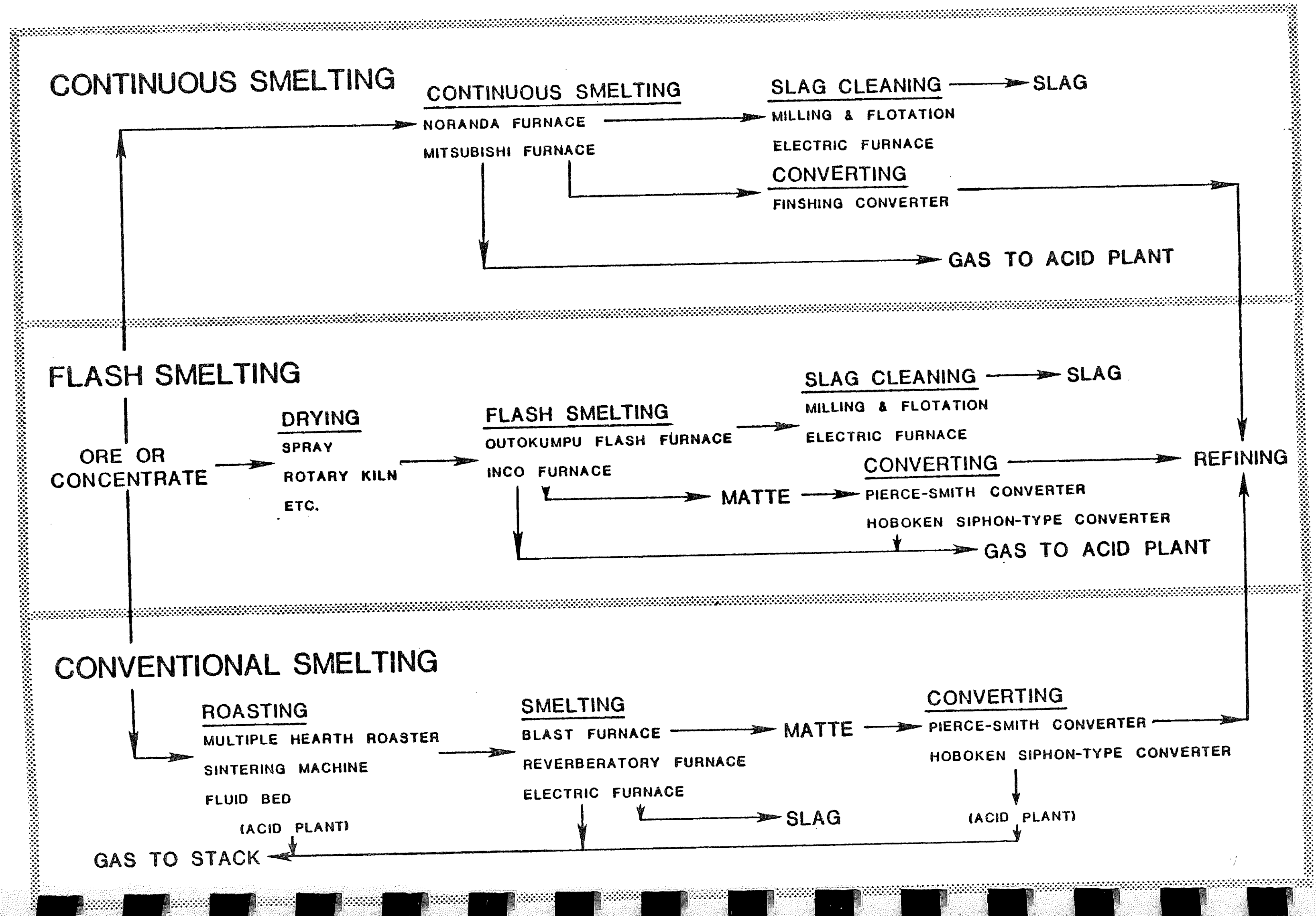
The processes of drying (or roasting), smelting, and converting are common to each of the individual pyrometallurgical systems. Though the basic steps have not changed, the actual equipment and hardware used have been modified or changed to accommodate new pyrometallurgical technology.

Conventional metallurgy, using either reverberatory or electric furnaces, as the name implies, involves three distinct and separate operations of drying (or roasting), smelting and converting. Each takes place in a separate and distinct unit or vessel. Flash smelting metallurgy involves the drying (roasting) and smelting of ores simultaneously in one unit or vessel, followed by a separate stage of converting. Continuous smelting metallurgy involves the simultaneous drying (roasting), smelting, and converting of an ore in a single unit or vessel.

Typical types of smelting equipment include:

EQUIPMENT	TYPE
Conventional Blast Furnace	
Reverberatory Furnace	Conventional Smelting Furnaces
Electric Furnace	
Outokumpu Furnace	Flash Smelting Furnaces
Inco Furnace	

FIGURE 8 COMBINED FLOWSHEET SHOWING VARIETY OF CHOICES IN CURRENT AND DEVELOPING TECHNOLOGY OFFERED TO COPPER SMELTER DESIGNERS



Noranda Furnace	Continuous Smelting Furnaces
Mitsubishi Furnace	

4.3.1 Conventional Blast Furnace

The blast furnace consists essentially of a tall vertical hollow shaft, rectangular in cross section, surmounting a hearth or crucible (1.5 m X 7 m X 5 m). Air required for combustion is supplied by a blower; it passes into the blast main surrounding the furnace and from there to the tuyeres. In a blast furnace, the tuyeres are water-cooled metal tubes which pass through the refractory lining of the bosh (the section of the blast furnace extending upward from the tuyeres to the plane of maximum diameter). The air then passes into the furnace. Where the air enters the furnace, very high temperatures (1100-1300°C) are generated by the combustion of fuel, and as the products of combustion ascend, they yield up their heat to the charge. Gases and fumes (3-5% in SO_2 concentration) escape from the top of the furnace through a flue located just below the charging floor. Metal and slag separate according to their specific gravities and are tapped from the crucible. The blast furnace, although simple in construction, is elastic in operation and is capable of high efficiencies. Capacities exceeding 1,000 mtpd of concentrate or charge feed are obtainable. The typical blast furnace uses relatively small amounts of fuel, generally as coke. Coarse or sintered ore is required for efficient working (Treilhard 1973).

Blast furnace smelting was used extensively in the past for producing large quantities of matte from lump sulfide ores. It was also used at one time to produce a crude, iron-contaminated "black copper" from oxide ores. However, depletion of rich lump ores and the increasing prevalence of froth flotation concentrates have gradually eliminated the blast furnace from matte smelting. The blast furnace is unable to directly treat finely-ground flotation concentrates because they are quickly blown out of the furnace by the rising combustion gases. However, the blast furnace still finds some use, usually with a sintered charge, in Africa where mixed oxide-sulfide ores are treated, in Canada for nickel-copper concentrates, and in Japan (Bendersky et al, 1976). Figure 9 illustrates in generalized form the flowsheet of the Falconbridge Smelter in Canada which utilizes a blast furnace in the treatment of nickel-copper concentrates.

Figure 9

4.3.2 Reverberatory Furnace

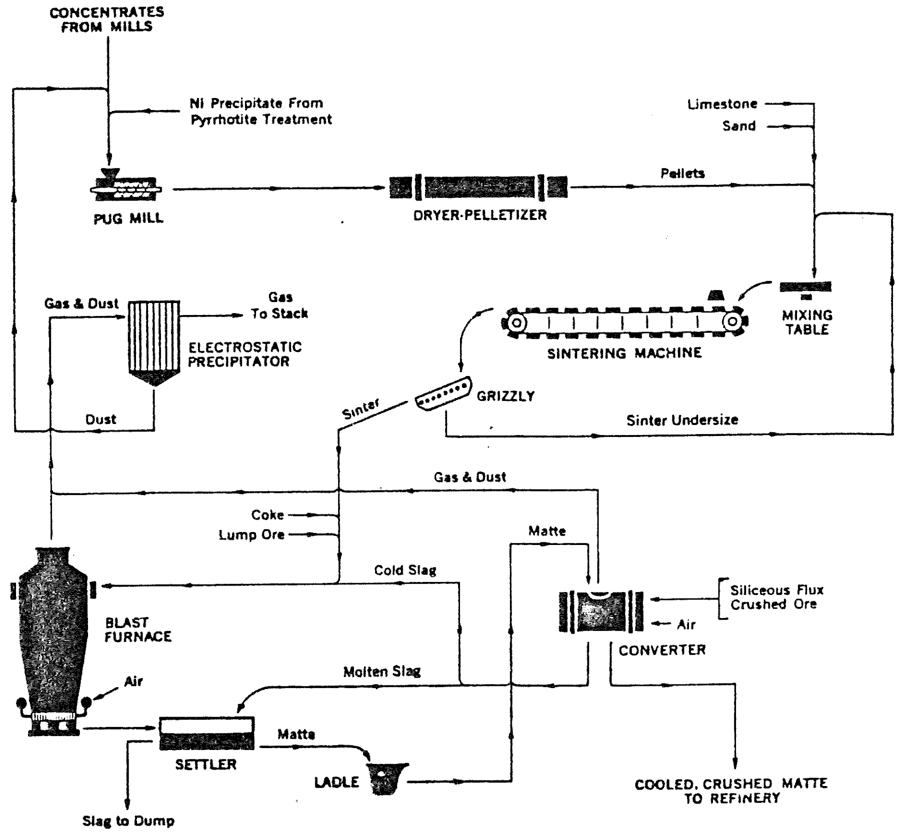
The reverberatory furnace is the most widely used unit in use today for matte smelting. It is a fuel-fired hearth furnace in which concentrates or roaster calcines are melted to produce separate layers of liquid matte and slag. The dimensions of reverberatory furnaces vary considerably, but modern furnaces are typically 33 m long (inside), 10 m wide, and 4 m high (hearth to roof) (Bendersky et al. 1976).

The reverberatory furnace is composed of a shallow hearth with side and end walls surmounted by an arch roof. The hearth is well constructed, being built of concrete overlaid with silica brick and sintered sand or slag. Side walls are of silica brick with frequently two or more courses of magnesite brick at the level of the slag line. The arch, or roof, is composed of a span of silica or magnesite bricks held in place by iron plates which run along the longer

FIGURE 9

FLOWSHEET OF FALCONBRIDGE SMELTER

(SOURCE: BOLDT, 1967)



sides of the furnace and are bolted to cast-iron uprights set in the foundations. The plates take up the thrust, the weight resting on the side walls. Horizontal tie-rods across the top of the furnace, bolted to the vertical uprights, serve to hold the furnace rigid. Heating is usually by pulverized fuel or gas injected into the furnace via burners inserted in the end wall. The ore is charged either through holes in the roof or through openings in the side walls (Treilhard 1973).

Furnaces of this type generally produce in the order of 500-800 net of matte grading 35-40% Cu and 500-900 net tons of discard slag per day. A smelter complex usually has from one to 3 such furnaces. The reverberatory furnace is also used, simultaneously with smelting, to recover copper from recycled, molten converter slag.

The extensive use of reverberatory furnaces is due to their high degree of versatility. The heat for smelting is provided by burning fuel in the furnace and by passing the hot combustion gases over the charge. Temperatures ranging from 1100-1700°C are not uncommon for such furnaces. All types of material, lumpy or fine, wet or dry, can be readily smelted.

During the melting phase in a reverberatory furnace, approximately 20-50% of the sulfur in the charge is oxidized depending upon feed chemistry. The range of sulfur dioxide concentration in the wet offgas is 0.5 to 2.5% depending on the feed and operating conditions. Of the sulfur in the charge, 70-80% is removed in the matte, 18-30% in the flue gas, and 1-2% in the slag. The low concentrations of SO_2 in the furnace off-gas poses a treatment problem since the concentration is below the minimum of 3.5-4% required for effective operation of a sulfuric acid plant. Applicable scrubbing techniques in this concentration range have been utilized in Japan, but not in the United States to date. Such treatment methods for reverberatory furnaces were considered to be unreasonably costly by the EPA. However, since other technologies (electric and flash smelting) exist which allow for the generation of gas streams which are economically treatable using acid plants, air quality emission regulations for new installations reflect the attainable SO_2 removal for these cases. This acts as a strong discouragement for the construction of new reverberatory furnaces (EPA 1976a).

Dust carry-over from the reverberatory furnace is also a substantial problem. Heavier particles settle below the waste heat boilers and into the hoppers of the balloon flues or settling chambers. Practically all of the copper smelters use drag or screw conveyors for the removal of dust from places of accumulation. Collected dust is returned to the system.

Figure 10 illustrates in generalized form the flowsheet of the Copper Cliff and Coniston smelters in Canada which utilize a reverberatory furnace in the treatment of nickel concentrates.

Figure 10

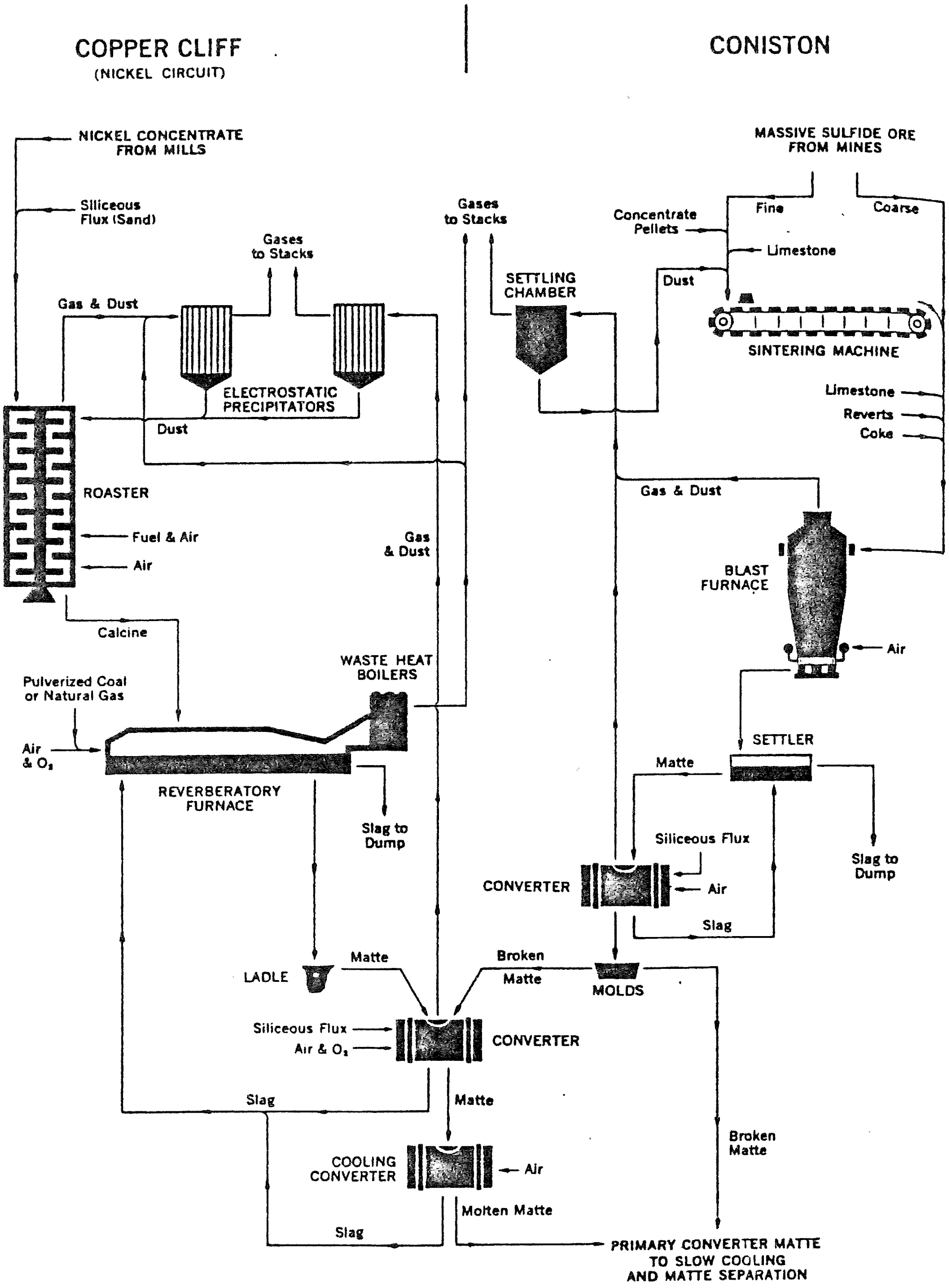
4.3.3 Electric Furnace

The electric furnace is an electrically heated hearth furnace which performs the same functions as that of the reverberatory furnace. Electric furnaces are rectangular in cross section, with a firebrick sprung-arch roof and a basic brick inverted-arch bottom. Walls are of magnesite basic brick to above the slag line, followed by three or four courses of transitional chrome magnesite brick, followed by firebrick to the roof level.

FIGURE 10

FLOWSHEET OF COPPER CLIFF AND CONISTON SMELTERS

(SOURCE: BOLDT, 1967)



Typically, matte is tapped from either of two regularly-rotated outer matte tapholes. Slag is tapped from one of 3 regularly-rotated tapholes situated at one end of the furnace. A converter slag-return launder enters above bath level at the opposite end of the furnace.

Power is supplied to the bath by inline Soderberg electrodes, either 3, 4, or 6 in number, extending down from the center line of the furnace. Surrounding each immersed electrode is an annular ring of superheated slag, and the free-flowing charge of calcine or dried concentrates is charged by drag chain conveyors to as close to the electrodes as possible. The heat for smelting is generated by electrical resistance in the slag, and correct slag composition, 35.5% to 38.5% SiO_2, must be maintained for proper slag resistivity. Normal slag depths are about 24 in. for a 6000 KVA furnace, 40 in. for a 30,000 KVA furnace, and 50-60 in. for a 50,000 KVA furnace (Treilhard 1973).

The electric smelting furnace is used where electrical energy is inexpensive or in the handling and/or treating of slags which cannot be handled in reverberatory furnaces, for example, a slag which is chemically high in MgO. It may also be used where SO_2 evolution from the smelter must be tightly controlled. The electric furnace and the reverberatory furnace are equally suitable for obtaining the relatively low temperatures, 1200-1300°C, of copper-nickel matte smelting. It is completely versatile and can be used to smelt any and all materials (Bendersky et al. 1976).

The electric furnace has an environmental advantage over the reverberatory furnace in so far as it produces smaller quantities of effluent gases due to the absence of gaseous combustion products. This results in a minimum amount of effluent gases, and consequently a minimum amount of dilution air leaving the furnace to be treated in a sulfuric acid plant.

The principal disadvantage of the electric furnace is the fact that premium fuel, namely electrical power, is required for successful operation, implying that treatment is costly in high power cost areas.

The electric furnace has the same versatility as the reverberatory furnace, and this factor plus the environmental advantages have led to its adoption for new smelting capacity in several environmentally sensitive areas (Bendersky et al. 1976).

Mattes and slags produced in electric furnaces are similar in nature to the mattes and slags produced from the reverberatory furnace. Sulfur dioxide gas emissions generally range from 2-4% with minimal dust losses, a consequence of low gas velocities.

Figure 11 illustrates in generalized form the flowsheet of the Thompson smelter in Canada which utilizes an electric furnace in the treatment of nickel concentrates.

Figure 11

4.3.4 Flash Furnaces

Flash furnaces for smelting are of 2 types:

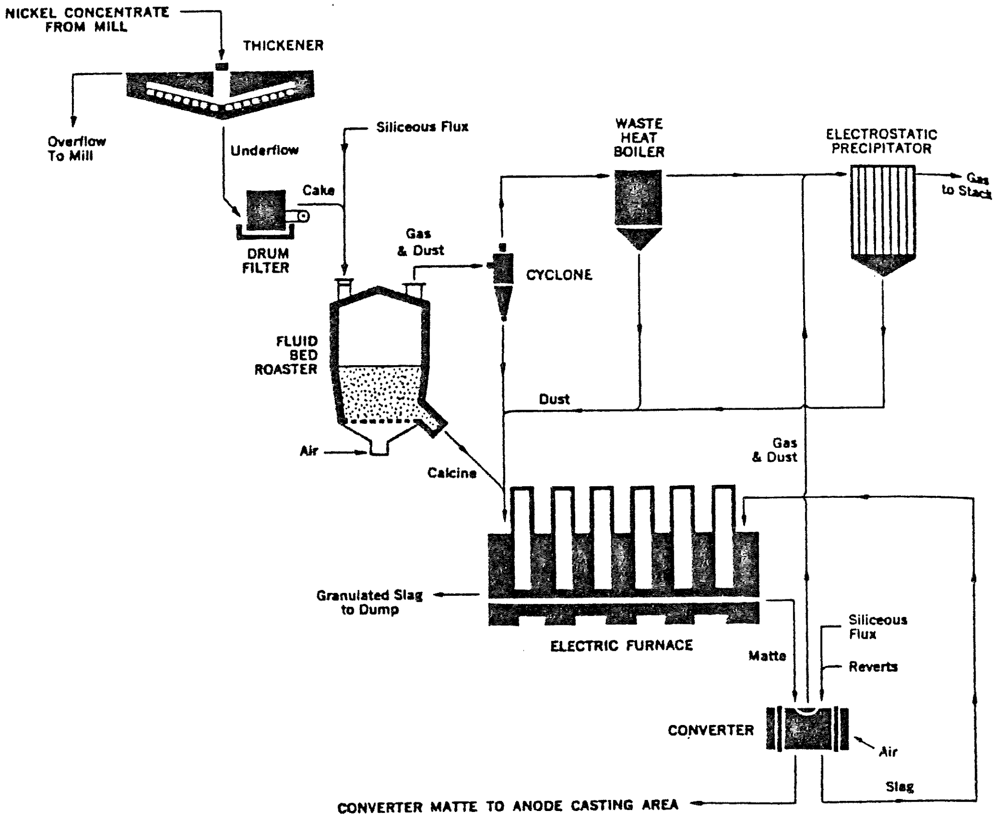
1) The Outokumpu Furnace
2) The Inco Furnace

In the flash smelting process, flotation concentrates are injected along with flux and either preheated air or oxygen into a combustion chamber maintained at smelting temperature by "flash" combustion of iron and sulfur while the par-

FIGURE 11

FLOWSHEET OF THOMPSON SMELTER

(SOURCE: BOLDT, 1967)



ticles are in suspension. The heat of the exothermic oxidation reactions is used in the smelting, with any heat deficiency augmented by a small addition of fuel, preheating of combustion air, enrichment of the combustion air with oxygen, or a combination of the above.

Flash furnaces utilize the heat evolved from oxidizing part of their sulfide charge to provide much or all of the energy required for smelting. The principal advantage of the flash smelting processes is that their energy costs are considerably lower than those of reverberatory and electric-furnace smelting. Flash furnaces are also excellent from an environmental point of view in that they produce SO_2-rich effluent gases from which the SO_2 can be efficiently removed as sulfuric acid or liquid SO_2. For these reasons, flash furnaces have accounted for most of the new matte smelting capacity since 1965 (Bendersky et al. 1976).

The principal product of flash furnace smelting is a high grade liquid matte ranging from 45-55% Cu. The gaseous product of the sulfide oxidation reactions is SO_2, and considerable quantities are produced by the flash smelting reactions. The effluent gases produced by the Inco process contain approximately 80% SO_2. The SO_2 from the Outokumpu reactions is diluted by nitrogen from the incoming combustion air and by hydrocarbon combustion products. Outokumpu effluent gases contain approximately 10-15% SO_2. Sulfur dioxide is efficiently removed from flash furnace gases as liquid SO_2, in the Inco process, or as sulfuric acid in the Outokumpu process.

Outokumpu Furnace: Concentrate, dried to less than 0.2% moisture, is mixed with heated air in a burner at the top of a reaction shaft. The melted droplets collect in a settler and develop the two normal liquid layers--matte and slag.

The offgas has a sulfur dioxide content, specifically determined by ore mineralization and matte grade but generally sufficient for processing to acid. There is also a dust burden of 6-10% of the charge which is collected and recycled. Matte grades ordinarily vary between 50% and 70% copper. The slag contains too much copper to discard, an inherent disadvantage of the process, and must be cleaned by settling in an electric furnace, or by casting, slow cooling, grinding, and treating by conventional flotation-concentration methods. The latter method of treatment has considerable advantage in reducing fugitive emissions. The high matte grade substantially reduces the amount of converter processing which follows. However, the amount of secondaries such as ladel skulls, scrap, and spillage which can be smelted as coolant in the converter is limited. The amount of heat available to flash smelting depends upon the iron and sulfur content of the concentrate (Treilhard 1973).

Principal advantages of the Outokumpu flash smelting system are:

1) The physical structure of the furnace supports a large throughput.
2) It is very economical in its use of fuel, with the greater portion of energy used for air heating; therefore, only a low quality fuel need be required.

3) The effluent gas produced is a good feedstock for an acid plant.
4) Direct production of elemental sulfur in the flash smelting emission control system is being developed.

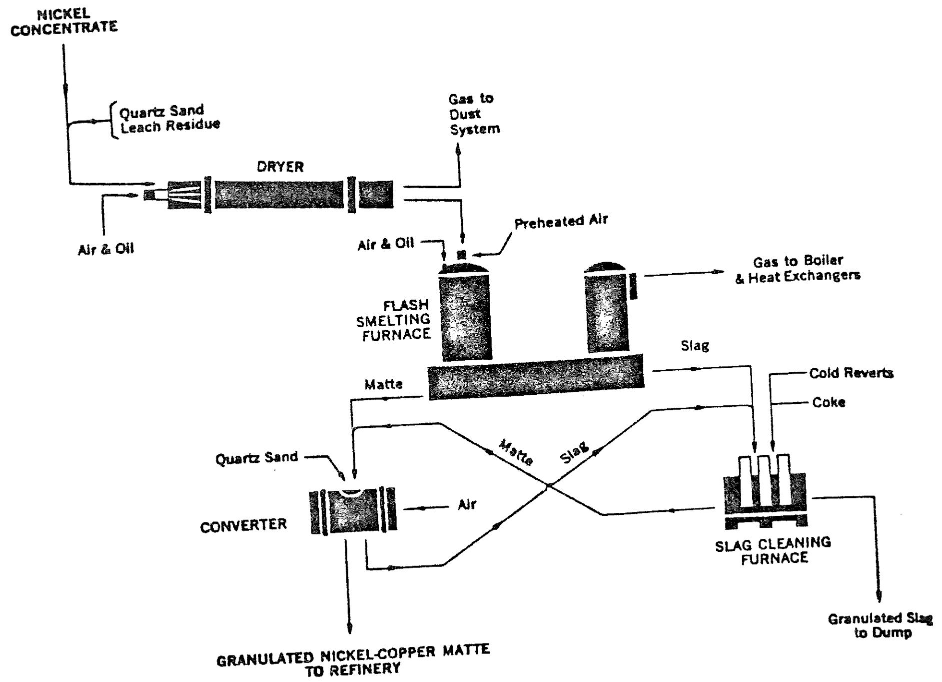
Figure 12 illustrates in generalized form the flowsheet of the nickel smelter at Harjavalta, Finland, which utilizes a flash smelting furnace in the treatment of nickel concentrates.

Figure 12

FIGURE 12

FLOWSHEET OF NICKEL SMELTER AT HARJAVALTA

(SOURCE: BOLDT, 1967)



Inco Furnace: The Inco flash furnace uses commercially pure oxygen in the flash smelting of sulfide concentrates. The concentrates are dried to approximately 0.1% moisture and partially oxidized with the oxygen in burners located in the ends of the furnace. A furnace of modest proportions offers a high throughput. The gas volume is very small, containing approximately 80% SO_2 which can be scrubbed and liquified by compression and cooling. The slag developed in the furnace is low enough in metal content to discard, but the converter slag is returned for cleaning. Thus, slag-cleaning facilities must be included in the smelter design. The oxygen flash furnace is dependent solely upon the oxidation of a portion of the iron and sulfur for the furnace's energy so that its application generally covers the same concentrate grade ranges as the Outokumpu furnace (Treilhard, 1973).

Principal advantages of the Inco flash smelting system are:

1) It has a much lower overall energy requirement.

2) Its volume of effluent gas (per metric ton of charge) is small due to the absence of nitrogen and hydrocarbon combustion products which means that its gas-collection equipment requirement is small.

3) The SO_2 concentration in its effluent gas is very high which simplifies SO_2 removal as sulfuric acid, liquid SO_2, or elemental sulfur.

4) Dust losses are low due to a relatively small volumetric gas-flow rate.

5) Its productivity (metric tons of charge per day/square meter of hearth area) is higher than that of other smelting furnace processes.

Figure 13 illustrates in generalized form the flowsheet of the Copper Cliff smelter which utilizes the Inco flash smelting furnace in the treatment of copper concentrates.

Figure 13

4.3.5 Continuous Furnaces

Continuous smelting furnaces producing copper directly combine the steps of roasting, smelting, and converting into a continuous, and perhaps autogenous, single-step operation for producing blister copper directly from concentrates. Input materials to the process are concentrates, fluxes, and air. The products are blister copper, a gas of high SO_2 strength, and a slag sufficiently low in copper to be directly discarded.

The potential advantages of such a single-step process for producing blister copper would be:

1) A reduced amount of material handling due to the absence of intermediate steps.

2) A low or zero energy requirement due to efficient use of the energy obtained by oxidizing sulfides continuously in a single vessel.

3) The production of a single stream of high SO_2 strength gas suitable for sulfuric acid or elemental sulfur recovery.

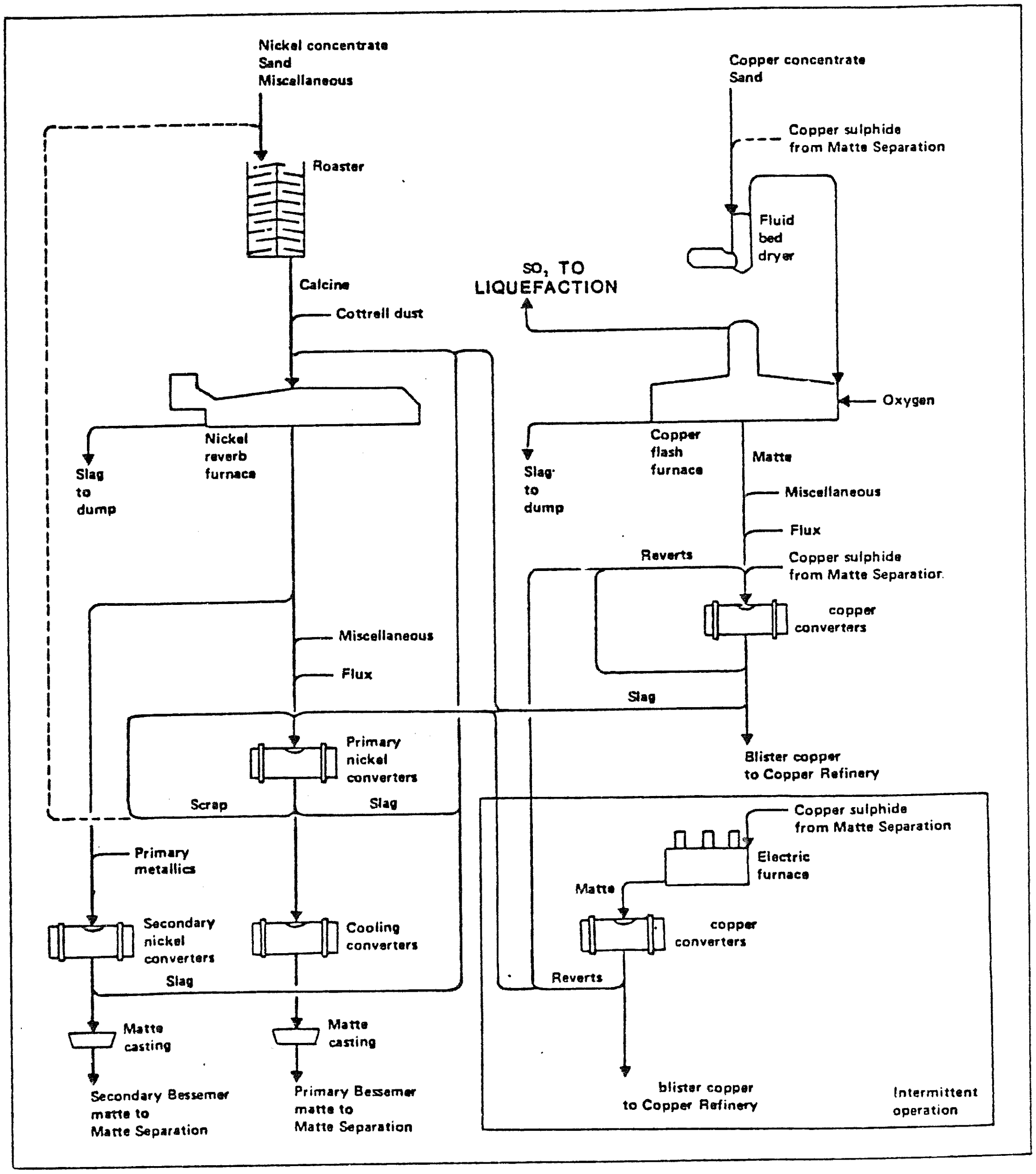
4) The ability to apply on-line automatic computer control to the entire copper making process.

5) Low capital cost requirements of a single unit as compared to multiple-unit operations.

FIGURE 13

SIMPLIFIED FLOWSHEET OF THE COPPER CLIFF SMELTER

(SOURCE: SCHABAS, 1977)



The Noranda and Mitsubishi processes are continuous processes operating on an industrial scale and further installations of both are planned.

Noranda Furnace: The Noranda process is based on two considerations: by combining smelting and converting in the same furnace, the fuel consumption can be minimized, and dynamic conditions can be created in the bath which will allow the production of copper while charging copper concentrates in the furnace.

Pelletized concentrate and flux are fed through a slinger belt into a cylindrical furnace of the same diameter but twice the length of a large converter. As oxygen enriched air is introduced through tuyeres, 3 layers generally are produced and coexist in the furnace: slag, matte, and copper.

Matte and slag flows are controlled as they move slowly to the tapping ports. Oxidizing gas is introduced into the matte to oxidize the FeS. Continued injection of the gas into the resulting white metal gradually oxidizes Cu_2S to metallic copper, which is tapped periodically after it separates by settling.

Slag tapped from the reactor is a low-silica, high copper product, which is treated by milling to yield a high grade concentrate, which is recycled, and a low copper (approximately 0.5% Cu) tailing which is discarded.

Figure 14 illustrates in generalized form the flowsheet of a smelter which utilizes the Noranda continuous smelting furnace in the treatment of copper concentrates.

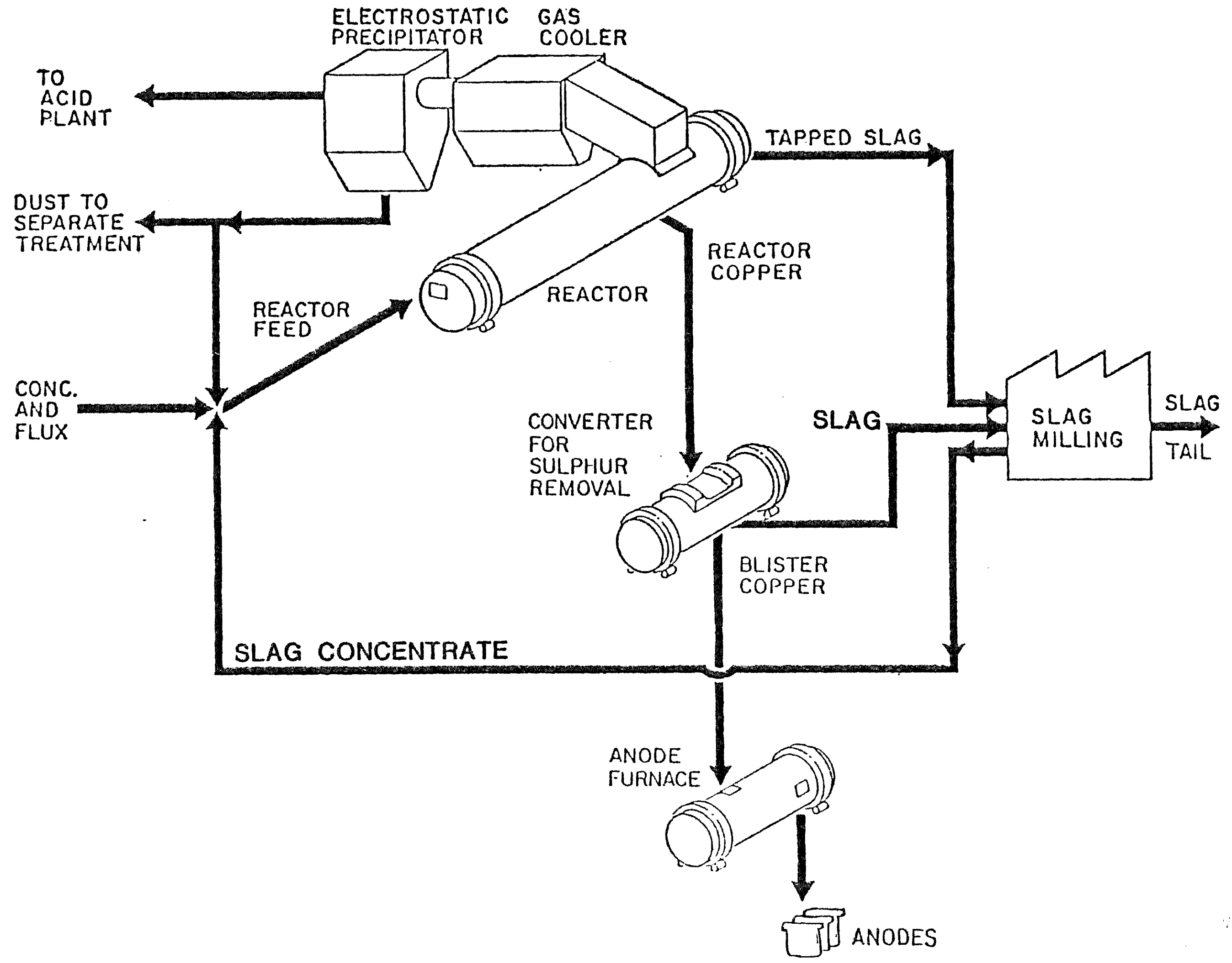
Figure 14

Mitsubishi Furnace: Sulfide ores are normally treated in two stages, the matte making stage, in which matte and slag are produced by smelting, and the con-

FIGURE 14

GENERALIZED FLOWSHEET OF NORANDA CONTINUOUS SMELTING PROCESS

(SOURCE: MACKEY ET AL. 1975)



verting stage, in which iron and sulfur in matte are progressively oxidized for production of blister copper. Although the chemical reactions in both process steps are oxidations, there is a significant difference in the required level of oxidation. The first stage is less oxidizing so that low copper can be produced, while the second stage is strongly oxidizing so that iron and sulfur can be sufficiently removed from blister.

The Mitsubishi process is a relatively recent development and utilizes three separate furnaces. In the first furnace, concentrates are dispersed in air jets which impinge against the surface of the melt, and are smelted and partially converted to approximately a 60-65% Cu matte. This matte then flows into a second furnace and is converted by air lances, while the slag is treated pyrometallurgically in an electric furnace. The basic elements of the Mitsubishi process are similar to those of the flash smelting process, with the exception that the three furnaces are interconnected and transfer of slag and matte between them is by gravity flow (Treilhard 1973).

One of the most important features of the Mitsubishi process is the simplicity of the design, construction, and operation. Furnaces are all stationary-type. Driving mechanisms such as tilting of the furnace, tuyere punching, and hood driving, which are all necessary for conventional converters, are not required. Molten products are transferred by gravity to the next furnace through a launder, thus not requiring big ladles or a crane system. Molten products overflow continuously through the outlet hole of the furnace. Therefore, such operations as matte tapping and slag skimming, which are inevitable in conventional practices, are not necessary, thus making the furnace operation easy and simple.

Figure 15 illustrates in generalized form the flowsheet of the new smelter at Timmins in Canada which will utilize the Mitsubishi smelting furnace in the treatment of copper concentrates.

Figure 15

Table 4 lists the salient features of each principal piece of pyrometallurgical equipment found in Figure 8, and Figures 16 through 27 pictorially and illustratively show the major equipment items.

Table 4, Figures 16-27

4.3.6 Possible Applications

It is appropriate here to give an overview of the possible applications of the pyrometallurgical technology discussed above to the resource found in Minnesota, in order to recover copper, nickel, cobalt, and precious metals in marketable form. It is important to realize that the resource poses unique problems in that copper is present in much larger amounts than the other metals and will dominate the choice of recovery processes. The principal product material flow will consist of copper which will most likely move through a fairly conventional process of smelting to a high grade matte, converting to blister copper, with subsequent conventional fire and electrolytic refining, which are discussed in the next section. The recovery of the precious metals, Au, Ag, Pt, and Pd will take place in the electrolytic copper refinery according to standard procedures.

Against this dominant process flow, a variety of possibilities exist for recovery of the nickel and, secondarily, of the cobalt. As discussed earlier, these processes are conveniently divided into approaches using a bulk flotation con-

FIGURE 15

MITSUBISHI PROCESS SMELTER FLOWSHEET

(SOURCE: AMSDEN ET AL, 1978)

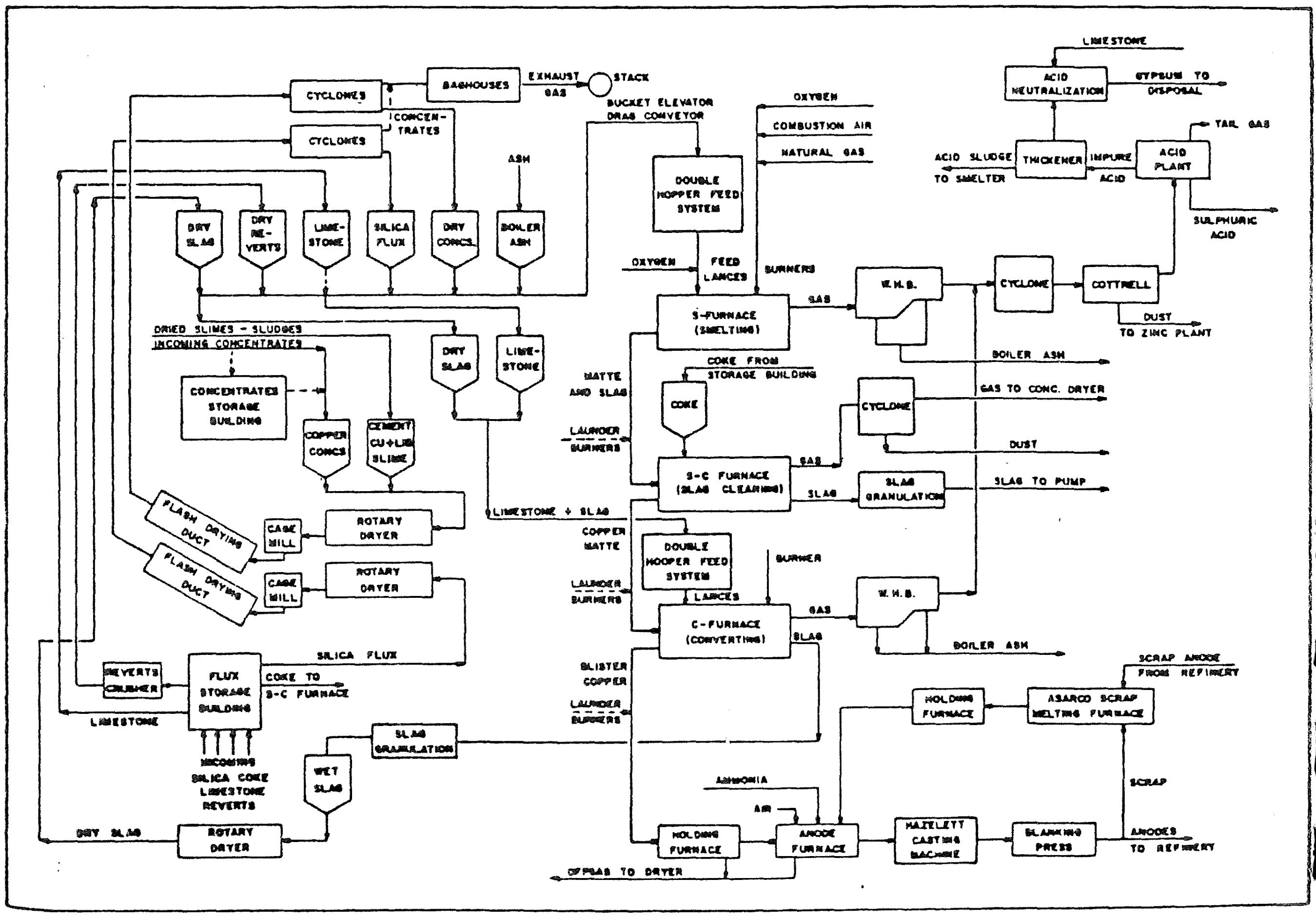


Table 4. Salient features of pyrometallurgical equipment and apparatus (values shown in this table are intended merely to be representative of typical operating practice).

APPARATUS AND DESCRIPTION	CAPACITY	GAS GRADES	MAJOR DISADVANTAGES	MAJOR ADVANTAGES
Multiple Hearth Roaster				
Cylindrical-brick-lined vessel approx. 6 m diameter; 15 m height	100-500 tpd concentrate	2-6% SO_2	More expensive to operate in comparison to other calcining operations. Calcine carryover of 6% in outlet gases.	
Fluid Bed Roaster				
Cylindrical-refactory-lined steel shell approx. 7 m diameter; 6 m height	200-1600 tpd concentrate		Processing difficulties result if gas velocity drops Excessive calcine carryover of 80% in outlet gases.	No moving parts in the combustion chamber. High SO_2 concentration in off-gases. Uniform bed temperature and composition are maintained in the fluid bed. Little excess air is required.
Conventional Blast Furnace				
Rectangular in plan with vertical sides at the top, inwardly sloping sides in the center section, and a vertically sided hearth at the bottom. 1.5 m x 7 m x 5 m	250-1300 tpd concentrate	approx. 5% SO_2	The blast furnace is unable to treat finely ground flotation concentrates.	The blast furnace has a high productivity rating the typical blast furnace uses a relatively small amount of fuel.

Table 4 continued.

APPARATUS AND DESCRIPTION	CAPACITY	GAS GRADES	MAJOR DISADVANTAGES	MAJOR ADVANTAGES
Reverberatory Furnace				
A long horizontal furnace with a roof designed to reflect flame down onto a charge on the hearth.	1200-1600 tpd concentrate	.5-1.0% SO_2	Thermal efficiency of the reverberatory is lower than certain other furnaces.	Furnace possesses flexibility with respect to feed.
36-46 m long; 9-12 m wide			Low SO_2 concentration in off-gas makes treatment difficult.	Capable of handling large tonnages of hot charge per day.
High temp. 1400-1700°C Tapping temp. 1100-1300°C				
Gas temp. 1100°C				
Electric Furnace				
Rectangular in cross-section with a firebrick spring-arch roof and a basic-brick inverted-arch bottom.	500-1400 tpd concentrate	2-8% SO_2	High hydrostatic heads attributable to deep layered slags constitute a definite furnace operating hazard.	It is completely versatile and can be used to smelt any and all materials. It produces small volumes of effluent gas
			Bath runaways are a major hazard.	
			Copper matte is more difficult to produce than nickel matte.	
			Furnace makes little use of the energy which is potentially available from oxidizing the sulfide minerals of the charge.	The SO_2 concentration of its effluent gas is readily controlled by adjusting the amount of air which is infiltrated into the furnace.
			The operating costs tend to be high due to the high price of electrical energy.	It makes efficient use of electrical energy.

Table 4 continued.

APPARATUS AND DESCRIPTION	CAPACITY	GAS GRADES	MAJOR DISADVANTAGES	MAJOR ADVANTAGES
Flash Furnace (INCO) (autogenous)				
Small hearth-type furnace using high purity oxygen for combustion. approx. 16m X 6m X 4.5m	1500-1600 tpd	75-80% SO_2	Slags are too high in copper content to be discarded. Additional treatment is needed for both flash furnace slag and converter slag.	It has much lower overall energy requirement. Its volume of effluent gas (per tone of charge) is small due to absence of nitrogen and hydrocarbon combustion products, which means that its gas-collection equipment requirement is small. The SO_2 concentration in its effluent gas is very high (80%) which simplifies SO_2 removal as sulfuric acid, liquid SO_2, or elemental sulfur. Dust losses are low due to a relatively small volumetric gas-flow rate. Its productivity (tons of charge per day/m^2 of hearth area) is approximately 30% higher than that of the Outokumpu process.

Table 4 continued.

APPARATUS AND DESCRIPTION	CAPACITY	GAS GRADES	MAJOR DISADVANTAGES	MAJOR ADVANTAGES
Flash Furnace (Outokumpu) (not autogenous)				
Requires 1/2 the fuel of an equivalent (dry) reverberatory smelting process. approx. 20m X 7m X 3m	1200-1900 tpd concentrate	10-14% SO_2	Slags are too high in copper contents to be discarded. An additional electric furnace is needed to treat both flash furnace slag and converter slag.	Its small physical size supports a large thrughput. It is very economical in its use of fuel, the greater portion used for air heating, and therefore of low quality. The gas produced is a good feedstock for an acid plant. Direct production of elemental sulfur in the flash-smelting emission system is being developed.
Pierce-Smith Sideblown Converter				
Cylindrical steel vessel lined with basic refractory bricks. approx. 4m diam; 9m length	100-200 tpd blister copper	2-9% SO_2	Relatively low concentration of SO_2 in outlet gas. Difficult to control fugitive SO_2 emissions.	Very efficient as a smelting machine under certain modified conditions.
Hoboken Horizontal Syphon-Type Converter				
approx. 4 m diameter; 11.5 m length	50-200 tpd blister copper	8-13% SO_2	Capital costs higher than Pierce-Smith converter, but not when emission control costs are included.	Higher SO_2 gas concentration makes acid plant operation more efficient. Design reduces fugitive SO_2 emissions considerable.

Table 4 continued.

APPARATUS AND DESCRIPTION	CAPACITY	GAS GRADES	MAJOR DISADVANTAGES	MAJOR ADVANTAGES
<u>Mitsubishi Process</u> (continuous)				
3 separate furnaces in a gravity flow relationship	500-1500 tpd concentrates	12-15% SO_2	The Mitsubishi process may not be suitable for treating high impurity concentrates. Concentration of impurities in the blister copper is likely to be high. The multi-step Mitsubishi process produces SO_2-bearing gas in each of its 3 furnaces and a more extensive gas-collection system is required.	The system facilitates pollutioncontrol, all exit gases have an SO_2 content greater than 10% which will which will permit recovery of sulfur as sulfuric acid. Capital investment is 70% of that needed to build a conventional smelter. Operating costs are reduced due to a smaller work force. Blister copper requires relatively little fire refining due to its relatively low (0.1-0.9%) sulfur content. Slag recycle to the melting furnace is kept to a minimum by the small production of slag.

Table 4 continued.

APPARATUS AND DESCRIPTION	CAPACITY	GAS GRADES	MAJOR DISADVANTAGES	MAJOR ADVANTAGES
Noranda Process (continuous)				
Horizontal cylindrical furnace with a raised hearth at one end, and a depression near the middle in which the copper collects. approx. 4 m diameter; 18 m length	800-1600 tpd concentrate	6-7% SO_2	The sulfur content of Noranda process blister copper (1-2%) is considerably higher than that of conventional converter copper and hence requires more air and an oxidation period in the anode furnace. The Noranda process may not be suitable for treating high impurity concentrates. (Concentration of impurities in the blister copper is likely to be high.)	The process takes advantage of energy released during the converting reaction to offset supplemental fuel requirements for the smelting reaction.
Top-Blown Rotary Converter				
Canted cylindrical steel vessel, refractory lined and capable of continuos rotation. approx. 3 m diameter; 5 m length	50-150 tpd blister copper	approx. 50% SO_2	Multiple units are required for large capacity operations due to the small size of each unit. The capital costs are higher for Pierce-Smith Converter. Maintenance costs are high.	The unit is versatile and may be used for smelting, converting, slag cleaning, and fire refining. The tight hood design minimizes air leakage and results in high SO_2 gas concentrations for easier emission control.

FIGURE 16

CUTAWAY VIEW OF A MULTIPLE HEARTH ROASTER

(SOURCE: BISWAS 1976)

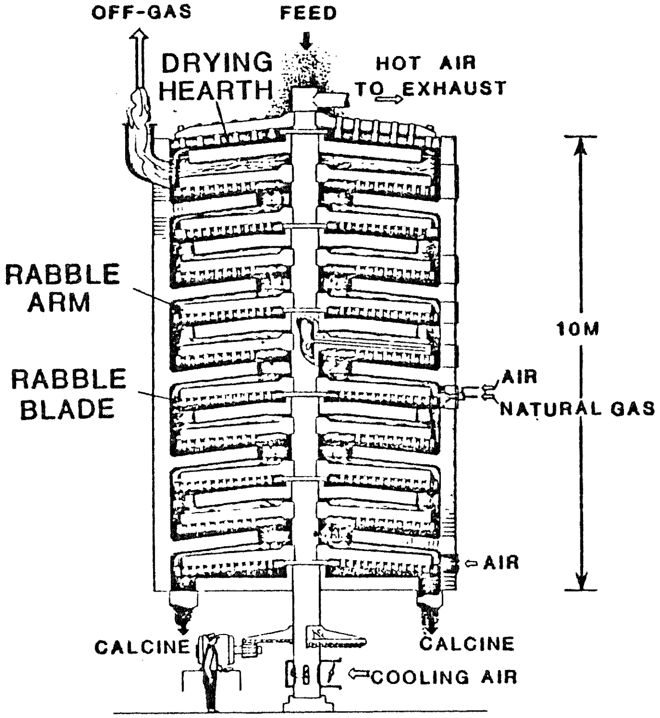


FIGURE 17

CUTAWAY VIEW OF A FLUID-BED ROASTER

(SOURCE: BISWAS 1976)

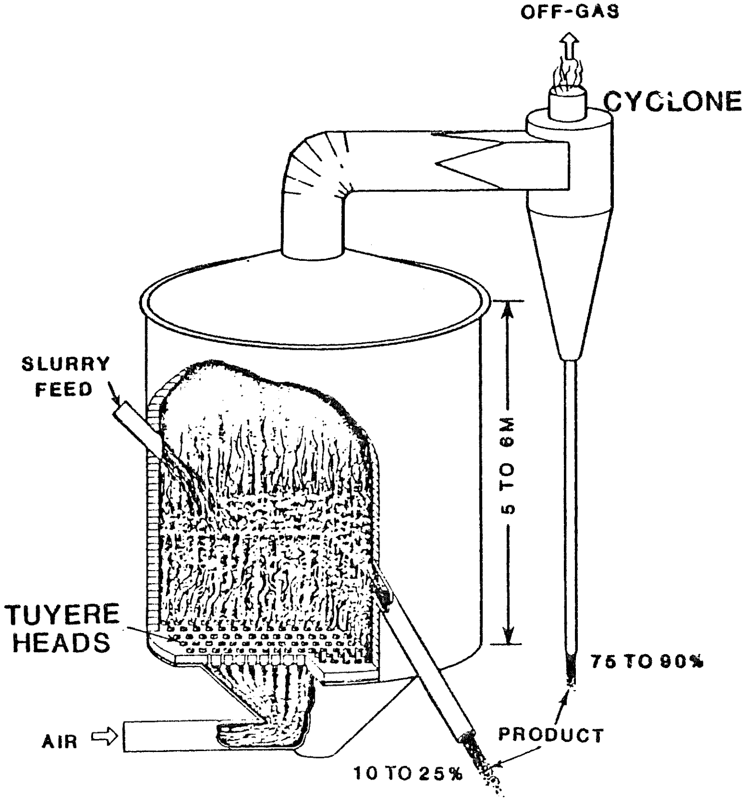


FIGURE 18

CUTAWAY VIEW OF A BLAST FURNACE FOR PRODUCING COPPER MATTE FROM SULFIDE ORES

(SOURCES: BISWAS, 1976, BOLDT, 1967)

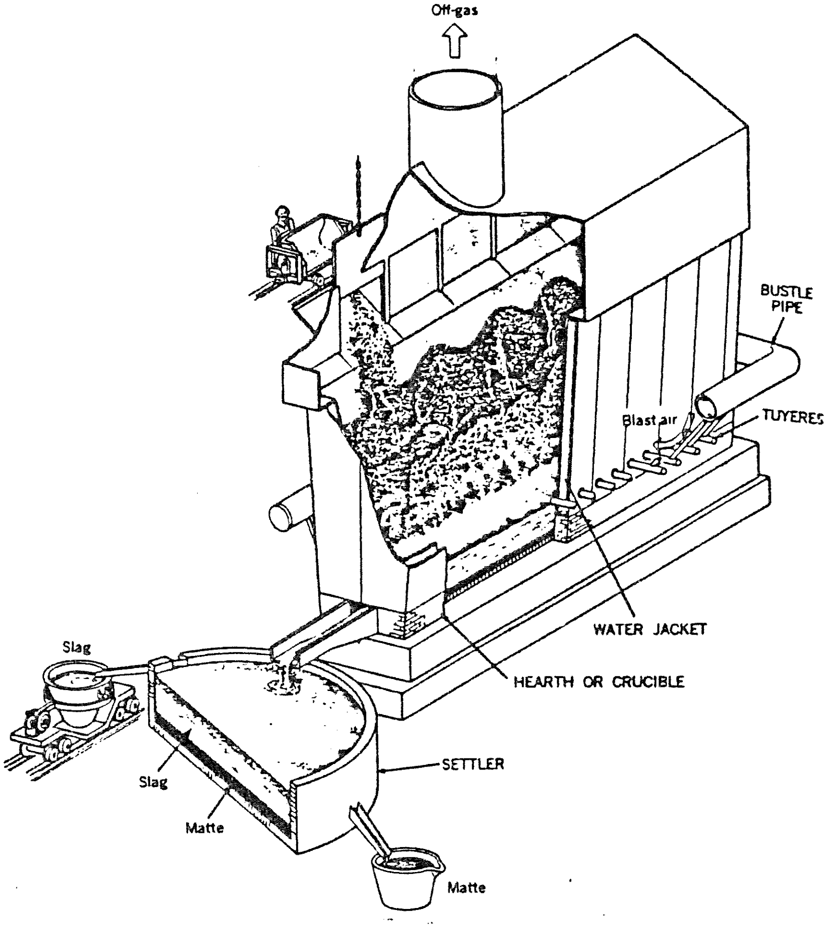


FIGURE 19

CUTAWAY VIEW OF A REVERBERATORY FURNACE FOR THE PRODUCTION OF COPPER MATTE FROM SULFIDE CONCENTRATES OR ROASTED CALCINES

(SOURCE: BOLDT, 1967)

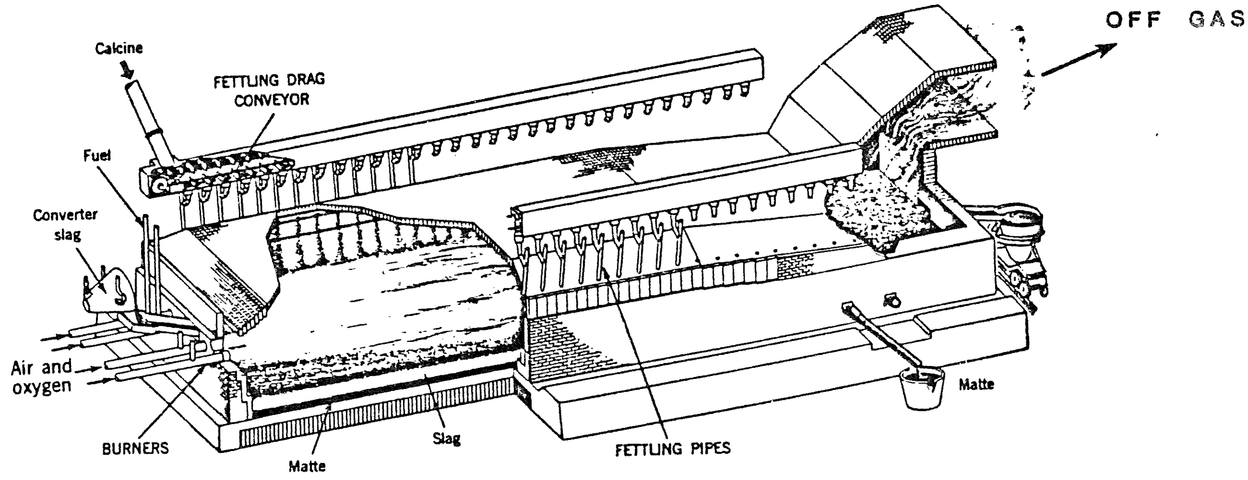


FIGURE 20

CUTAWAY VIEW OF A SUBMERGED ARC ELECTRIC FURNACE FOR THE PRODUCTION OF MATTE FROM DRY SULFIDE CONCENTRATES OR ROASTED CALCINES

(SOURCE: BOLDT, 1967)

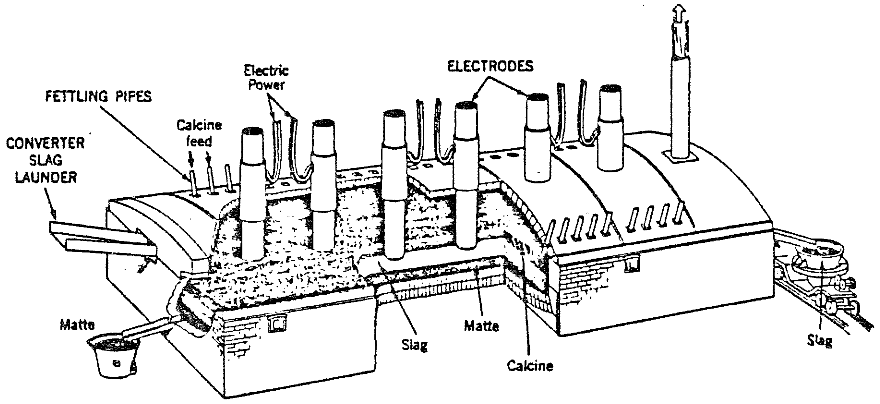


FIGURE 21

CUTAWAY VIEW OF AN INCO OXYGEN FLASH SMELTING FURNACE

(SOURCE: BOLDT, 1967)

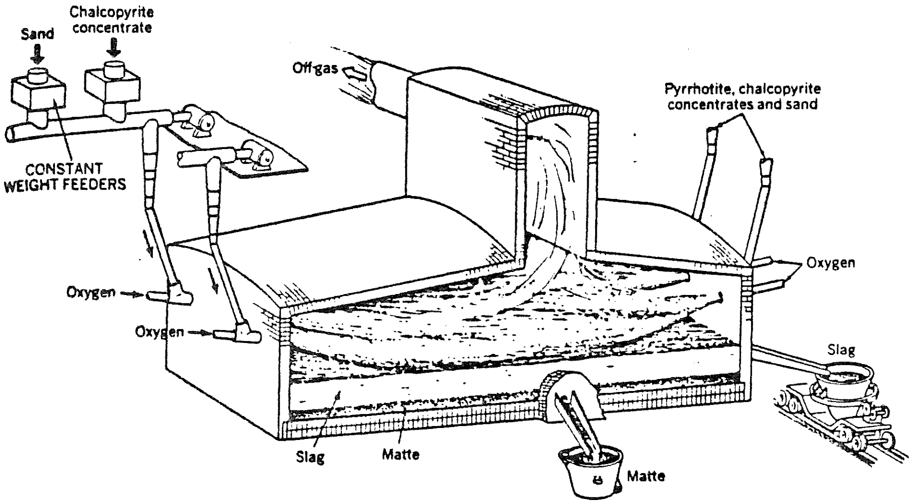


FIGURE 22

CUTAWAY VIEW OF AN OUTOKUMPU FLASH SMELTING FURNACE

(SOURCE: BOLDT, 1967)

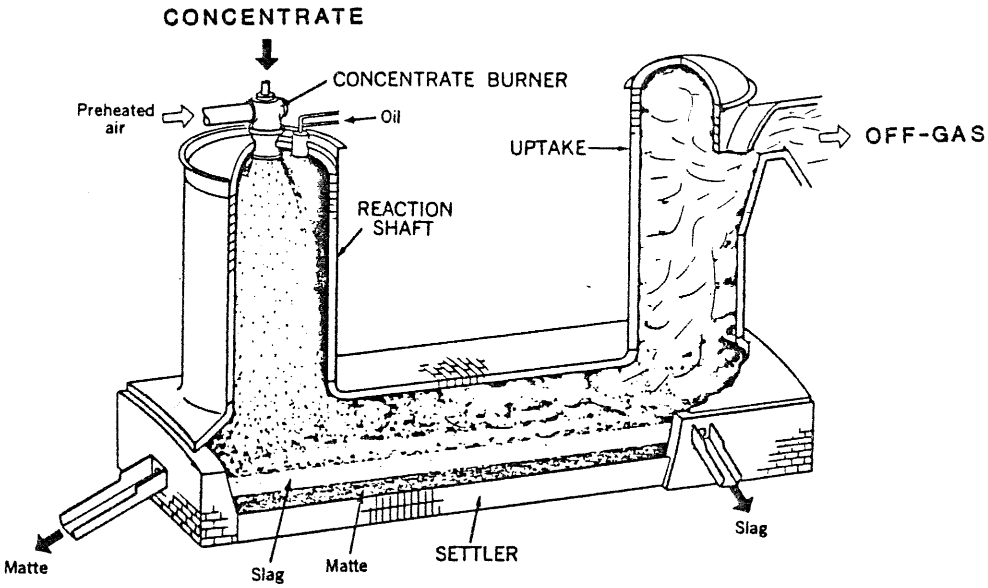
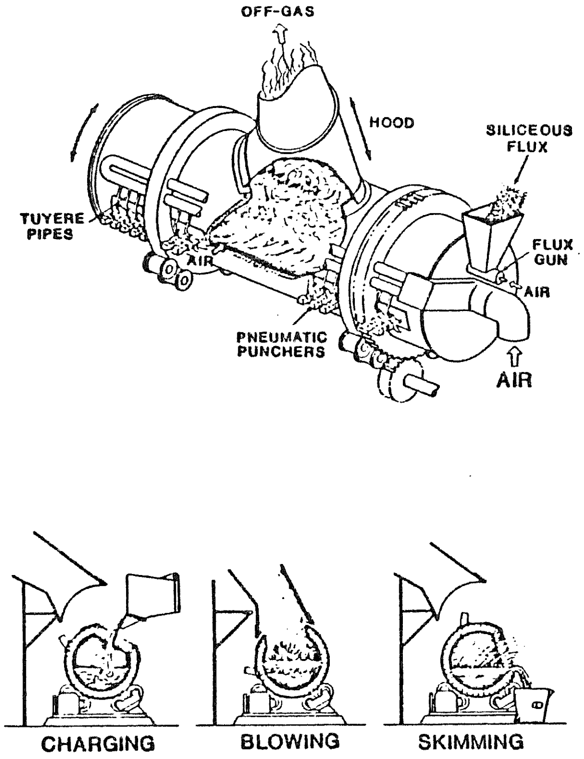


FIGURE 23

CUTAWAY VIEW OF A HORIZONTAL SIDE-BLOWN PIERCE-SMITH CONVERTER FOR PRODUCING BLISTER COPPER FROM MATTE

(SOURCES: BISWAS, 1976, BOLDT, 1967)



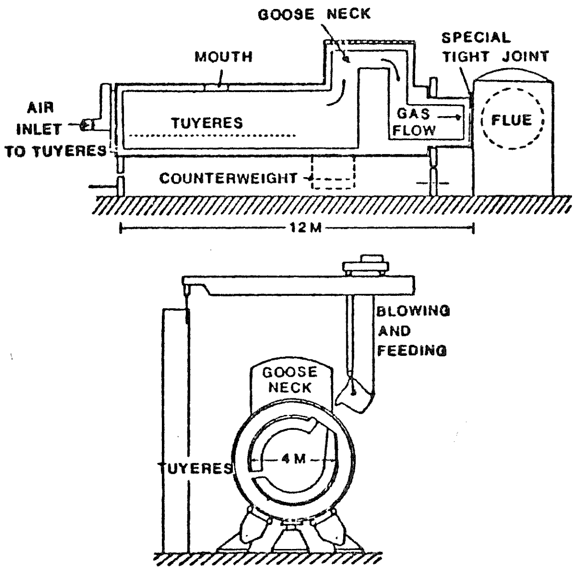
CHARGING BLOWING SKIMMING

FIGURE 24

END AND SIDE VIEW OF THE HOBOKEN OR "SYPHON" CONVERTER

(SOURCE: BISWAS, 1976)

LONGITUDINAL SECTION



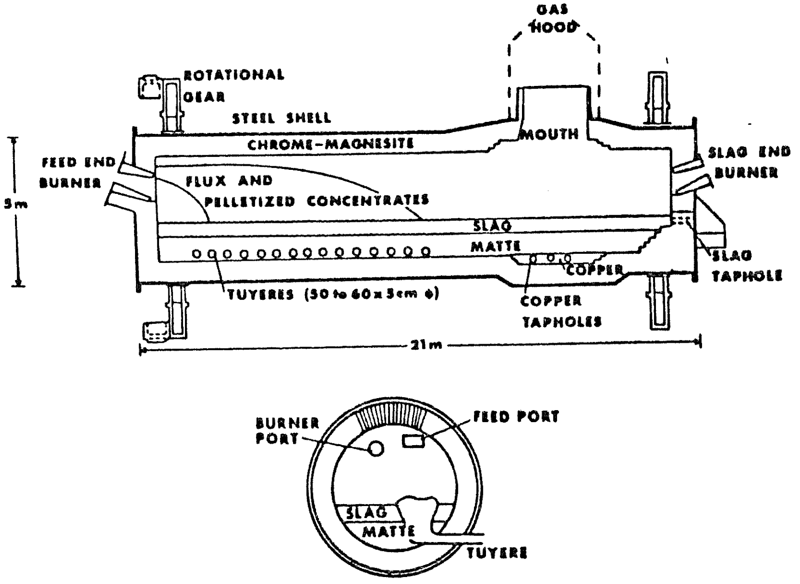


FIGURE 25

SCHEMATIC LONGITUDINAL AND END VIEWS OF THE INDUSTRIAL NORANDA SINGLE-STEP REACTOR

(SOURCE: BISWAS, 1976)

FIGURE 26

SCHEMATIC PLAN AND ELEVATION VIEWS OF THE MITSUBISHI CONTINUOUS SMELTING SYSTEM

(SOURCE: BISWAS, 1976)

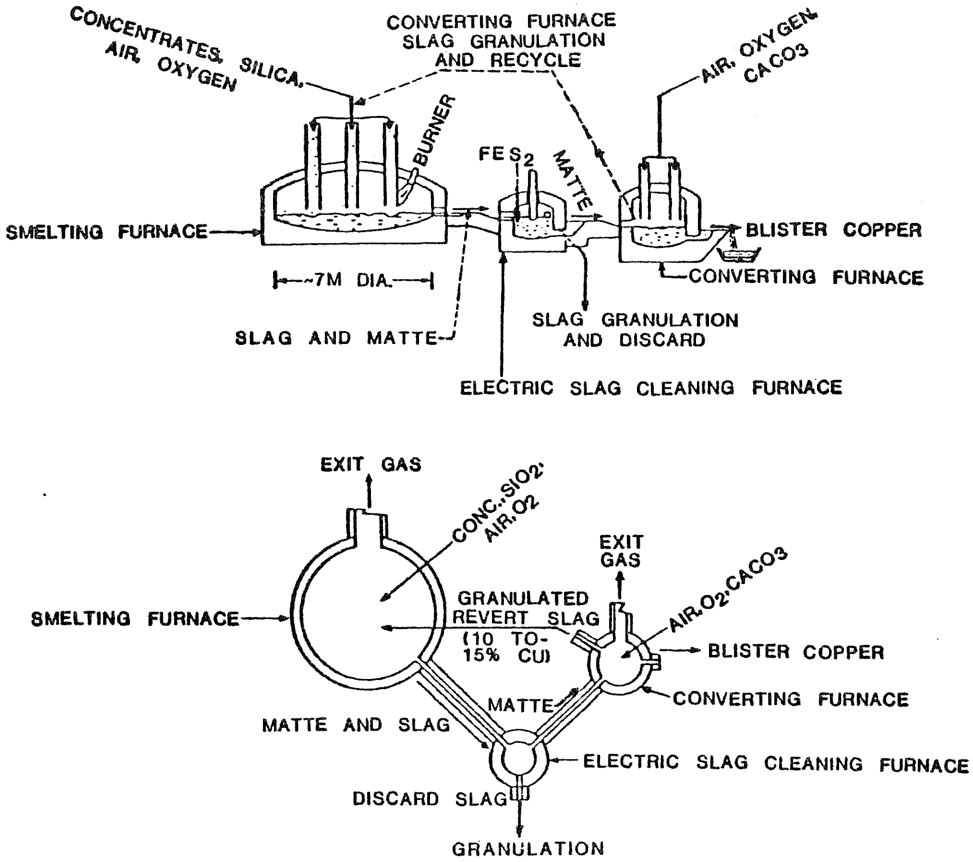
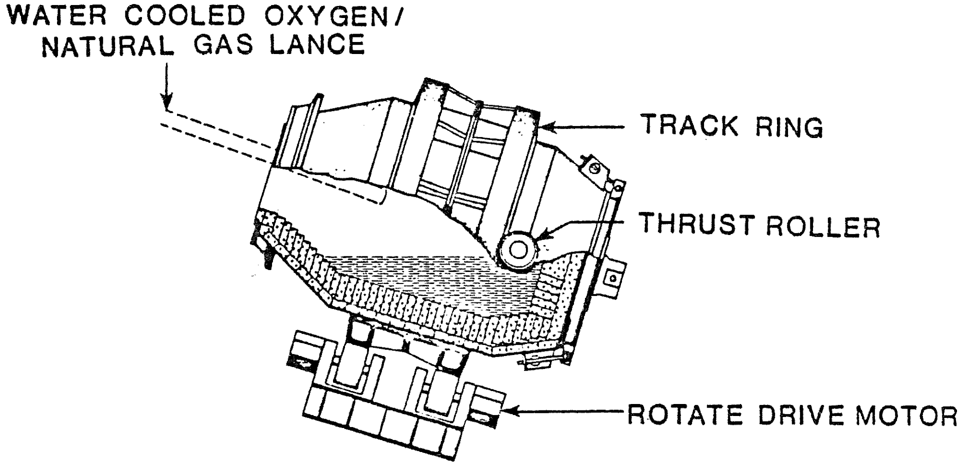


FIGURE 27

CROSS-SECTION OF A TOP BLOWN ROTARY CONVERTER FOR COPPER MATTE CONVERTING

(SOURCE: BISWAS, 1976)



(VESSEL IS SHOWN IN BLOWING AND ROTATING POSITION) centrate on the one hand, versus those using a selective or differential flotation scheme to produce 2 distinct concentrates on the other hand (see Figure 4).

4.3.6.1 Case 1: Bulk Flotation--Here the problem of physically separating the great portion of the copper from the nickel is solved in the smelter/refinery complex. Initially, a single matte is produced using any one of a number of possible smelting techniques. One method for separating the nickel at this point may be to slowly cool the matte, then crush, grind, and separate the bulk of the copper from the nickel by flotation. This method is used by Inco at Copper Cliff. However, the process is unproven on mattes of the low nickel content expected here, so that the application of this method is questionable. An alternative separation method makes use of the fact that cobalt and nickel both have a higher affinity for oxygen than does copper. Following iron, they are oxidized during slagging in both the smelting and converting operations. This explains the fact that approximately 50% of the cobalt in the concentrate is expected to be lost in the slag. However, the remainder, along with the bulk of the nickel should be recoverable in a nickel-copper matte. This matte is produced in one or more slag cleaning furnaces where trapped sulfides are settled from the slag, and cobalt and nickel oxides are reduced and recovered in the matte. The result of this approach is a blister copper devoid of significant cobalt or nickel, and a nickel-copper matte containing comparable amounts of both metals. This matte contains the recoverable cobalt and is suitable for metal recovery by proven hydrometallurgical methods or by using the slow cooling-granulation method of Inco.

4.3.6.2 Case 2: Selective or Differential Flotation--The possibilities here are clearly seen in light of the previous discussion. The copper concentrate will follow a conventional flowsheet. Any residual nickel which goes with the blister may be recovered in the electrolytical refinery. Any cobalt will go to the slag, along with a portion of the nickel. The matte produced in slag cleaning can be sent to the circuit treating the nickel-copper concentrate for further processing. The nickel-copper concentrate will be smelted in a separate furnace and treated by slow cooling and matte granulation, or by hydrometallurgical methods as noted earlier. The recoverable cobalt will move with the nickel and likely be recovered as a cobalt hydroxide precipitate in the nickel refinery, as discussed in the following section.

4.4 REFINING PRINCIPLES AND PRACTICES

Blister copper is an impure intermediate product in the refining of copper, produced by blowing copper matte in a converter, the name being derived from the large blisters on the cast surface that result from the liberation of SO_2 and other gases. The blister coming from converting often has a composition which falls into the ranges listed in Table 5.

Table 5

The comparable nickel product must be derived from the nickel-copper matte discussed earlier, probably by slow cooling, with subsequent matte granulation and flotation, or by selective leaching to dissolve the copper prior to the production of Ni anodes. These anodes, based on data from Canadian operations have a typical composition which falls into the following ranges (Boldt 1967):

ELEMENT	Ni ANODES (range of percent)
Cu	4 - 17
Fe	0.8 - 2
Ni	76.5 - 93.5
Co	1 - 1.4
S	0.6 - 1.4
Pb	0.01 - 0.05
As	0.05 - 0.5

Copper and nickel from the converting stage must be subjected to a refinery process in order to remove the various impurities present. Generally speaking, there are 2 methods of refining, pyrometallurgical and electrolytic. With the

Table 5. Representative analyses of blister copper.

ELEMENT	BLISTER COPPER (Range of Percent)
Cu	-7.5 - 99.5
Fe	0.01 - 0.1
Ni	0.1 - 0.5
S	0.03 - 0.3
Zn	0.0 - 0.03
Pb	0.05 - 0.26
Sb	0.0 - 0.3
As	0.0 - 0.12
Sn	0.0 - 0.1
Bi	0.0 - 0.05
Se	0.0 - 0.1
Te	0.0 - 0.1
O	0.0 - 0.1
Ag	0.0 - 0.1
Au	0.0 - 0.005

pyrometallurgical process it is only possible to obtain low grades of copper and nickel, since the impurities are not completely removed in the process. In order to remove the impurities most completely and to recover the valuable elements, the crude metals must be subjected to both forms of refining. Figure 28 presents a generalized flow diagram showing both fire and electrolytic refining of blister copper (EPA 1975).

Figure 28

4.4.1 Fire Refining

In fire refining, purification principally to remove sulfur and oxygen is carried out in rotary-anode refining furnaces resembling Pierce-Smith converters, or in small hearth furnaces. The temperatures of operation are approximately 1130 to 1150°C which provides sufficient superheat for the subsequent casting of anodes. There is very little heat produced by the refining reactions. Therefore, some combustion fuel such as natural gas is necessary to maintain the temperature of the furnace.

The essential reaction for the removal of dissolved sulfur by air in the case of copper refining is:

$$[S]_{Cu} + O_2(g) = SO_2(g) + Cu$$

while simultaneously oxygen is dissolving in the copper by the reaction:

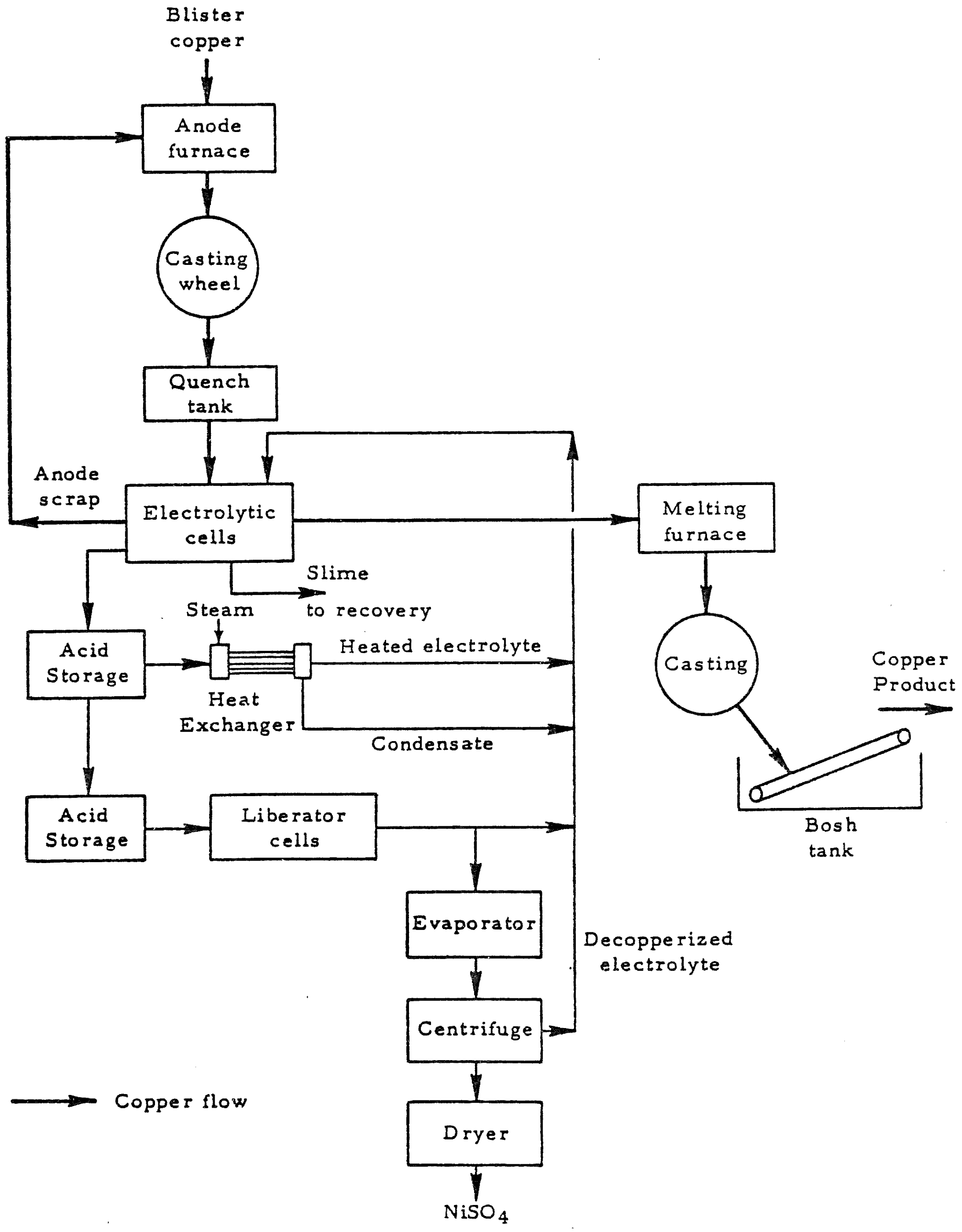
$$Cu + O_2(g) = 2[O]_{Cu} + Cu$$

The oxygen in the desulfurized metals is then reduced and removed from the molten copper with hydrocarbons such as natural gas (CH_4), reformed natural

FIGURE 28

GENERALIZED FLOW DIAGRAM SHOWING BOTH FIRE AND ELECTROLYTIC REFINING OF BLISTER COPPER

(SOURCE: EPA, 1975)



gas ($CO + H_2$), propane (C_3H_8), or wood, producing carbon monoxide, carbon dioxide, and water as residual products from the chemical reactions.

In the past, a final metal product, anodes (special shaped metal slabs, resulting from the refinement of converter products) was produced by fire refining in this manner. However, many impurities, such as nickel, cobalt, and precious metals, are not removed by this technique and the product must undergo electrorefining to meet the standards of purity required by many modern consumers of copper (Biswas 1976).

4.4.2 Electrorefining

The electrorefining of copper consists of the electrochemical dissolution of copper from the impure anodes and the plating of pure copper, without anode impurities, onto copper cathodes. The electrolyte is generally an aqueous solution of H_2SO_4 and $CuSO_4$, usually with a trace amount of chlorine. Many of the anode impurities such as silver, gold, bismuth, lead, platinum, and tin are insoluble in this electrolyte and do not interfere with the electrolysis. Other impurities such as arsenic, iron, and nickel are partially or fully soluble and must be kept to a low concentration in the electrolyte to prevent them from being occluded with the copper on the cathode, thus contaminating it. This is accomplished by continuously bleeding part of the electrolyte through a purification circuit (Biswas 1976). As noted earlier, no significant amount of cobalt is present in the copper anodes, since it has been oxidized and removed with the slag during smelting and converting.

Typical anode-to-cathode voltages are 0.20 to 0.25 v at current densities of 200 a/m^2 of cathode.

The energy required to deposit one metric ton of copper is given by the equation

$$W(\text{KWH/mt cathode copper}) = \frac{V \times 8.4 \times 10^5}{1000^* \times CE/1000} \text{ (ampere hours/mt copper)}$$

(*-conversion to kilowatts)

Refer to Table 6 for symbol identification.

Table 6

The equation shows that the energy requirement is directly proportional to the applied voltage and inversely proportional to the current efficiency (Biswas 1976).

An example energy calculation using a typical operating voltage of 0.25 v and a current efficiency of 95% gives the energy requirement as 225 KWH/mt of cathode. This energy is for DC current so that the actual energy requirement must be divided by the AC/DC energy conversion efficiency which industry-wide is approximately 0.95. Thus, the energy (AC) employed directly in the electrolysis per metric ton of cathode copper is approximately 240 KWH (Biswas 1976; Ettel 1977).

The total electrical energy (AC) used in a copper-refinery tankhouse for all functions, machinery, electrolyte purification, and general use as well as electrolysis, is in the order of 275-350 KWH/mt of cathode copper (Biswas 1976; Ettel 1977).

Copper and nickel can also be recovered in marketable form by electrowinning from strong leach solutions or from the electrolytes produced by solvent-extraction techniques which are discussed later. Electrowinning is similar to

Table 6. Symbols used in copper refining, their meaning, and units.

SYMBOL	MEANING	UNITS
F	Faraday's constant, 96,500 coulombs. Faraday's Law states that 96,500 coulombs will theoretically plate 1 gram equivalent weight copper (or any metal). In the case of the reaction $Cu^{2+} + 2e^- \rightarrow Cu^o$ this is equal to 3.0×10^3 coulombs per gram or 8.4×10^5 ampere hours per metric ton of copper	
CE	Current efficiency (cathode)[a] $= \frac{\text{Weight of Cu actually plated}}{\text{Weight of Cu expected by Faraday's Law}} \times 100$	% %
V	Voltage applied between the anodes and cathodes of a cell	Volts

---

[a] Anode current efficiency is the efficiency at which copper enters the electrolyte from the anodes. It is slightly higher (approx. 1/2%) than the cathode current efficiency.

electrorefining except that the anode is composed of an inert material, usually antimonial lead. The overall reaction for copper electrowinning may be written:

$$CuSO_4 + H_2O_{2V} \rightarrow Cu_{cathode} + 1/2O_{2\ anode} + H_2SO_4$$

Copper is produced at the cathode which is started on a copper base. Oxygen gas evolves at the anode, and sulfuric acid is regenerated for reuse as a leachant (Biswas 1976).

Electrowinning requires approximately ten times the voltage used in electrorefining, typically 2-2½ volts, and thus it uses considerably more electrical energy. Since the electrical energy per metric ton of cathode copper is directly proportional to cell voltage,

$$W = \frac{V \times 8.4 \times 10^5}{1000 \times CE/100}$$

it can be seen that the energy consumed in electrowinning is approximately 10 times that of electrorefining (2000-2500 KWH/mt DC energy, 2100-2700 KWH/mt ton AC energy)(Biswas 1976; Ettel 1977). In addition, the cathode product is less pure than electrorefined copper, mainly because of contamination from the lead anode which is not completely inert (Dasher 1976).

Most of the electrolytic nickel sold today is produced by electrolytic refining in a sulfate/chloride electrolyte using soluble anodes. The anodes are either of the metallic type or are cast from a sulfur-deficient nickel matte, in which case the process is often called electrowinning with a soluble anode. Smaller quantities of nickel are also produced by electrowinning from sulfate electrolyte using insoluble anodes and diaphragms (Dasher 1976).

The chief difference between the nickel refining and copper refining process is the need to use a neutral and therefore less conductive electrolyte with nickel, and also to employ a diaphram separating the pure catholyte from the impure anolyte. In the case of the sulfide anode process, there are also 2 other important differences. First, the process has a distinct thermodynamic energy requirement, as the anode and cathode reactions are not identical (Dasher 1976):

$$\mathrm{Ni_3S_2 = 3Ni^{+2} + 2S + 6e} \qquad E^o = 0.10V$$

$$\mathrm{Ni^{+2} + 2e = Ni^o} \qquad \underline{E^o = -0.25V}$$

$$E_{MF} = -0.35V$$

Secondly, the incomplete dissociation of the anode leaves a porous layer of elemental sulfur on the anode surface, causing a substantial ohmic potential loss, which increases during the life of the anode (Dasher 1976).

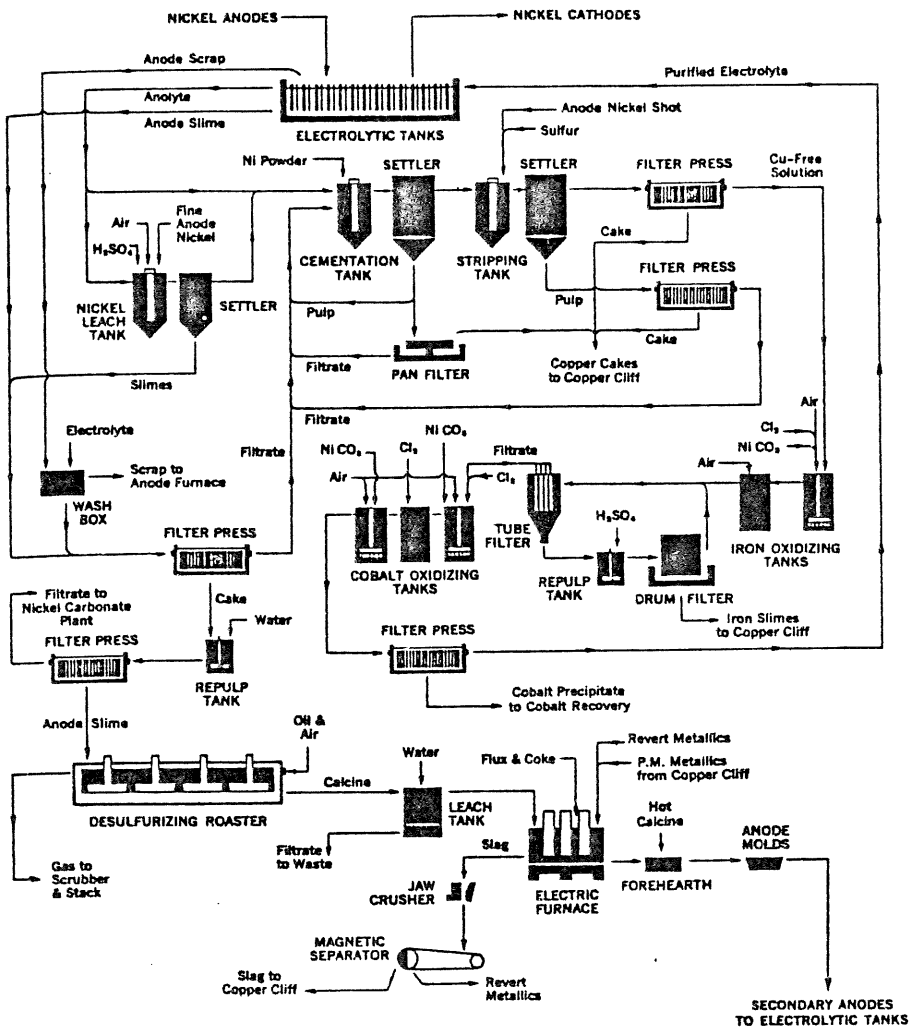
The electrorefining of nickel involves the dissolution of nickel and some of its associated impurities from the anode into the adjacent electrolyte (the anolyte). This solution is pumped from the refining cells, treated for removal of impurities, then returned to the cell as catholyte (the electrolyte adjacent to the cathode). Nickel from the catholyte is then deposited on the cathode (Boldt 1967).

The energy consumed in the electrorefining of metallic nickel anodes is approximately 1900 KWH/mt DC energy (2000 KWH/mt AC energy)(Ettel 1977). Figure 29 illustrates in generalized form INCO's Port Colborne nickel anode electrolysis operation where nickel is recovered from nickel anodes. Note the cobalt recovery from the anolyte. Cobalt is precipitated as cobaltic hydroxide and further processed to metallic cobalt.

Figure 29

FIGURE 29

FLOWSHEET OF PORT COLBORNE
NICKEL ANODE ELECTROLYSIS
(SOURCE: BOLDT, 1967)



Pure nickel cathodes may also be produced by electrowinning. Two different methods of electrowinning nickel are currently in use:

1) Electrolysis of soluble anodes of nickel sulfide, mentioned earlier.

2) Utilization of insoluble non-nickel anodes to extract nickel from a leach liquor.

Nickel sulfide anodes may be cast directly from low-copper converter matte or from melted nickel sulfide concentrate produced by the matte separation process. Controlled cooling is necessary to make anodes with satisfactory mechanical properties. The anodes are essentially Ni_3S_2.

Electrowinning with nickel sulfide anodes involves anodic reactions in which sulfur is oxidized to the elemental state accompanied by the release of metal ions into solution and electrons to the anode. The reaction is summarized below (Boldt 1967).

$$Ni_3S_2 = 3Ni^{+2} + 2S + 6e^-$$

The cathodic reaction is represented by:

$$3(Ni^{+2} + 2e^-) = 3Ni$$

and the net cell reaction is represented below as:

$$Ni_3S_2 = 3Ni + 2S$$

The energy consumed in nickel electrowinning where soluble sulfide anodes are used is approximately 3500 KWH/mt DC energy (3700 KWH/mt AC energy)(Dasher 1976). This is roughly twice the requirement when metallic anodes are used. Figure 30 illustrates in generalized form the Thompson refinery where nickel is recovered in cathode form from nickel sulfide anodes. Again, cobalt is recovered here as a precipitate.

Figure 30

Nickel electrowinning with insoluble anodes also provides a means of recovering the nickel metal from leach liquors. Since the nickel being extracted at the anode enters the electrolyte by a leaching reaction, the only function of the anodes is to transfer electrons to the external circuit for delivery to the cathode. For this reason the anodes are made of an insoluble material, such as antimonial lead, that has a long life in sulfate electrolytes. Thus, there is no need to cast and handle anodes or to collect tank slimes (Boldt 1967).

The energy consumed in nickel electrowinning where insoluble anodes are used is approximately 3700 KWH/mt DC energy (3900 KWH/mt AC energy). Figure 31 illustrates in generalized form the Outokumpu refinery at Harjavalta where nickel, copper, and cobalt are recovered from leach liquors using insoluble anodes. The leach liquors result from hydrometallurgical treatment of nickel-copper matte.

Figure 31

4.5 HYDROMETALLURGY PRINCIPLES AND PRACTICES

As was stated earlier, the processing of copper-nickel concentrates is readily accomplished in the nonferrous metals industry by treating the concentrates either pyrometallurgically or hydrometallurgically. For copper-nickel sulfide ores, pyrometallurgy is utilized extensively, with hydrometallurgy utilized to a lesser extent.

FIGURE 30

FLOWSHEET OF THOMPSON REFINERY

(SOURCE: BOLDT, 1976)

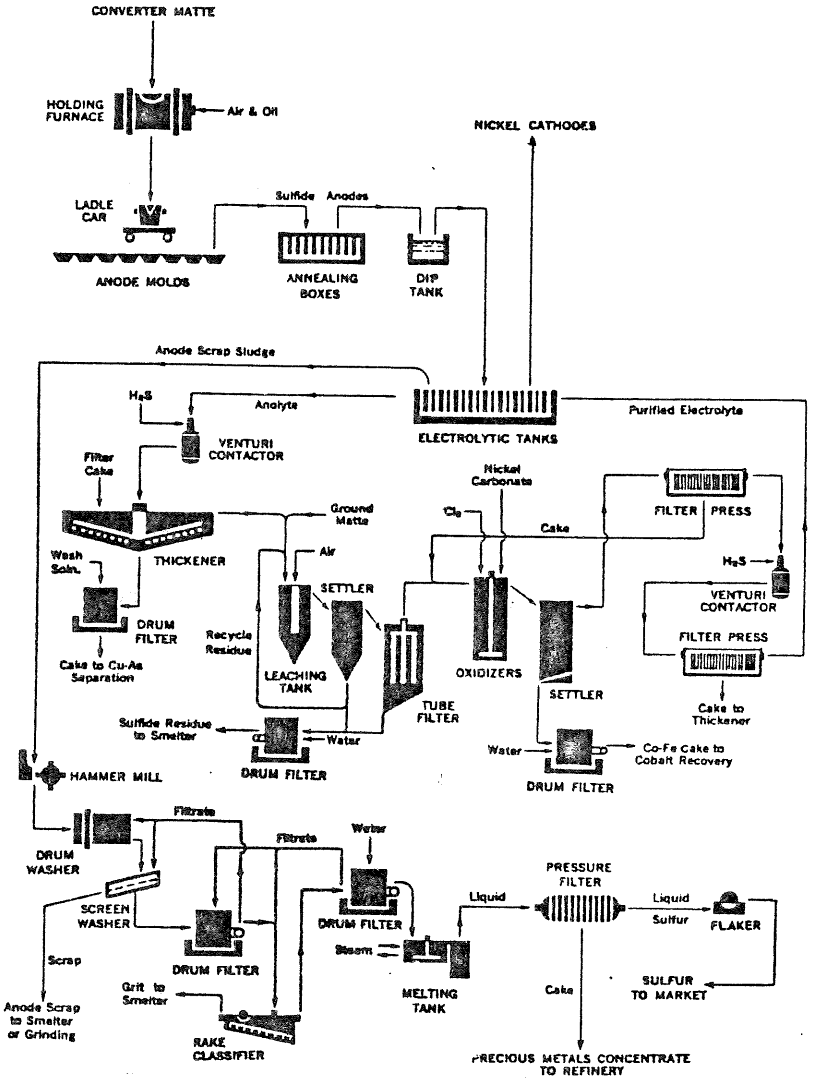
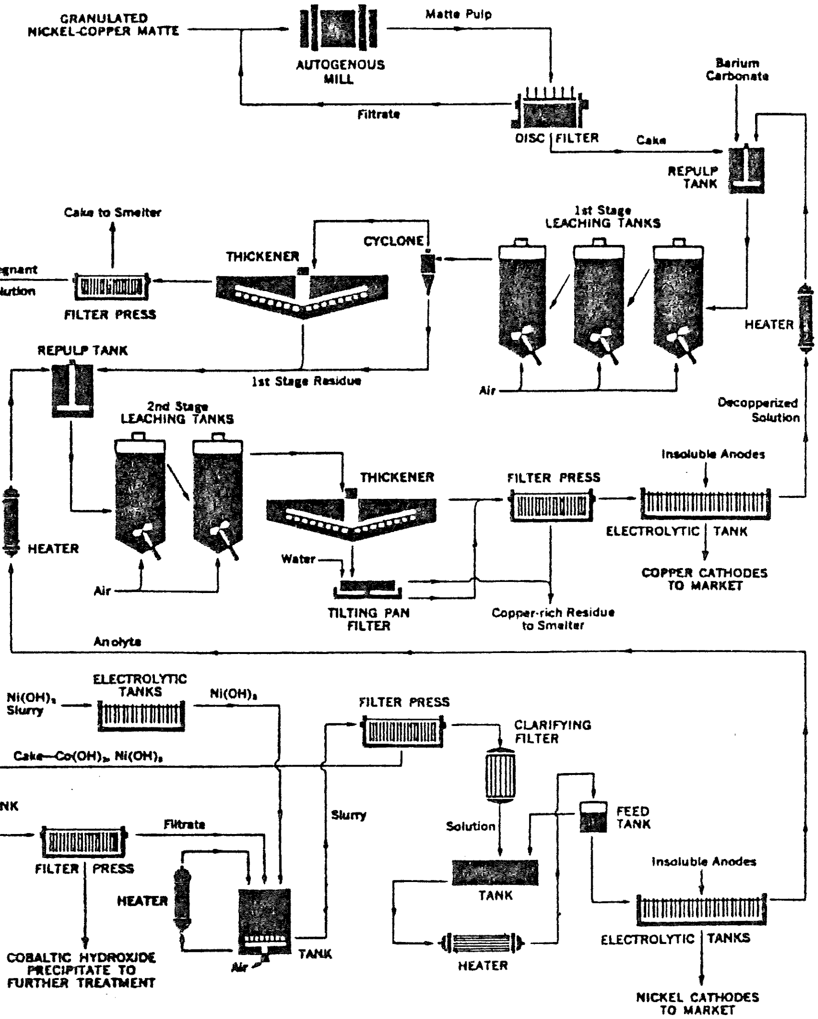


FIGURE 31

FLOWSHEET OF OUTOKUMPU REFINING OPERATIONS AT HARJAVALTA

(SOURCE: BOLDT, 1967)



Hydrometallurgy is the treatment of ores, concentrates, and other metal-bearing materials by aqueous solutions, usually involving the dissolution of some component, and its subsequent recovery from the solution. This process can be applied either to recover the desired metal directly from an ore by dump or heap leaching, or as an integral part of a complex metallurgical scheme to recover the desired metal by a combination of procedures. The former method will not be considered in detail here because physical properties such as density, porosity, and permeability do not appear to encourage the treatment of Minnesota copper-nickel material by direct leaching methods. Tables 7 and 8 generalize the major hydrometallurgical systems currently available for consideration, showing their reagent requirements and output products. Each system includes a primary leaching phase, with some utilizing an additional distinct leaching step.

Hydrometallurgy, as a secondary vertical stage in a complex metallurgical scheme to recover a desired metal, particularly nickel, by a combination of procedures, can be used to treat intermediate metallurgical products produced during smelting operations. Hydrometallurgical treatment in such cases is not considered to be the principal metal extraction method, and usually the operations are much smaller in size when compared with pure hydrometallurgical plants treating ores and/or concentrates. Leaching generally occurs in contained and controlled vessels or tanks under atmospheric as well as pressurized conditions. Hydrometallurgical treatment of this type generally follows smelting and converting operations, but precedes refining operations, such as electrowinning using insoluble anodes and nickel recovery from leach liquors.

Figure 31, shown previously, illustrates in generalized form the Outokumpu refining operations at Harjavalta where nickel and copper are recovered from leach liquors resulting from the hydrometallurgical treatment of granulated nickel-copper matte. Nickel and copper cathodes are produced for market. Cobalt is also recovered here.

Essentially, hydrometallurgy involves leaching, the feed material being treated with a solvent to dissolve the metallic mineral, leaving the gangue unaffected. After filtration from the gangue, the metal in the solution is recovered either by chemical precipitation or by electrolysis. It is essential that the metal be in a soluble form, often requiring preliminary treatment. To ensure efficient leaching, the feed must be of the proper size distribution. Hence, the first step is usually crushing.

Hydrometallurgical techniques are not yet highly developed, particularly for sulfur ores like those found in northeastern Minnesota. Many of the systems are in the pilot plant stage and most have not yet been proven to be efficient, economical, or successful on a large-scale commercial basis. The positive features of hydrometallurgical systems include:

1) gaseous sulfur emissions are negligible
2) costs are comparable with small scale pyrometallurgical processes
3) there is flexibility in handling different feedstocks

The principal negative features are:

1) dissolution rates are unsatisfactory
2) precious metals are difficult to recover
3) pollution control of solid and liquid waste is both difficult and costly
4) large quantities of water are required
5) the commercial potential of such systems is unknown

4.6 INTRODUCTION TO POLLUTION CONTROL IN SMELTING AND REFINING

All of the primary steps in the metallurgical processing of nonferrous minerals, whether pyrometallurgy and/or hydrometallurgy, emit materials to the environment either in a gaseous, liquid, or solid form.

In the case of a possible smelter/refinery complex treating Minnesota copper-nickel concentrates, the complex can be broken into 3 vertical operations possibly separated from each other by great distances if necessary. These are:

1) A copper-nickel smelter, including an acid plant operation, which treats copper-nickel concentrates to produce blister copper and nickel-copper matte, respectively.

2) A copper refinery which treats the blister copper to produce cathode copper of very high purity, as well as precious metals.

3) A nickel refinery which treats the nickel-copper matte to produce cathode nickel of high purity, cathode copper, possibly of high purity, various other nickel products, cobalt precipitates, and precious metals.

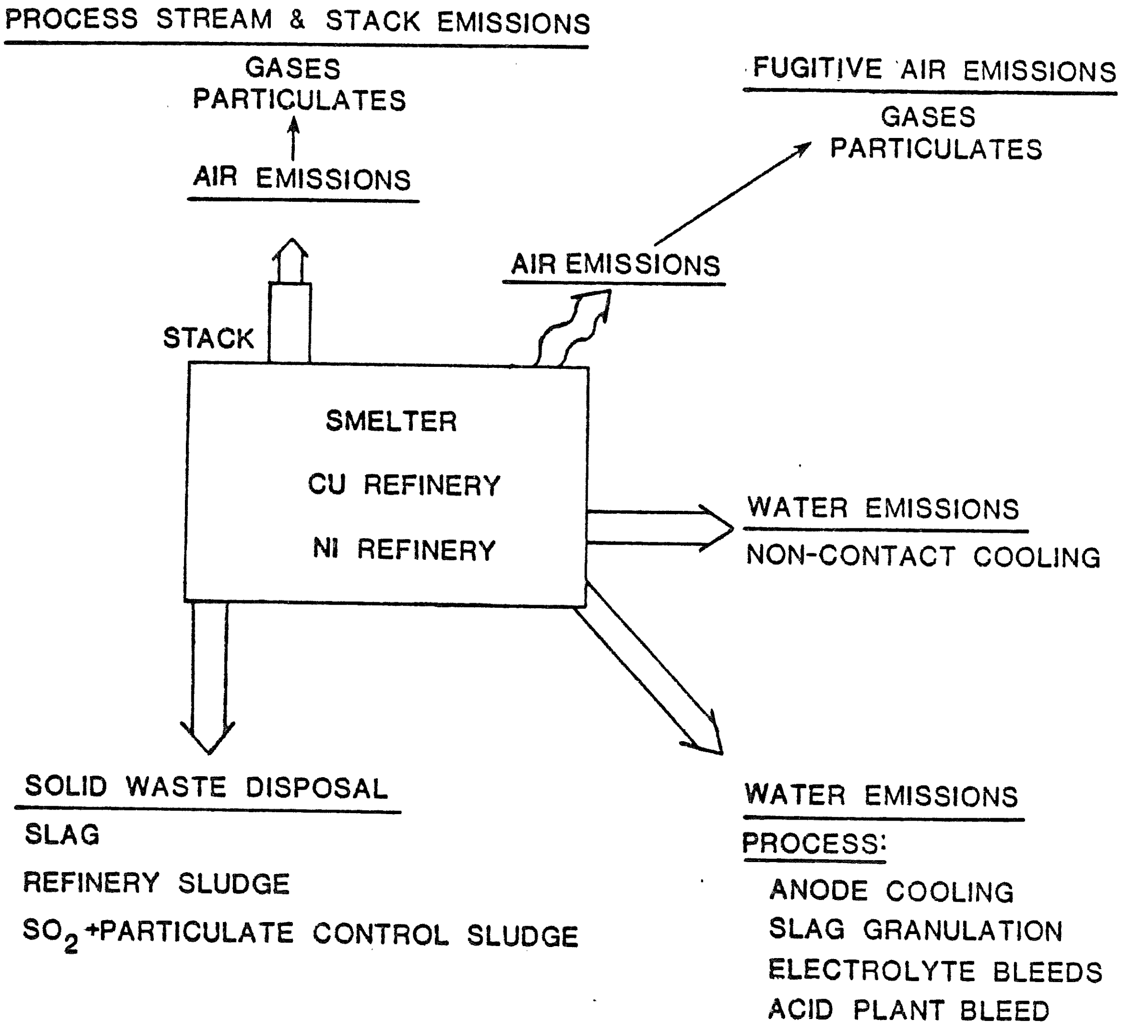
Each vertical operation can function by itself, hence each operation will represent a source for potential pollutants. These pollutants can all be placed into one of three categories; air emissions, solid waste products, or water emissions. See Figure 32 for a diagramatic summary of these emissions. Each of these emission types are briefly described below.

Figure 32

1) Air Emissions

FIGURE 32

OVERVIEW OF POSSIBLE ENVIRONMENTAL EMISSIONS FROM SMELTER AND REFINERY OPERATIONS

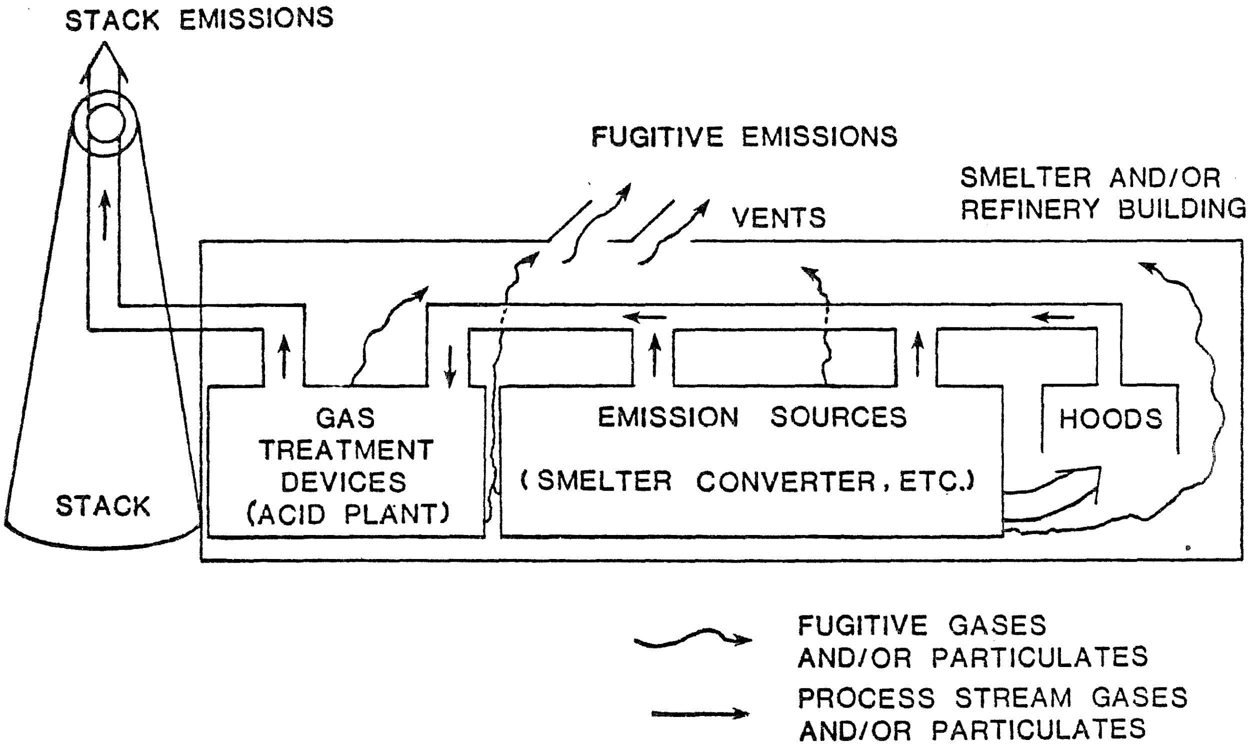


Emissions in this category can be broadly divided into 2 types, process stream stack emissions and fugitive emissions. Stack emissions are those constituents which originate as process air streams from various sources required by the smelter or refinery technology used. These process air streams are collected, combined, and ducted either directly to a stack for exit to the atmosphere or are first treated by various air pollution control systems and then the remaining constituents are emitted via a stack to the atmosphere. Examples here include the offgases from the smelting furnace and the copper converters. Fugitive emissions, on the other hand, are those which leak from process air stream ducts and treatment systems, or which escape collection altogether. In some cases, no collection system is provided for minor sources. These emissions initially enter the occupational environment of the smelter or refinery building and are eventually vented to the atmosphere, typically at low elevations and exit velocities, via roof or wall vents or other building openings. These might include, for example, emissions from open ladels of molten matter in transit to the converters and molten slag in transit to disposal, and uncaptured leakage from matte and slag launders on the smelting furnace. Figure 33 illustrates the distinction between stack and fugitive emissions.

Figure 33

Each of the above emission categories contains constituents which are either in a solid or a gaseous state. Thus, emissions can be discussed in terms of particulate emissions, or gaseous emissions. The principal gaseous constituent of concern is sulfur dioxide, SO_2. For modern smelters using best available air pollution control methods the quantity (by weight) of fugitive and stack SO_2 emissions can be of the same order of magnitude. Under conditions with a lesser degree of control, stack emissions are usually greater in quantity than fugitives. This does not necessarily mean that stack emissions are of greatest concern

FIGURE 33 SOURCES OF STACK AND FUGITIVE EMISSIONS



pertaining to ambient air quality impacts since fugitive emission are released at or near ground level. (See Volume 3-Chapter 3 for a discussion of air pollutant emissions and their ambient air quality implications.) The oxides of nitrogen, NO_x, will also be present. However, present information indicates that the quantities of NO_x produced will be relatively low, and not of serious concern. Particulate emissions of concern include dust from the concentrate and certain volatile elements which leave the smelting furnace or converter as gases at elevated temperatures and then condense as particulates prior to or just after being released to the atmosphere. Elemental constituents of concern in these two cases include Cu, Ni, Co, Cd, As, Pb, and Hg.

2) Solid Waste Production

The nature of the smelting and refining processes dictate that a portion of the output from the operation will be a discardable solid waste of no intrinsic value in the context of the base metals market. For the smelter, this waste consists principally of the iron silicate slag left after the removal of the copper and nickel as anodes or as a sulfide matte.

For refineries, the waste is typically a sludge containing various impurities which must be regularly cleaned from the electrolyte used in any electrolytic purification to prevent contamination of the refined product. In addition, the use of various air pollution control devices generates another category of solid wastes. These usually consist of a variety of sludges containing constituents such as sulfur and trace metals that have been cleaned from process air and water streams. Some sludges may be reused or treated by other processes, while others are disposed of as wastes.

3) Water Emissions

A variety of water requirements in the smelting and refining operations lead to the potential for water discharges. In principal, all water discharges could be eliminated by appropriate treatment and conversion of any undesirable constituents to a solid or sludge for land disposal. In practice, such treatment may be uneconomical or unnecessary, with discharge being the alternative, so the possibilities must be understood. Water serves two basic functions in the operations of concern here. The first is as a cooling medium. The water is isolated from any contaminants except for heat, and it may leave the operation at a higher temperature than it entered. The second function served by water is the process function, which includes all operations in which water acts directly in contact with other constituents to allow the operation to function. Such processes include slag quenching and granulation, anode cooling, gas scrubbing and acid production in the sulfuric acid plant, and use as a base for the electrolytic solutions in the refineries. Such uses result in contamination of the water by other constituents involved in the processes. The need to prevent buildup of these constituents in the water may then lead to a discharge of polluted water, or the treatment and subsequent reuse of the water.

In the remainder of this section, each of these possible emissions will be considered in turn, with an emphasis on the amounts involved, the constituents of concern, and the various technologies available for their control. To aid in the understanding of the relative magnitudes of possible emissions and their corresponding potential environmental impacts, a series of models will be presented throughout the course of the following discussion. The various models are all designed to be compatible with a new, totally integrated mining, processing, and smelting/refining operation designed to produce a total of 100,000 mtpy of copper and nickel metal. The principal assumptions involved in this model are discussed in Chapter 5 of this report. It must be realized throughout that the various models presented are meant only to generally characterize the magnitudes of the various parameters involved. Parameter values in actual or proposed future operations may vary considerably from the model values selected here. Correspondingly, the resulting environmental impacts would be expected to vary.

4.7 AIR EMISSIONS AND CONTROLS

4.7.1 Introduction

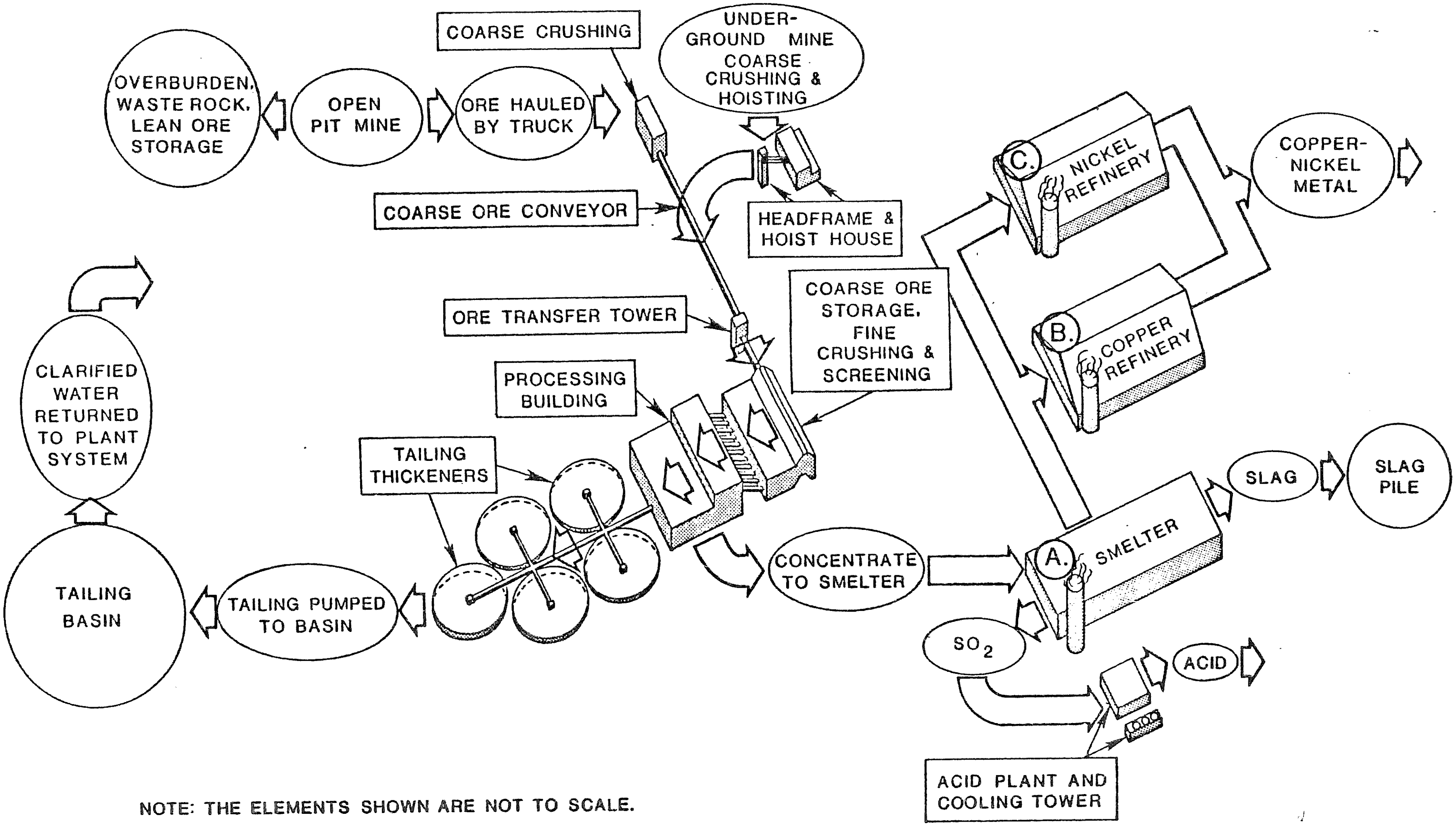
Figure 34 schematically identifies the basic mining component relationships necessary in the treatment of copper-nickel ores. Several potential sources for air emissions exist. The smelter/refinery complex is shown with its 3 basic vertical operations, labeled A, B, and C, separated by an unlimited distance. The acid plant and cooling tower, though possibly housed separately, must be close to the smelter building and so, for considerations of interest here, can be taken as part of the smelter complex. If the operations are physically separated, a minimum of three exit gas stacks, each representing a point source location for air emissions, would be required for successful operation. In many instances, more than one stack per vertical stage is required. This, of course, depends upon the complexity of the particular stage or treatment process selected. Table 9 breaks down the various types of air emissions and the operations which generate them. The figure emphasizes that from the point of view of quantity of air emissions the focus of concern is on the smelter, and the emissions of principal interest are SO_2 and total particulates. These 2 constituents will be focused on in the following discussion. Since emissions will include trace amounts of heavy metals which are of qualitative importance, they are also a focus of concern even though emission rates will be very small as compared to SO_2 and total particulation.

Figure 34, Table 9

Prior to a discussion of the smelter, a comment on the emission potentials shown for the refineries is warranted. Briefly, the origin of the atmospheric

FIGURE 34

PRINCIPAL MINING COMPONENT RELATIONSHIPS IN THE PRODUCTION OF COPPER AND NICKEL METAL



NOTE: THE ELEMENTS SHOWN ARE NOT TO SCALE.

Table 9. Sources of air emissions by operation.

EMISSION	OPERATION[a]		
	SMELTER	Cu REFINERY	Ni REFINERY
Gases			
SO_2	XX	X	X
NO_x	X	T	T
Other (Sg-Hg)	X	T	T
Particulates	XX	T	T

[a] XX = major source, potentially greater than 1,000 mtpy.
X = minor source, probably less than 1,000 mtpy.
T = possibly trace emissions.

emissions from the copper and nickel refineries is principally from the burning of fuels needed to supply energy during operation. These may include the need to heat electrolytes and other liquid baths, melt and cast both cathodes and residual anodes, and provide general space heating. Possible fuels include coal, oil, and natural gas, all of which may release some SO_2, NO_x, and possibly fly ash and metal vapors such as mercury. The quantities involved, however, are expected to be insignificant in comparison to the smelter emissions and will not be discussed further. It should be noted that in the event that one or both of the refineries are located at the smelter site, some of these heating requirements may be met using smelter waste heat, thereby reducing the fossil fuel requirements and consequent air emissions. Also, the fire refining process, though strictly speaking a part of copper refining, is in practice included as part of the smelter operation. Its air emissions are discussed later, since anode refining and casting are typically integrated into the processes performed at the smelter site.

The possibility of acid mist emissions from the copper or nickel refinery must also be mentioned. As discussed earlier, the electrolytic purification of copper and nickel involves the use of an electrolyte solution, generally containing sulfuric acid. Particularly in the case of electrowinning with insoluble anodes, in which gaseous oxygen bubbles from the solution at the anode, physical disturbances of the surface of the electrolyte can lead to the emission of droplets of electrolyte into the occupational environment. The resulting acid mist is of concern principally as an occupational hazard, but typically ventilation fans are used to exhaust this mist from the tankhouse, creating emissions to the ambient air. No data is available concerning emission quantities or resulting ambient concentrations. The droplets would tend to settle in the vicinity of the plant, posing possible corrosion problems for nearby metal structures and vehicles normally parked in the area. Mitigating measures include the use of a floating layer of plastic spheres on the electrolyte surface to trap emitted droplets.

4.7.2 Smelter Air Emission Sources

In discussing air emissions from the smelter operation, it is useful to describe the characteristics of the important emission sources. The principal sources of interest here include:

1) dryer or roaster
2) smelting furnace
3) copper and nickel converters
4) slag cleaning furnaces
5) anode furnace
6) ladels for transport of molten matte and slag, and anode casting machine

Each of these sources will be discussed in turn.

During the discussions, typical values or ranges of values will be cited to give a quantitative perspective to the important parameters being presented. These parameters include process material tonnages, air flow rates, process temperatures, and concentrations of constituents in gas streams. Once again, it should be understood that actual values may vary considerably from the representative figures given here. Tonnage estimates are based on a hypothetical model smelter/refinery operation processing some 635,000 mtpy of Minneosta copper-nickel concentrate to produce approximately 85,000 mtpy of refined copper and

15,000 mtpy of refined nickel. See Chapter 5 for a detailed discussion of this model.

As noted earlier, the focus of these discussions is on the emission of SO_2 and particulates, although NO_x is listed as a gaseous emission. Data on NO_x emissions from either copper or nickel smelters could not be located in the literature. Data provided by a smelting company indicated that a Japanese copper smelter measured 4 ppm NO_x at the outlet of their TCA SO_2 scrubber (approximately 200,000 SCFM). The value of 4 ppm seems reasonable because of the following (Coleman 1978b):

1) No fuel nitrogen of the form R-N is present in the concentrate.

2) All NO_x present in smelting furnace off-gases comes from thermal fixation of molecular nitrogen (N_2) in the combustion air.

3) The smelting reactions occur at temperatures lower than those needed for significant NO_x generation (i.e. below 3000°F).

4) Local temperatures on the concentrate particles in a smelter should be lower than the temperature on coal particles as in a power plant. This is the case first, because of the lower heat of reaction and second, because the copper and iron present act as a significant heat sink.

5) The expected residence time, approximately 20 sec, and average temperature, approximately 2800°F, are not sufficient to generate significant NO_x concentrations based on reported reaction rate calculations for the following reaction:

$$N_2 + O_2 \rightarrow 2NO$$

These qualitative statements can be supported by using the following equation:

$$\frac{d[NO]}{dt} = A_f e^{-E_f/RT} [N_2][O_2]^{1/2} - A_r e^{-E_r/RT} [NO]^2 [O_2]^{-1/2} \text{ g moles/cc/sec}$$

where: $\frac{d[NO]}{dt}$ = net formation rate for NO_x (assumed constant for this calculation),

A_i = Frequency factor,

T = 2500°F for the case with no oxygen enrichment; 2800°F with 300 Nm^3 O_2/mt Cu, and

E_f, E_r = Forward and reverse reaction activation energies.

assume:
a) $N_2:O_2$ mole ratio is 0.54:0.46 for oxygen enriched case,
b) Furnace residence time is 20 sec, and
c) Flash furnace shaft is a homogeneous reactor.

These approximations allow the NO_x formation rate (moles/sec) and the NO_x concentration (ppm) to be calculated. For the no oxygen enrichment case, an NO_x concentration of 3 ppm NO_x was calculated. For the case of 300 Nm^3 O_2/mt Cu, a concentration of 15 ppm NO_x was calculated.

These numbers are certainly on the same order of magnitude as the 4 ppm NO_x figure reported by the Japanese smelting company. Of course, the 4 ppm NO_x value includes approximately 2 volumes of dilution air for every one of process gas. The 3 ppm and 15 ppm NO_x calculated above do not.

For comparison, Table 10 presents some information on power plant NO_x emissions which will place potential smelter NO_x emissions in perspective. The power plant data are for different types of firing mechanisms, i.e. different flame temperatures. A typical gas flow from a 500 MW coal-fired power plant should range from 1.0 to 1.25 X 10^6 SCFM depending on the coal heating value and moisture content. Obviously, the NO_x emissions from a smelter (approximately 200,000 SCFM, 4 ppm NO_x) would be insignificant compared to a 500 MW power plant, and thus will not be discussed further.

Now smelter SO_2 and particulate sources will be discussed.

Table 10

4.7.2.1 Dryer or Roaster--Depending on the type of smelting technology used, incoming concentrate may require drying to remove excess moisture, as in the case of electric or flash smelting, or more extreme heating (roasting) to begin the process of sulfur removal, as may be the case using reverberatory furnaces with a concentrate containing sulfur in excess of 30%. Drying takes place at low temperatures (200-500°C) and thus does not involve the evolution of SO_2. The emission of concern here is particulates in the form of concentrate dust entrained in the exiting dryer air. For the model operation considered here, typical gas flows are on the order of 60,000 SCFM. Depending on the type of dryer used, up to 10% of the input concentrate may be entrained as dust in this gas stream, clearly indicating an economic, as well as environmental control incentive to remove and recycle this dust. This air stream does contain sulfur in the solid form, but the process is not a source of sulfur in the gaseous form. However, the heat required by the drying process may be obtained by directing the hot gases from other operations, such as the slag cleaning furnaces and anode furnace, through the dryer. As a result of this measure to more fully utilize waste heat, the gases inputed to the dryer may contain SO_2 in low concentrations (0.1-1% by volume) and thus the dryer may appear as an SO_2 source when SO_2 controls are being planned.

Table 10. Concentration ranges of NO_x from coal-fired power plants.

TYPE OF FIRING	TYPICAL NO_x CONCENTRATION, ppm[a]
Vertical	225 - 310
Horizontally opposed	340 - 375
Spreader (stoker)	400 - 470
Tangential (corner)	420 - 500
Front wall	390 - 600
Cyclone	800 - 1200

SOURCE: Coleman 1978b.

[a] Gas flows typically range from 1-1¼ X 10^6 SCFM for a 500 MW power plant.

In the event that a roaster is used, high temperatures (500-700°C) are employed in order to force sulfur in the concentrate to react with oxygen and evolve as SO_2. Thus, not only are high levels of particulates present in the exit gases, as with the dryer, but also high SO_2 concentrations. With a gas flow in the range of 25,000 SCFM, SO_2 concentrations will be in the range of 2-16% by volume. This gas flow also contains sufficient particulate matter to warrant control for economic reasons alone. Further, the SO_2 concentrations here are likely to be near the higher end of the range shown, particularly if a fluid bed roaster is used, and provide an economic incentive to recover the SO_2 as a marketable product such as sulfuric acid. If for some reason a smelting furnace such as a reverberatory furnace is chosen, then use of a roaster, such as a fluid bed roaster, with high levels of SO_2 in the off-gas optimizes the possibilities for efficient, economic recovery of SO_2 in the roaster off-gases.

Both dryers and roasters would be operated continuously and thus would produce reasonably constant levels of SO_2 and/or particulates during normal operation.

4.7.2.2 Smelting Furnace--Following the drying or roasting operation, the concentrate and added flux and fuel move on to a smelting furnace. In terms of air emissions, one of the principal functions of the furnace is the oxidation of sulfur and evolution of SO_2. Thus the operation is clearly a principal source of SO_2. In addition, oxygen and/or air is blown into the furnace to provide oxygen for the smelting reaction and for combustion of fuels that may be used, depending on the type of furnace. The resulting volume of exhaust gases and consequent SO_2 concentrations vary greatly as a function of the type of furnace although the furnace is a reasonable continuous emission source during normal operations. Table 11 summarizes typical SO_2 concentrations for a variety of furnace types.

Table 11

The reverberatory furnace is the type most widely in use world-wide, but is unlikely to be chosen for a new facility, partly as a result of its low SO_2 concentration off-gas. This gas cannot be economically treated by an acid plant and so poses serious problems in light of air pollution laws applicable to new smelters. As a result, this type of furnace is not considered further here.

The electric furnace, possibly combined with a roaster, is a potential candidate for use with Minnesota concentrate if the hurdle of high costs for electric power can be overcome. The off-gas provides a satisfactory acid plant feed, with flows in the range of 12,000 SCFM. Particulate matter is also contained in this stream and would require removal prior to treatment of the SO_2 in the acid plant.

The flash furnace, coupled with a dryer, is another major candidate for use in treating a Minnesota concentrate. Gas volumes vary considerably depending on whether oxygen enrichment is used. The Outokumpo furnace without oxygen enrichment would produce approximately 100,000 SCFM of off-gases. This gas would contain considerable amounts of entrained dust, up to 10% of the input charge, with a clear economic incentive to recover and recycle this material. The gas then provides suitable feed for an acid plant. As oxygen enrichment is used, the concentration of SO_2 in the off-gas increases, with the Inco flash furnace as the extreme case.

In addition to the smelting furnaces mentioned, a variety of continuous processes are also available, notably the Noranda process, in use at the new

Table 11. SO_2 concentrations (volume %) in the off-gas of various smelting furnaces.

FURNACE TYPE	VOLUME (%)
Reverberatory	0.5-1.0
Electric	2-8
Flash (Outokumpu)	10-14
Flash (INCO)	75-80

Kennecott smelter at Garfield, Utah, and the Mitsubishi process, being installed by Texasgulf at Timmins in Ontario. These processes are capable of combining smelting and converting in one continuous process. From an air emissions point of view both of these processes produce gas streams of sufficient SO_2 concentration to feed an acid plant. However, though they may be applicable to treatment of Minnesota concentrates, data is not available to allow their performance to be further discussed. For purposes of controlling air emissions, it is likely that the discussions and conclusions based on use of a flash or electric furnace are also applicable to these continuous processes.

4.7.2.3 Copper and Nickel Converters--Following smelting, the metal product or matte moves to the converting stage. The nickel is separated from the bulk of the copper just prior to or during converting to produce 2 mattes, a copper matte and a nickel-copper matte. The copper matte is converted to blister copper in a copper converter, by oxidation of the bulk of the remaining sulfur to SO_2. The nickel-copper matte may also be treated in another converter to remove remaining iron and silica, and adjust the sulfur content of the matte prior to sending it to the nickel refinery. Sulfur dioxide and particulates are thus present in the off-gas from both of these operations, though the copper converter is a source of gas at a high SO_2 concentration (2-12%) while the nickel converter gas is likely to be at concentrations below 1% SO_2.

Two basic types of converters, the Pierce Smith and the Hoboken could be utilized. The Pierce Smith is the type in common use, and produces SO_2 gas concentrations in the range of 2-9%. This gas is collected by means of a large hood over the outlet of the converter, and at this point the process gas stream is diluted, typically 100%, by the uptake of outside air. The resultant concentration of SO_2 is still adequate to feed on acid plant with flows in the range of 50,000 SCFM. However, a superior acid plant feed (8-12% SO_2) (Verney 1978) is achieved by use of the Hoboken converter. The design of this converter reduces the potential for gas stream dilution which is inherent in the Pierce Smith design. However, the improved air control features also introduces complications which make operation of this type of converter more difficult (Billings 1977b). These operating problems affect both the converting process and the air pollution control processes down stream. Possibly as a result of these complications, the Hoboken has not been widely used, but with the advent of more stringent air emission regulations it is expected to gain wider acceptance.

One problem assoicated with either type of converter is the fact that converting is a batch operation, rather than being continuous. As a result the concentration of SO_2 in the gas to the acid plant varies greatly over time periods as short as a few minutes. Figure 35 illustrates this variation. This has a negative effect on the removal efficiency of the acid plant, but can be partly offset by operating several converters in a sequence timed to minimize fluctuations of SO_2 content in the combined gas stream. This is a point in favor of a large operation, capable of supplying 2 or more converters continuously.

Figure 35

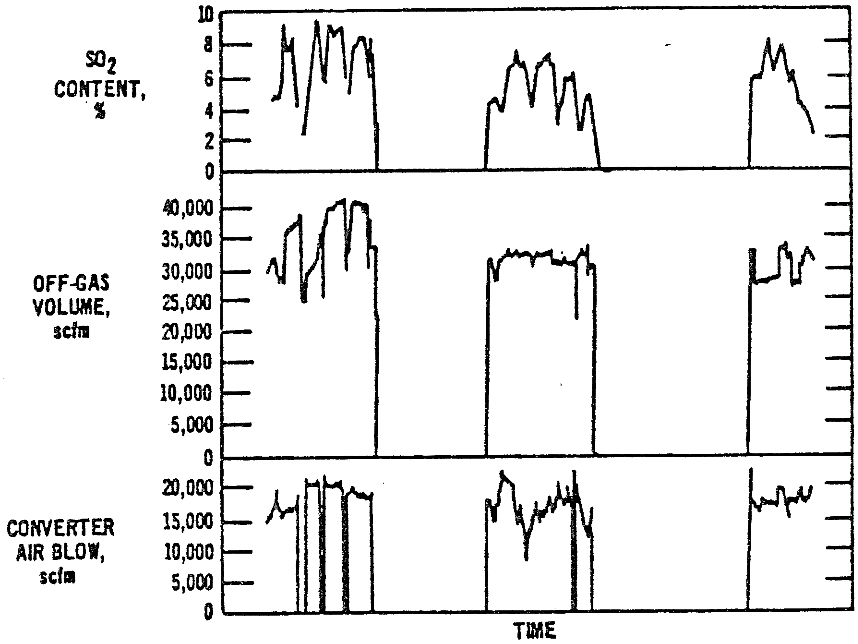
4.7.2.4 Slag Cleaning Furnaces--The slag produced during smelting, especially using a flash furnace, and during converting contains entrained droplets of valuable matte, as well as oxides of economic metals, particularly nickel and cobalt. As a result, the slag will be treated in one or more slag cleaning furnaces. Here a reducing atmosphere will convert some of the metals back to a matte/alloy phase, and entrained matte will be allowed to settle out. These

FIGURE 35

FLUCTUATIONS IN CONVERTER OFF-GAS VOLUME AND SULFER DIOXIDE CONCENTRATION

(SOURCE: AMSDEN, 1974)

* THE CHART REPRESENTS A TOTAL ELAPPED TIME OF APPROXIMATELY 24 HOURS



furnaces will likely be the source of the bulk of the nickel-copper matte sent to the nickel refinery. Since a supply of oxygen is not needed, but rather a reducing atmosphere is desired, the electric furnace seems the best choice here. Some SO_2 will be evolved during this operation, but flows will be small (a few thousand SCFM). Sulfur dioxide concentrations will be low, typically below 1%. Some particulate emissions also occur.

4.7.2.5 Anode Furnace--Blister copper is fire refined in an anode furnace which resembles a Pierce-Smith converter. Here the small amount of sulfur (0.03-0.3% by weight) remaining in the copper is oxidized, which creates a source of SO_2. The amount of SO_2 is low, producing a flow of a few thousand SCFM at a fraction of a percent SO_2 concentration. Small amounts of particulates are also released. The furnace operates on batches of blister transferred from the converters, and so constitutes an intermittent source of SO_2 and particulate.

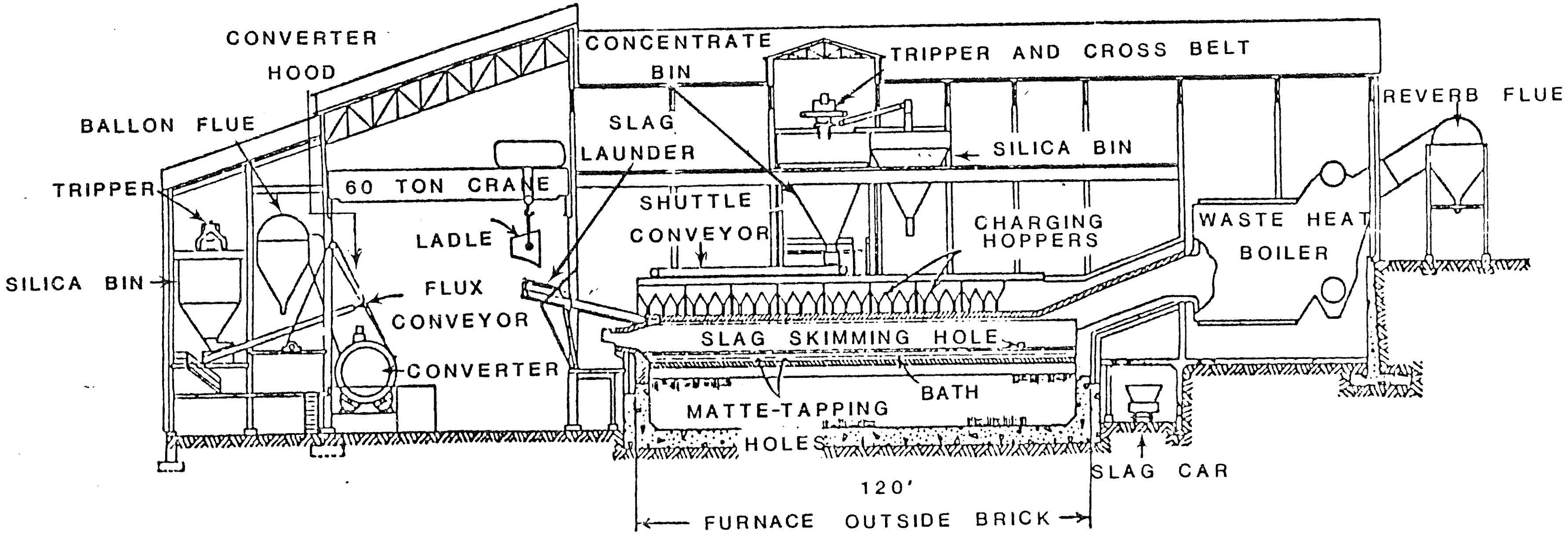
4.7.2.6 Ladels for Transport of Matten Metal and Slag; Anode Casting Machine--Large open ladels are typically used to transport motten matte and slag between the smelting, converting, and slag cleaning furnaces. Anode casting also involves the exposure of surfaces of molten metal to the occupational environment in the smelter building. There are no specific gas flows associated with these operations, so volumes of air connot be quantified. However, the various materials do contain sulfur and the surface is exposed to oxygen. As a result, SO_2 and particulates in some quantities (small in comparison to emissions from the other sources discussed, do escape to the atmosphere. To aid in visualizing these various sources, Figure 36 shows a specific example of a smelter layout (Billings 1977a).

Figure 36

FIGURE 36

TYPICAL REVERBERATORY FURNACE AND CONVERTER LAYOUT

(SOURCE: KIRK-OTHMERS, 1963-1970)



4.7.2.7 Summary, SO_2 and Particulates

SO_2--All of the devices discussed above constitute sources of SO_2 and particulates in the smelting operation. Some of the sources produce strong gas streams with high levels of SO_2, as well as high dust loadings. These include the dryer or roaster, the smelter, and the converters, particularly the copper converters. For example, with the use of a flash furnace, a hypothetical sulfur balance (Coleman 1978b) indicates that approximately 63% of the input sulfur leaves the flash furnace as SO_2 and 30% is emitted from the converter. All the other sources plus sulfur in the waste and metal products account for the remaining 7%. A similar balance for an electric furnace shows 50% of the input sulfur evolved as SO_2 from the roaster. The electric furnace itself accounts for 14%, with 30% coming from the converters. The roughly 6% remaining is distributed among the other sources or leaves the operation in the solid waste or metal products. Clearly, roasters, smelting furnaces, and converters require gas handling ducts, hoods, and fans to contain the exhaust gases either for treatment or controlled discharge if only to maintain a viable occupational environment. The various ducts, hoods, and fans, are themselves then sources of air emissions wherever minor leaks occur. These leakage emissions join a variety of other emissions from sources of high SO_2 concentration gases. These other emissions include gases which escape from slag and matte taps during removal of these materials from the smelting furnace, and releases from roasters while calcine (roasted concentrate) is being removed. These emissions combine with the lower concentration gases from devices such as the slag cleaning furnaces, anode furnace, ladels, and anode casting machine to produce what could be termed weak gas streams. Such streams are physically created only if secondary hoods, ducts, and fans are installed to collect and control these emissions.

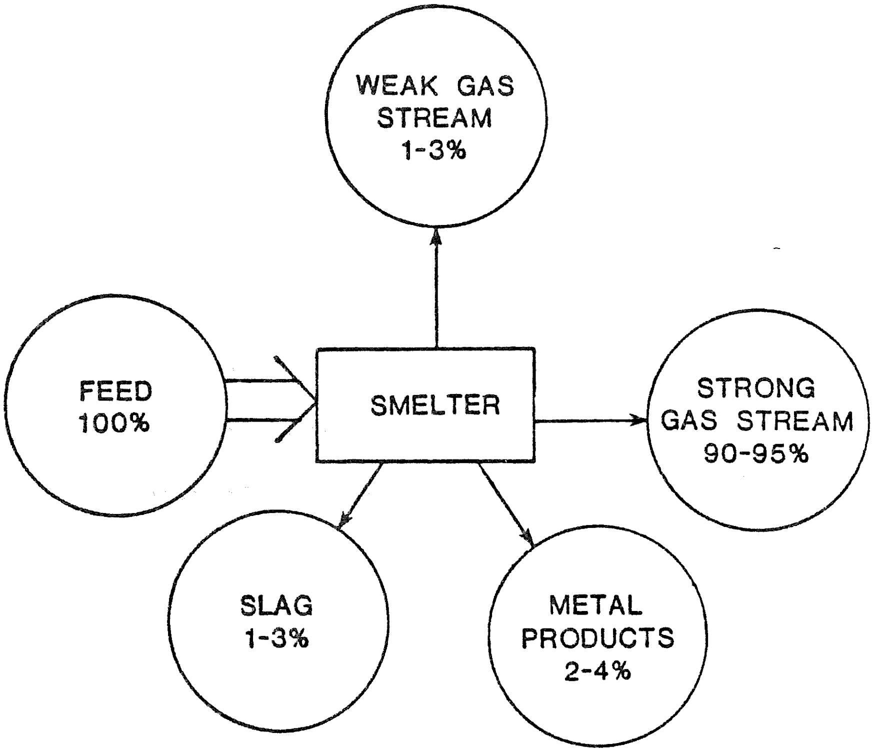
It is useful to summarize the above sources as "strong" (greater than 3.5-4% SO_2) and "weak" (less than 3.5-4% SO_2) gas streams since existing control devices can generally be grouped in terms of their applicability to one of these streams. Assuming a traditional reverberatory furnace would not be used to treat a Minnesota concentrate, a generalized sulfur balance for a new smelter during normal operation is shown in Figure 37. The numbers indicate the general ranges of expected sulfur distribution for a new facility using a flash or electric smelting furnace. The distribution of 2-3% of the sulfur to the metal products reflects the fact that the nickel will leave the smelting operation as a sulfide matte for treatment in the nickel refinery. The range of 1-3% shown for the weak gas stream also reflects the assumption that modern, efficient hooding and ducting will be used to contain the strong gas streams. Clearly this range would be much higher if poor collection of the strong gases is practiced.

Figure 37

Particulates--As indicated throughout this discussion, all of the operations considered are potential sources of particulates. Certain devices, such as spray dryers, fluid bed roasters, and flash smelting furnaces entrain a major fraction of the input feed as dust in exhaust air by the nature of their operation. Other operations (electric smelting, converting) have only incidental entrainment of particulates in exhaust air. Particles also may be created from fumes evolving from exposed matter, matte and slag. Very little data exists to date concerning the quantity and composition of dust from these various sources. For example, flash furnace exhaust gases may contain from 2 to 10% of the input charge as entrained dust (Biswas 1976). Comparable or greater amounts may be

FIGURE 37

GENERALIZED SULFUR BALANCE FOR A NEW SMELTER* INSTALLATION DURING NORMAL OPERATING CONDITIONS



* A REVERBERATORY FURNACE IS ASSUMED NOT TO BE USED

STRONG GAS STREAM SO_2 CONÇENTRATION 3.5-4% OR GREA

WEAK GAS STREAM SO_2 CONCENTRATION LESS THAN 3.5-4%

emitted from devices such as spray dryers and fluid bed roasters. Actual emissions cannot be predicted with the confidence reflected by the sulfur balance just shown. However, the general nature of the particulate generation and control problem will be discussed later in the report, using specific emission estimates to provide a picture of the behavior of the various devices involved.

It must be noted that the particulates essentially reflect the makeup of the feed to the smelter operation. This feed contains not only the concentrate produced in the milling and flotation operation, but additives such as silica flux, limestone or lime, and possibly fuel such as oil or coal, depending on the smelting technology used. One example (AMAX 1978a) indicates additions of silica flux in the amount of approximately 18% of the concentrate, and lime additions of about 3% of the concentrate. Coal is also added in amounts of about 6% of the concentrate. This illustrates that the concentrate might easily be augmented 25-30% by weight as a result of these additions. All of these constituents contribute to the various potential particulate emissions.

4.7.2.8 Smelter Models--As mentioned earlier, to illustrate the quantities of materials typically involved in a large modern smelting operation, a set of hypothetical smelter flowsheets were designed for this study. At this point it is useful to give some of these models to illustrate the general sulfur and particulate balances just described. The models chosen here primarily focus on a flash smelter, smelting some 635,000 mtpy of Minnesota copper-nickel concentrate containing approximately 25.9% sulfur, 13.8% copper, and 2.6% Ni (see the geology report, Volume 3-Chapter 1). The overall operation produces 100,000 mtpy of metal, approximately 84,600 mtpy of copper and 15,400 mtpy of nickel following refining. For this model, the sulfur balance analogous to the ranges shown in Figure 37 are given in Figure 38. The values are shown as both percent sulfur distribution and model values in metric tons of sulfur per year. Normal operating conditions are assumed, and an estimate of the sulfur content of coal added as a fuel is included.

Figure 38

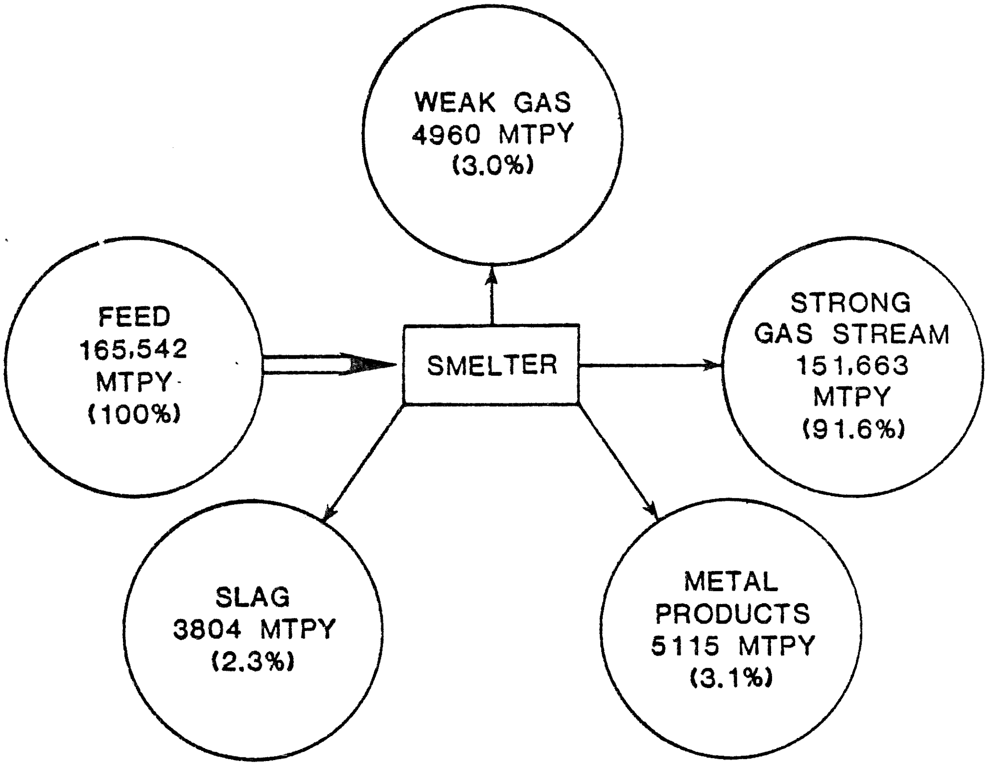
A model for the particulate distribution was also created. As noted, the quantitative validity of this model is much weaker than that for SO_2. However, it does serve to illustrate the order of magnitude of tonnages involved. Here, in addition to the 635,000 mtpy of concentrate, the smelter feed is also assumed to include 151,000 mtpy of pulverized lime and silica flux. The model assumes a flash furnace utilizing 40,000 mtpy of pulverized coal, of which some 7,600 mtpy is ash and sulfur. A model showing the various heavy metal constituents, as well as silica and other oxides, was created for the smelter feed. Available data for the composition of coal (Kessler et al. 1973), lime and silica flux (AMAX 1978a), and a model concentrate analysis (see geology report, Volume 3-Chapter 2) were used. Table 12 indicates the resulting model for the constituents in the smelter feed. The parameters shown include all the constituents in the concentrate which are known to be highly toxic in the environment and further, are present in amounts which could create toxic concentrations if released to the environment. This question is discussed further in section 4.7.4 of this chapter.

Table 12

A source model for particulates was generated assuming the modeled material provides the feed to a smelter facility, and 10% of this input would be released as

FIGURE 38

SULFUR BALANCE* FOR A MODEL SMELTER UTILIZING FLASH SMELTING TO PROCESS 100,000 MTPY OF COPPER & NICKEL METAL



* THE EXACT TONNAGES SHOWN IN THIS AND OTHERS MODELS DO NOT REFLECT THE ACCURACY IMPLIED FOR THE MODEL, BUT SIMPLY THE FACT THAT THE STREAM SHOWN IS PART OF A MATERIAL BALANCE REQUIRING INTERNAL CONSISTENCY DATA IS GIVEN BOTH AS METRIC TONS OF SULFUR PER YEAR, AND % OF IMPUT SULFUR. NORMAL OPERATING CONDITIONS ARE ASSUMED

Table 12. Model for the constituents in the feed to a flash smelter facility generating 100,000 mtpy of copper and nickel metal (all values shown are mtpy).[a]

	CONCENTRATE	FLUX Silica & Lime	SUPPLEMENTAL FUEL Coal	TOTAL INPUTS
SOLID FLOW MTPY	635,259	151,479	(40,000)	794,328[a]
Constituent				
Cu	87,825		7.2	87,832.2
Ni	26,815		2.4	16,817.4
S	164,342		1,200	165,542
As	32		0.4	22.4
Cd	25		0.12	25.4
Co	839		3.6	842.6
Be	0.04		0.12	0.16
Pb	39		1.44	40.44
Hg	0.11		0.02	0.13
Zn	722		3.2	725.2
Fe	190,584	2,826	480	193,890
Sb	1.08		0.08	1.16
Cl	70.89		60	130.89
F	2.02		4.4	6.42
SiO_2	68,656	110,668	3,512	212,836
Al_2O_3	21,789	10,416	1,739	33,944
MgO	16,326	2,603	232	19,161
CaO	10,228	22,820	344	33,392
Other[b]	26,973	2,146	--	29,119

---

[a] Includes only the constituents shown for the coal contribution. The exact tonnages shown in this and other models do not reflect the accuracy implied for the model, but simply the fact that the stream shown is part of a material balance requiring internal consistency.

[b] Includes oxides of Na, K, Ti, P, Mn, Cr, and Fe.

particulates in the smelter strong gas streams (Coleman 1978b). Additionally, 10% of the feed to a dryer is assumed to be released in the resulting weak gas stream as well, for the model utilizing a dryer with a flash smelter. These are conservative estimates. The actual amount is believed to be smaller. Figure 39 shows the resulting particulate source models for 2 cases, with and without a dryer. The dryer coupled with a flash smelter is the same as the model which was given for the sulfur balance. The model for an electric smelter without a dryer is shown for comparison. Note that the electric smelter feed does not include coal.

Figure 39

The models shown are for particulates in the strong gas streams and the dryer weak gas stream. Of course, the other weak gas streams also contain particulates. However, no data is available to provide even a qualitative basis for modeling these sources. Rather, the question must be approached simply as one of the overall fugitive emissions likely to escape from the smelter building. This will be discussed in section 4.7.4 on minor and trace metals.

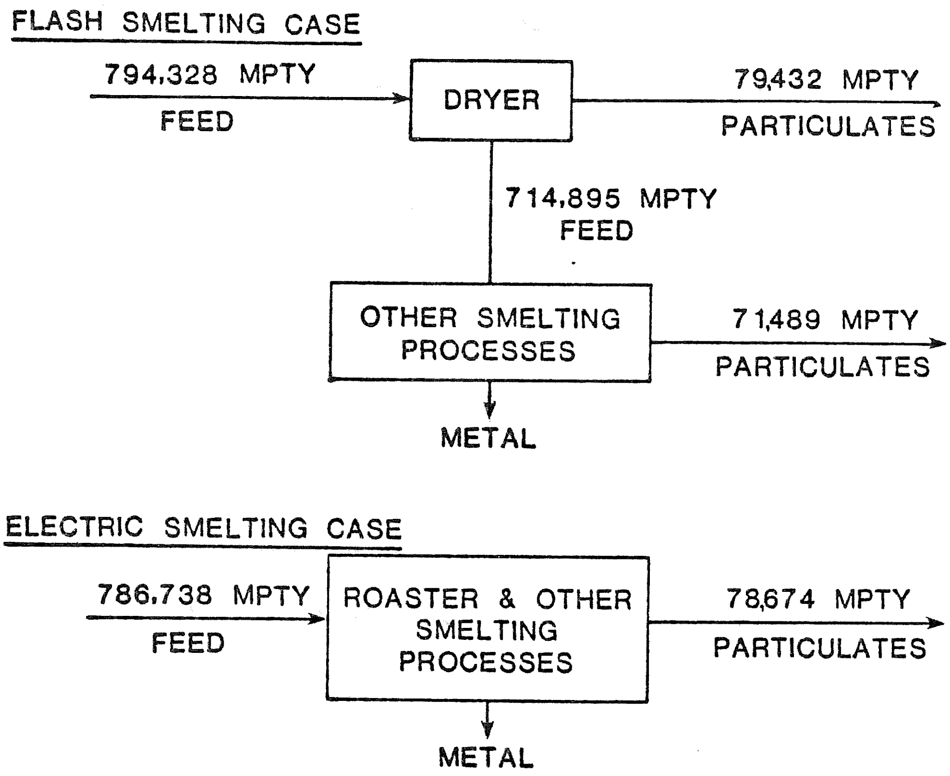
4.7.3 Smelter Air Emission Control Devices

This section will discuss the various devices available to remove SO_2 and particulates from the sources just reviewed. It is convenient to organize this discussion as follows:

1) Strong Gas Streams
    a. SO_2 removal devices
    b. Particulate removal devices

FIGURE 39

PARTICULATE SOURCE MODELS*
FOR TWO SMELTER CASES,
EACH PRODUCING 100,000 MPTY
OF COPPER & NICKEL METAL



* MODELS ASSUME 10% OF DRYER FEED AND 10% OF FEED TO OTHER SMELTING PROCESSES (PRODUCING STRONG GAS STREAMS) IS CARRIED OFF AS ENTRAINED PARTICULATES IN EXIT GASES.

2) Weak Gas Streams
    a. SO_2 removal devices
    b. Particulate removal devices

To illustrate the economic and emission implications of various control configurations, a set of smelter emission models are again presented during the course of this discussion. As before, each model is based on an integrated operation producing 100,000 mtpy of copper and nickel metal.

4.7.3.1 Strong Gas Streams--As discussed, these are gas streams originating from a roaster (if used), the smelting furnace (except for the reverberatory furnace) and the copper converters. Although some SO_2 and particulates escape from these sources to join the weak gas stream, the bulk of these constituents pass through ducts to various control devices for removal of SO_2 and particulates.

SO_2 Removal Devices--The removal of SO_2 from strong gas streams has been a problem receiving considerable attention in recent years. Although SO_3 and H_2SO_4 mist will be present in smelter stack emissions, SO_2 will be the major form in which sulfur will exit a smelter facility in the absence of any gas treatment. Thus, gas treatment technology focuses on control of this constituent. The principal devices to be discussed here include:

1) sulfuric acid plants
2) elemental sulfur plants
3) DMA scrubbers (with liquid SO_2 production)

Sulfuric acid plants are the most common technique for control of emissions of sulfur oxides from copper-nickel smelters. They involve catalytic oxidation of sulfur dioxide to sulfur trioxide in the controlled smelter off-gas streams for the production of sulfuric acid.

Contact sulfuric acid plants can be designed to produce acid from gas streams ranging from a fraction of a percent sulfur dioxide up to the highest concentrations feasible in smelting operation. However, economic considerations usually restrict the application to concentrations greater than 3.5-4%. The acid produced would be sold if a market is available, or disposed of by neutralization if necessary. Neutralization poses its own problems, including potentials for liquid and solid waste releases to the environment, as well as an added economic burden to the mining company.

Sulfuric acid mist and smelter off-gas contaminants in the strong gas stream can present difficulties in the production of sulfuric acid due to corrosion of heat exchanger tubes, plugging of catalytic beds, or partial deactivation of the catalyst. These difficulties must be minimized by adequate design and proper maintenance of the gas purification and treatment system. This includes the use of scrubbers, demisters, and electrostatic precipitators which remove 99.9% of the particulate matter in the feed gas, prior to its entering the acid plant.

Two types of acid plants, single and double contact, are available. The double contact or double absorption type, essentially operates as two single contact acid plants in series. EPA figures (EPA 1976a) indicate SO_2 removal efficiences of 97% for single contact plants, and 99.5% for double contact plants. Newer double contact plants are designed for even higher efficiences. New copper smelters in the U.S. are effectively required to employ double contact acid plants with their high removal efficiences in order to meet new federal air emission regulations (EPA 1976a).

Figure 40 is a generalized flowsheet for both the single contact and double contact sulfuric acid plant.

Figure 40

The various source off-gases are cooled and cleaned to remove particulates and volatile metals, acid mist is removed in an electrostatic mist precipitator, and the gases are dried with 93% sulfuric acid. The cool, dry gases then pass through a series of gas-to-gas heat exchangers to heat the off-gases to the optimum temperatures for catalytic conversion of sulfur dioxide to sulfur trioxide (SO_3). Single-stage absorption acid plants use 3 of 4 stages of converter catalyst, whereas dual-stage absorption plants use 1, 2, or 3 stages of catalyst before the first absorption tower. Since the conversion of SO_2 to SO_3 is exothermic, the converter outlet gases must be cooled before passing through the absorption tower. These outlet gases are passed countercurrent to the inlet gases in the heat exchangers mentioned above. The SO_3 is then absorbed in 98% sulfuric acid in an absorption tower to yield the product. The remaining gases are then typically treated to remove acid mist and spray, and vented to the atmosphere if a single-stage absorption acid plant is employed. In a dual-stage absorption acid plant, the gases exhausted by the first absorption tower are passed through a second series of heat exchangers and catalytic converter stages to oxidize the sulfur dioxide remaining in the gases. Normally, this step employs 1 or 2 stages of catalyst. The gases then pass through a second absorption tower, where SO_3 is absorbed by sulfuric acid as in the first absorption tower. The waste, or tail, gases are then normally treated to remove acid mist and spray, and vented to the atmosphere. Tail gases could be routed to other treatment devices for further SO_2 removal prior to release, if necessary.

FIGURE 40 SULFURIC ACID PLANT

(SOURCE: AMSDEN, 1974)

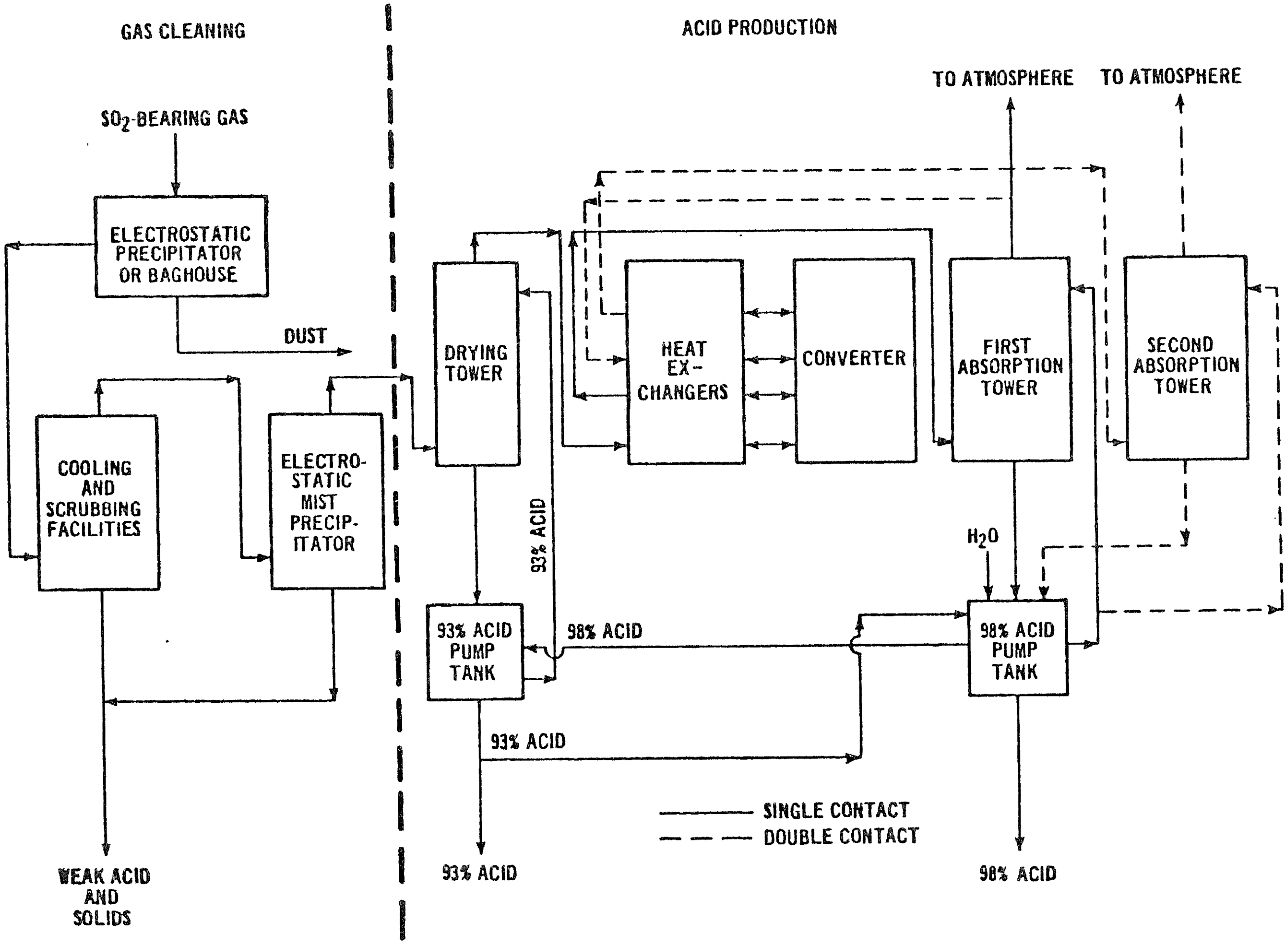


Table 13 is a list of some of the smelters using sulfuric acid plants, and estimated SO_2 removal efficiencies for the plants, based on data available in the literature. Note that the acid plants shown have the capability of removing up to 99.7% of the SO_2 in the acid plant feed gas. A distinction must be made here between the SO_2 removal efficiency of an acid plant, and the efficiency of sulfur recovery as sulfuric acid. For example, the best available technology employed to effect sulfur removal from the model 100,000 mtpy smelter (Coleman 1978b) removes 99.64% of the sulfur in the strong gas stream, leaving only 0.36% in the existing tail gas. However, only 97.44% of the input sulfur is converted to sulfuric acid, while the remaining 2.20% of input sulfur leaves the plant as a weak acid blowdown. Such blowdown may require treatment to prevent water pollution problems (see section 4.9.2).

Table 13

Estimates are available for the general range of acid plant capital costs as a function of gas treatment capacity (AMAX 1978d). For a single sulfuric acid plant where smelter gas flows generally range from 40,000-140,000 SCFM, capital costs of construction typically will range from \$16 to 39 X 10^6 for SO_2 gas concentrations ranging from 3.25-6.0%. For double contact sulfuric acid plants where gas flows also generally range from 40,000-140,000 SCFM, capital costs of construction will typically range from \$17.5 to 41 X 10^6 for SO_2 gas concentrations ranging from 4.25-8.0%. Costs listed above are for a plant commencing construction in 1978, with start-up in 1980.

Costs are shown in Figure 41 as a function of the daily production of sulfuric acid (Billings 1977a). The data includes actual costs from 7 smelters in Arizona, as well as the estimate for a model smelter designed by the U.S. Bureau

Table 13. Typical acid plant removal efficiencies.

SMELTER	OVERALL ACID PLANT SO_2 REMOVAL EFFICIENCY[a]
Kosaka: Dowa Mining Co. JAPAN[1]	94%
Onahama: Onahama Smelting & Refining Co. JAPAN[1]	greater than 99%
Saganoseki: Nippon Mining Co. JAPAN[1]	greater than 99%
Toyo: Sumitomo Metal Mining Co. JAPAN[1]	97%
San Manuael: Magma Copper Co. USA[2]	98%
Morenci: Phelps Dodge Copper Co. USA[3] (2 acid plants)	95.4%, 96.9%
McGill: Kennecott Copper Co. USA[4]	95%
Hayden: Kennecot Copper Co. USA[5]	99.7%
Hurley: Kennecott Copper Co. USA[6]	97%
El Paso: Asarco Copper Co. USA[7]	99.24%

[a] Most of the values shown were calculated from sulfur balance data available in the literature, and involve interpretations which require that the results be viewed as indicative of the range of actual experience, rather than firm specifications of performance.

[1] Rosenbaum et al. 1976.
[2] Weisenberg et al. 1976a.
[3] Weisenberg et al. 1976b.
[4] Weisenberg et al. 1976c.
[5] Weisenberg et al. 1976d.
[6] Weisenberg et al. 1976e.
[7] Weisenberg et al. 1976f.

of Mines. The solid line is the regression line, with the 2 dashed lines representing the 95% confidence limits.

Figure 41

As a reference, an acid plant treating the strong gases from the model flash smelter facility processing Minnesota copper-nickel concentrate would produce 1200-1300 mtpd (1350-1450 stpd) of 100% H_2SO_4 during normal operation. The plant would treat approximately 100,000 SCFM of gas, and is estimated to require a capital expenditure of $\$28 \times 10^6$ in 1977 dollars. This figure is for modeling purposes only, but may be considered as a reasonable estimate in the context of an accuracy of $\pm 30\%$.

Available information (Billings 1977a) on acid plant operating costs is based on copper production for plants producing only copper. Such data indicates a cost of 2¢-4¢ per pound of copper produced, exclusive of any value recovered through sale of the product acid, or use of the acid by the company itself. Assuming pounds of copper plus nickel can be used to scale for the costs of treating a Minnesota concentrate, this cost becomes $\$4$ to $\$8 \times 10^6$ per year. This should be high since, unlike a conventional copper smelter, approximately 1/3 of the metal output from the smelter is not processed through the copper converter to a low residual sulfur product, but rather leaves as a nickel-copper sulfide matte for refinery processing. Accordingly, for modeling purposes the lower end of the cost range, $\$4 \times 10^6$, was selected as a reasonable estimate of acid plant operating costs.

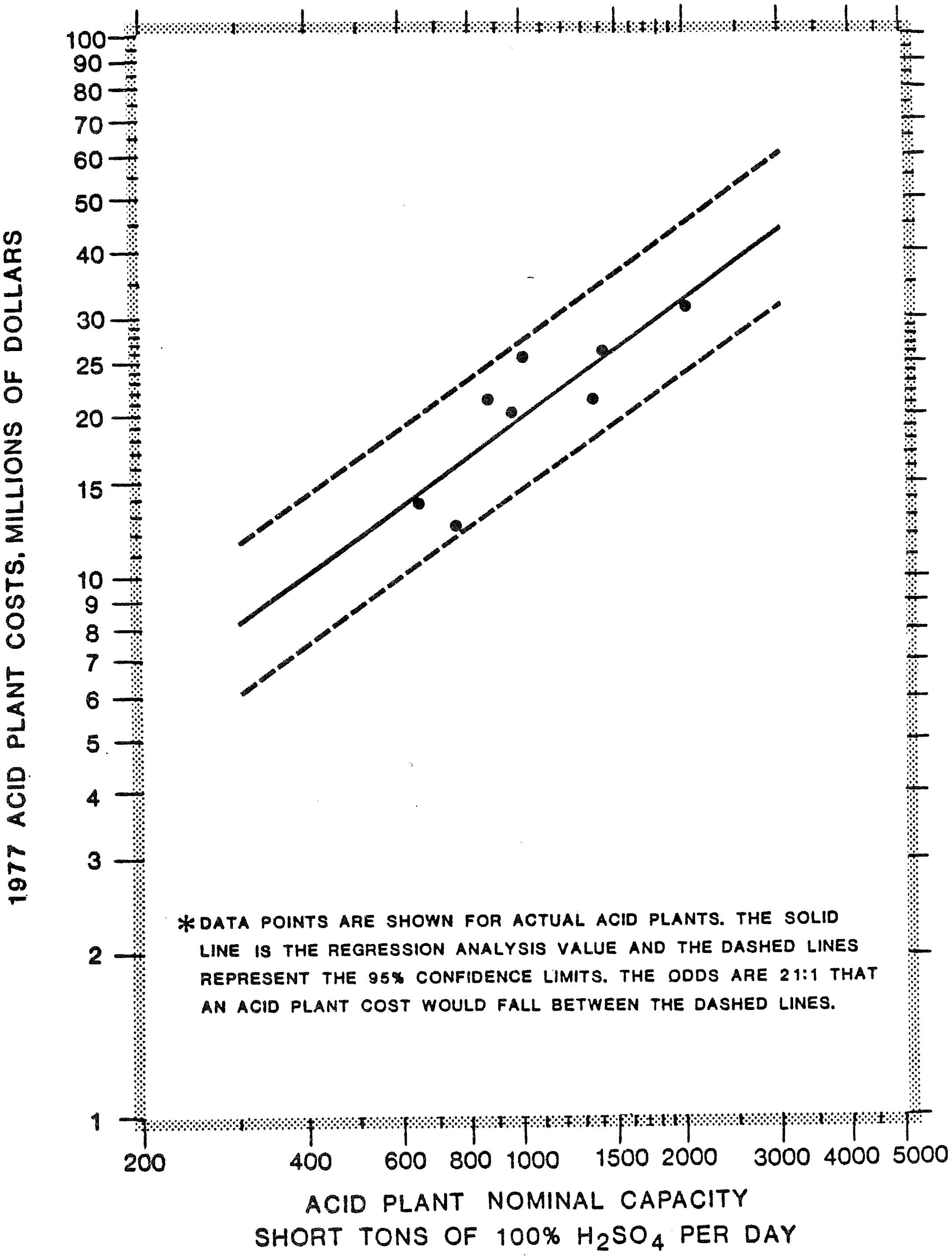
The focus for SO_2 removal from strong gas streams has been on the use of sulfuric acid plants, since this is the technology in widest use today.

FIGURE 41

1977 CAPITAL COSTS *

SMELTER SULFURIC ACID PLANTS

(SOURCE: BILLINGS, 1977A)



* DATA POINTS ARE SHOWN FOR ACTUAL ACID PLANTS. THE SOLID LINE IS THE REGRESSION ANALYSIS VALUE AND THE DASHED LINES REPRESENT THE 95% CONFIDENCE LIMITS. THE ODDS ARE 21:1 THAT AN ACID PLANT COST WOULD FALL BETWEEN THE DASHED LINES.

Further, available information on possible Minnesota copper-nickel operations indicate this device is quite likely to be the control device chosen for strong gas treatment from a new facility. However, other control possibilities do exist. Two of these deserve mention, and will be briefly discussed: those are plants producing elemental sulfur, and those producing liquid SO_2.

Elemental sulfur plants, which normally achieve sulfur dioxide reduction efficiencies of 90% have not achieved widespread use in the copper-nickel industry (Amsden 1974). The failure of this technology to achieve widespread application in most cases has not been due to technical limitations, but a matter of economics where other alternatives have been available. It is significant that the low removal efficiency here is inadequate to meet new federal air emission standards (EPA 1976a), putting this technology at a competitive disadvantage with respect to the double contact sulfuric acid plant.

Essentially, elemental sulfur plants consist of 2 basic process steps. A fossil fuel is mixed with the gas stream to be reduced, frequently in the presence of a catalyst to promote the reduction reactions. A portion of the sulfur dioxide in the gas stream is reduced to elemental sulfur and hydrogen sulfide. The extent to which elemental sulfur and hydrogen sulfide are formed and sulfur dioxide remains in the gas stream depends on temperature, pressure, and the carbon-to-hydrogen ratio in the fuel utilized as a reductant. With the reductant properly proportioned to the sulfur dioxide in the gas stream, the ratio of hydrogen sulfide to sulfur dioxide remaining will be approximately 2:1. Following reduction, a claus catalyst is utilized to react the hydrogen sulfide formed with the remaining sulfur dioxide, producing elemental sulfur according to the claus reaction.

$$4H_2S + 2SO_2 \rightarrow 3S_2 + 4H_2O$$

Figure 42 shows a flow diagram for an elemental sulfur production process developed by the Allied Chemical Corporation. Elemental sulfur plants are available commercially, and are capable of treating gas streams containing SO_2 concentrations ranging from less than 5% up to 100%. However, the oxygen content of the gas must be low (less than 5%) for the process to be attractive. As a result only the gas streams from fluid bed roasters and flash smelting furnaces appear to be suitable for application of this technology, and tail gases would still need further treatment to meet air emission standards. Since an acid plant can accept these gas streams, and would be needed to treat converter gases in any case, elemental sulfur technology appears to be the less likely choice over the more versatile and efficient acid plant. Both systems have, however, been installed at the new Hildago flash smelter in New Mexico (Judd 1978). The smelter is owned by the Phelps Dodge Corporation, one of the principal developers of the elemental sulfur production technology. Here, two double contact acid plants are also required. A small plant is required to treat converter off-gases while the elemental sulfur plant treats the flash furnace gases. A larger plant is also provided to treat the combined strong gas streams when the elemental sulfur plant is not operating.

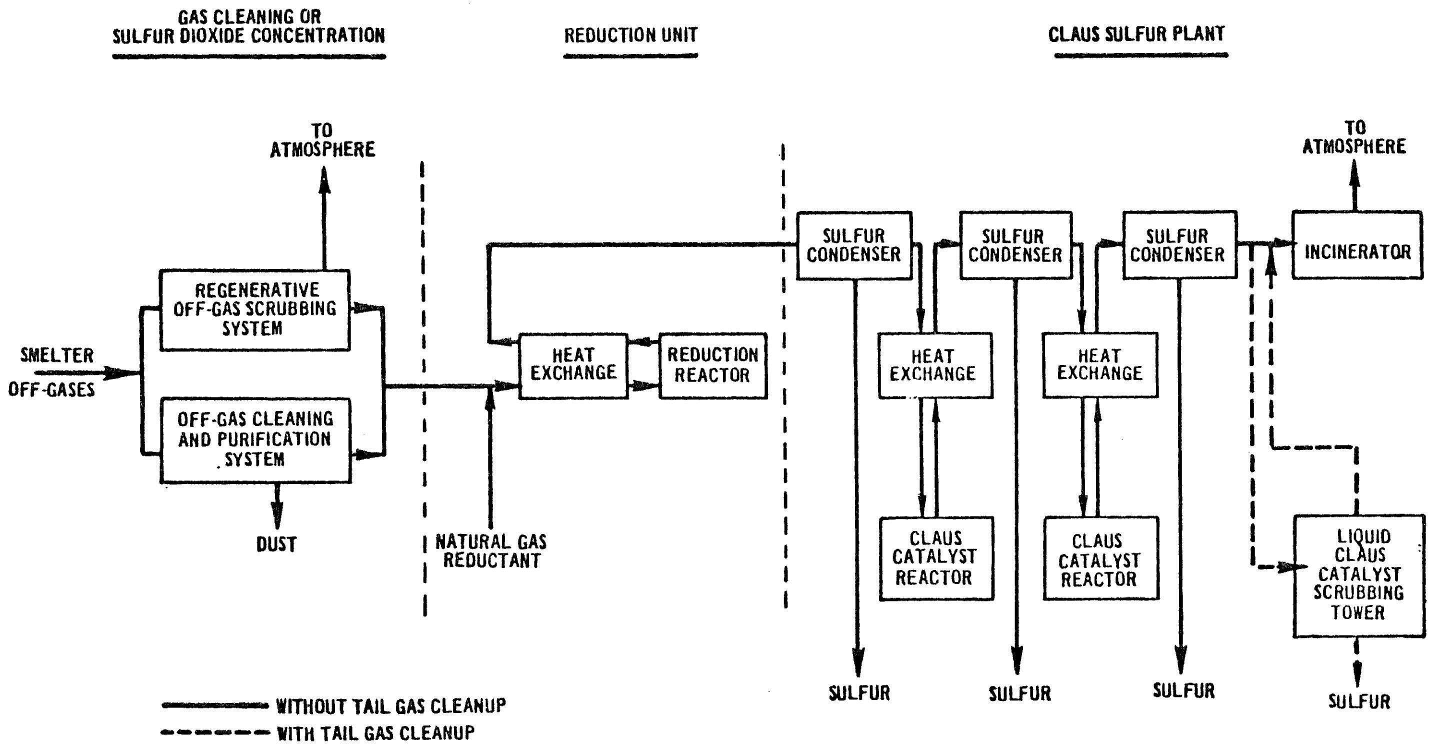
Figure 42

Several facilities currently in operation employ removal technologies that produce liquid SO_2 as a by-product. One such case is the Inco oxygen flash furnace at Copper Cliff (Merla et al. 1972). The use of 95% pure oxygen in the flash furnace allows the production of a strong gas stream containing approximately 80% SO_2. This stream is cleaned, dried, and liquified in multi-stages of

FIGURE 42

ALLIED CHEMICAL SULFUR DIOXIDE REDUCTION PROCESS

(SOURCE: AMSDEN, 1974)



compression and cooling. Again, since an acid plant would still likely be needed to treat the lower concentration converter gases, the selection of such a process appears unlikely. However, techniques do exist for concentrating the SO_2 in gas streams to a degree adequate for liquifaction. The dimethylaniline (DMA) scrubbing system accomplishes this concentration, and has been used with SO_2 liquifaction to treat smelter gases containing 4 to 10% SO_2. The process may also be able to treat weaker gas streams. This system, possibly coupled with an Inco style oxygen flash furnace, producing liquid SO_2 may be a viable process for SO_2 emission control. It's selection over the use of an acid plant may well depend on the existence of appropriate markets for the liquid SO_2 produced. For example, should Minnesota become a terminal for a pipeline carrying Alaskan oil, a market might develop using liquid SO_2 for treating petroleum refinery hydrogen sulfide by the klaus process (Billings 1977a). Therefore, it is worth discussing the DMA process in a bit more detail, even though extensive performance and cost data are not available.

Briefly, the DMA absorption system is a cyclic regenerative process. The system incorporates an absorption tower with numerous trays that allow for much greater gas phase mass transfer and reactant surface area than with other scrubbers such as the venturi or single-bed type. Liquid sulfur dioxide is recovered as a product, and the adsorbent is regenerated and recycled through the system. A small purge stream is required to eliminate sodium sulfate (in solution) from the regenerator section. A small amount of DMA is also included in the purge stream.

A simplified flow diagram for the DMA scrubbing system is depicted in Figure 43. Briefly, pretreated SO_2-laden process off-gases vent to the bottom of a bubble plate tower where most of the SO_2 is adsorbed in a counter-current stream of anhydrous DMA, a complex, aromatic organic compound, $C_6H_5N(CH_3)_2$. The gases, impoverished in SO_2 and enriched in DMA vapors, then pass to a second section of the tower where they are scrubbed with a weak sodium carbonate solution. The residual SO_2 in the gases converts the sodium carbonate to sodium sulfite or sodium bisulfite. The CO_2 is liberated in the gas stream. The effluent gases then pass to a third section of the scrubbing tower where they are scrubbed with a weak sulfuric acid solution and entrained vaporized DMA is recovered as DMA sulfate. The effluent then vents to the atmosphere.

Figure 43

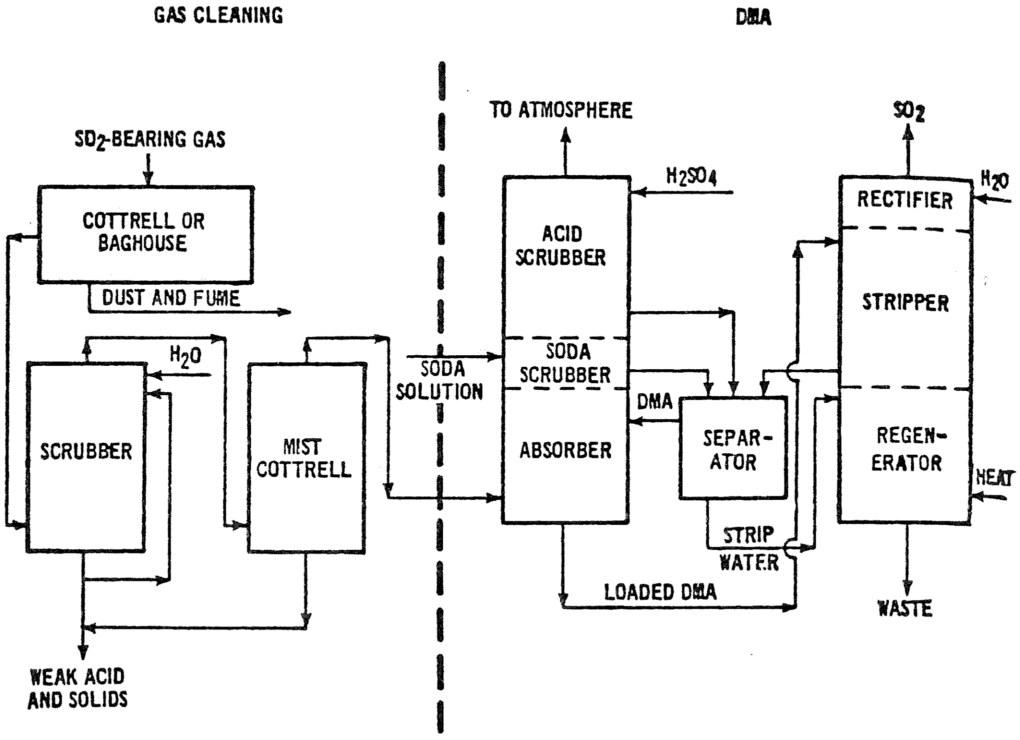
Pregnant DMA is heated by exchange and then passes to the center section of a bubble plate stripping tower. The liquid flows downward counter-current to a rising column of steam and sulfur dioxide vapors. The sulfur dioxide is stripped from the DMA and escapes upward through the tower. The recovered DMA is cooled and then passes to a series of separators where the absorbent floats on the water and can be physically separated and sent to the DMA surge tank for recycle.

The aqueous effluent from the soda scrubbing and acid scrubbing sections of the absorption tower passes to a collection tank where DMA is liberated as a result of the reaction between DMA sulfate from the acid scrubber and the sodium sulfite-bisulfite from the soda scrubber. Part of the DMA remains dissolved in the water as DMA sulfite. The water/DMA sulfite/sodium sulfate solution empties to a stripper water tank. This solution then passes to the bottom section (regenerator) of the stripping tower where the DMA sulfite is thermally decomposed and SO_2, DMA, and water are vaporized and vented into the stripper section of the tower. A small purge stream is drawn off the regenerator to remove sodium sulfate.

FIGURE 43

DMA SCRUBBING PROCESS

(SOURCE: AMSDEN, 1974)



The stripped SO_2 and residual DMA vapors pass from the stripping section into the top section (rectifier) of the stripping tower where they are bubbled through water. The DMA, by reacting with SO_2 in the presence of water, is recovered as DMA sulfite and passes back to the stripper section. The sulfur dioxide effluent stream from the rectifier is cooled to condense water, then scrubbed with cold water, and dried in a tower with 98% sulfuric acid. The gas is then compressed, cooled, liquefied, and run to storage.

Reportedly, this type of sulfur dioxide absorption system has few significant operating problems if the process off-gases are properly cleaned and conditioned. Scaling, erosion, mist elimination, and gas reheat are not major problems with existing units.

A brief summary of operating problems that could affect the operation or the sulfur dioxide removal efficiency of DMA scrubbing system is as follows:

1) Precleaning of process off-gases--Particulate removal equivalent to that required for a contact sulfuric acid plant treating metallurgical gas streams is required for successful application of the DMA process.

2) Waste sodium sulfate--The waste sodium sulfate formed in the DMA process depends primarily on the amount of sulfuric acid used for recovery of DMA vapor in the adsorption tower.

The adsorption reaction between SO_2 and DMA is exothermic; hence, intercoolers are required between each of the absorption tower trays to cool the absorbent. Cooling of the absorbent not only increases the capacity of a unit of DMA to transfer SO_2, but it also reduces the vapor pressure of the DMA, thus decreasing DMA losses. As a result of decreasing absorption temperatures, reagents are saved and sodium sulfate formation is reduced. With the absorbent being totally organic, oxidation plays a relatively minor role in waste sodium sulfate generation.

A decrease in the SO_2 concentration of the process off-gases requires an increase in the use of reagents and, consequently, an increase in the formation of sodium sulfate, as well as operating costs.

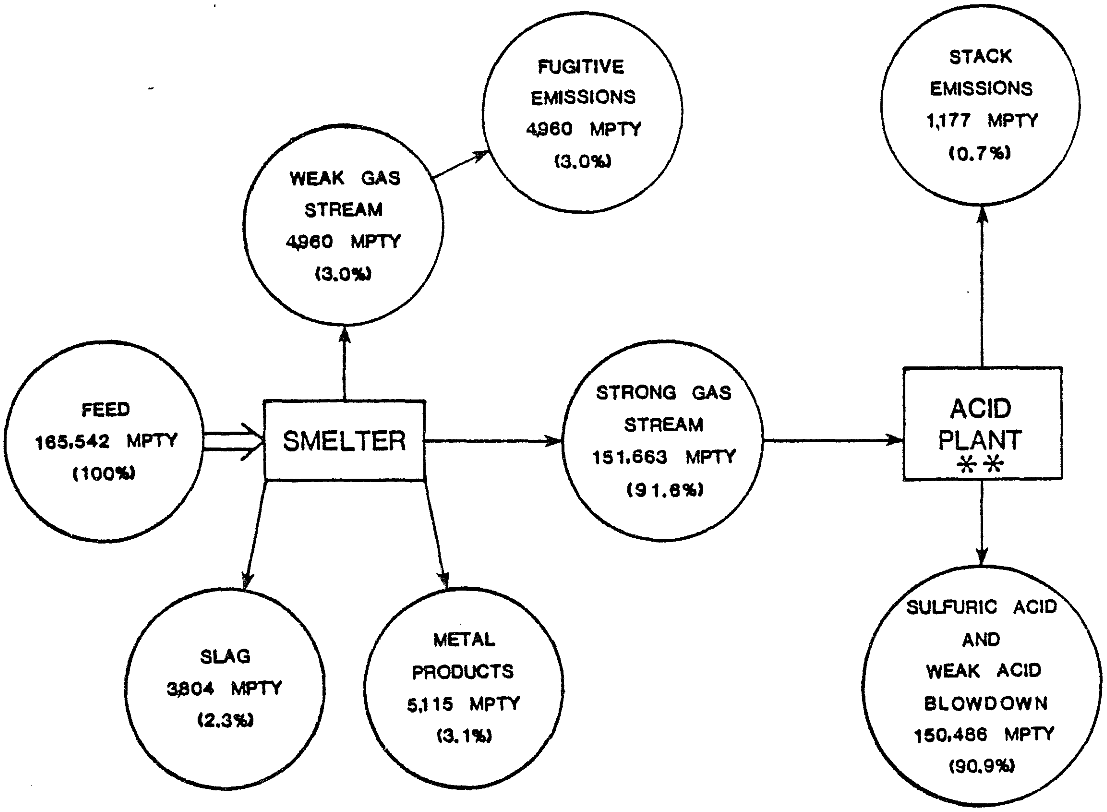
Smelter Models--To illustrate the emission control effect of these devices treating the strong gas stream, a sulfur balance was computed using the model shown earlier in Figure 38. As the most likely control device for a new facility, a sulfuric acid plant is assumed to treat the approximately 100,000 SCFM strong gas stream with a removal efficiency of 99.2%, sufficient to lower the SO_2 concentration in the strong gas stream to the 650 ppm indicated by the EPA's new source performance standards for primary copper smelters (EPA 1976a). Figure 44 indicates the effect of this treatment on the overall sulfur balance. The acid plant tail gas would contain some 1,175 mtpy of sulfur, which would be emitted to the atmosphere as 2,350 mtpy of SO_2. The weak gas stream is not collected, but escapes through vents and other building openings as low level emissions, termed fugitive emissions. The control system shown here is estimated to cost \$28 X 10^6 in capital costs, with \$4 X 10^6 (1977 dollars) in annual operating costs.

Figure 44

Upsets--It is important to comment here on the question of the reliability of emission control equipment. Clearly, a device such as an acid plant is relied upon to remove a considerable fraction of the SO_2 in smelter gas streams prior

FIGURE 44

SULFUR BALANCE* FOR A MODEL FLASH SMELTER UTILIZING AN ACID PLANT TO LOWER THE SO_2 CONTENT OF THE (APPROXIMATELY 100,000 SCFM) STRONG GAS STREAM TO 650 PPM SO_2



* THE EXACT TONNAGES SHOWN IN THIS AND OTHER MODELS DO NOT REFLECT THE ACCURACY IMPLIED FOR THE MODEL, BUT SIMPLY THE FACT THAT THE STREAM SHOWN IS PART OF A MATERIAL BALANCE REQUIRING INTERNAL CONSISTENCY. DATA IS GIVEN BOTH AS METRIC TONS OF SULFUR PER YEAR, AND % OF IMPUT SULFUR.
NORMAL OPERATING CONDITIONS ARE ASSUMED.

** SO_2 REMOVAL EFFICIENCY OF 99.22%, 88,852 SCFM TAIL GAS TO STACK to releasing those streams to the environment. It is important, therefore, to understand that these control devices can and do fail, resulting in either the forced shutdown of the entire operation, increased SO_2 emissions to the atmosphere, or both. Clearly, the specific problems involved and their consequences depend on the details of the particular installation involved. However, the record of previous experiences provides valuable insight into some of the problems that may be encountered.

Data from 2 Arizona smelters indicate that the acid plants at these operations were down for approximately 14% and 21% of the time, respectively, during 1976 (Billings 1977a). Not all of the outages were due to failures in the acid plants themselves, but the information was given as representative of the difficulty in operating and maintaining an acid plant. EPA figures (EPA 1976a) indicate availabilities of 94% and 93.5%, respectively, for single and double contact acid plants. This again confirms that, whether planned or accidental, any acid plant will be non-operational for a significant number of hours out of each year.

In the event of a failure of the acid plant, it is technologically feasible to bypass the plant and vent the entire strong gas stream to the atmosphere via the stack. Minnesota air quality regulations, however, require that in the event of a breakdown, "the owner or operator shall immediately take all practical steps to modify operations to reduce the emission of air contaminants" (APC 21, d.3.). However, even if the operator shuts the entire facility down completely, a certain amount of time is required to halt operations in an orderly fashion. During this time, emissions to the atmosphere would occur. To illustrate the possible effects, the air quality section of this report considers the ambient SO_2 concentrations in the vicinity of a smelter under normal operating conditions, as well as under conditions assuming one acid plant upset per month. See Volume 3-Chapter 3 for a discussion. Reliable data is not available to specify the expected frequency of acid plant outages. However, several new metallurgical acid plants are currently in operation worldwide, and the various problems encountered are being dealt with. Consequently acid plant performance might be expected to improve with this experience, and more reliable data should become available concerning this performance. Such up-to-the-minute data, not only with respect to acid plants, but all control devices, should be obtained in order to assess the potential air quality impacts of any specific proposed smelter facility.

Particulate Removal Devices--As noted earlier, the particulate load in the strong gas stream is so large that there has long been a clear economic incentive to remove these entrained particles. This is especially true of smelter and roaster off-gases. It also applies to the gases from a dryer, particularly a spray dryer, which do not contain SO_2. Consequently a variety of well-proven devices are available commercially for control of particulates including aerosols, in the strong gas streams. The principal devices to be discussed include:

1) settling chambers
2) cyclones
3) impingement separators
4) centrifugal separators
5) electrostatic precipitators
6) wet collectors

The design of gas cleaning equipment is primarily based on particle and carrier gas characteristics, and process and operating factors. Important particle characteristics are size distribution, shape, density, and such physio-chemical properties as hydroscopicity, agglomerating tendency, corrosiveness, stickiness, flowability, electrical conductivity, flammability, and toxicity. Ease of maintenance and the need for continuity of operation are operating factors which are considered. Important construction factors include the need for floor space and headroom, and material limitations imposed by the temperature, pressure, and/or corrosiveness of the exhaust gas stream.

Information on the particle size gradation in the inlet gas stream is very important in the proper design of gas cleaning equipment. Particles larger than 50 microns can be removed in inertial and cyclone separators, or simple, low energy wet scrubbers. Particles smaller than 50 microns require either high efficiency, high energy wet scrubbers, fabric filters, or electrostatic precipitators.

Wet scrubbers operate at variable efficiencies directly proportional to the energy expended, and can handle changing effluent flow rates and characteristics. Disadvantages of wet scrubbers include high power requirements, the possible need to treat the scrubber liquor, and the possibility that a visible plume may be emitted.

Fabric filters more readily permit reuse of the collected material and can collect combustible and explosive dusts. They do, however, have temperature limitations and are sensitive to process conditions. Electrostatic precipitators can operate at relatively high temperatures, have low pressure drop, low power requirements, and few moving parts. They are, however, sensitive to variable dust loadings or flow rates, and, in some cases, require special safety precautions.

The performance of various gas cleaning devices differs widely depending upon the particular application. Grade efficiency curves for selected gas cleaning devices are shown in Figure 45. Although based on silica dust emissions, it is important to note the collection efficiencies of the various systems in the lower micron regions, less than 10 microns. In this region, fabric filters, high energy scrubbers, and dry electrostatic precipitators are the most efficient. The small particle size of particulate emissions expected from smelter installations, which would result in high energy requirements for a high efficiency scrubbing system to limit particulate emissions, is probably one of the major reasons why scrubbing systems have not found widespread application in the smelting industry. Consequently, fabric filters and electrostatic precipitators are the most widely employed particle emission control systems within the smelting industry.

Figure 45

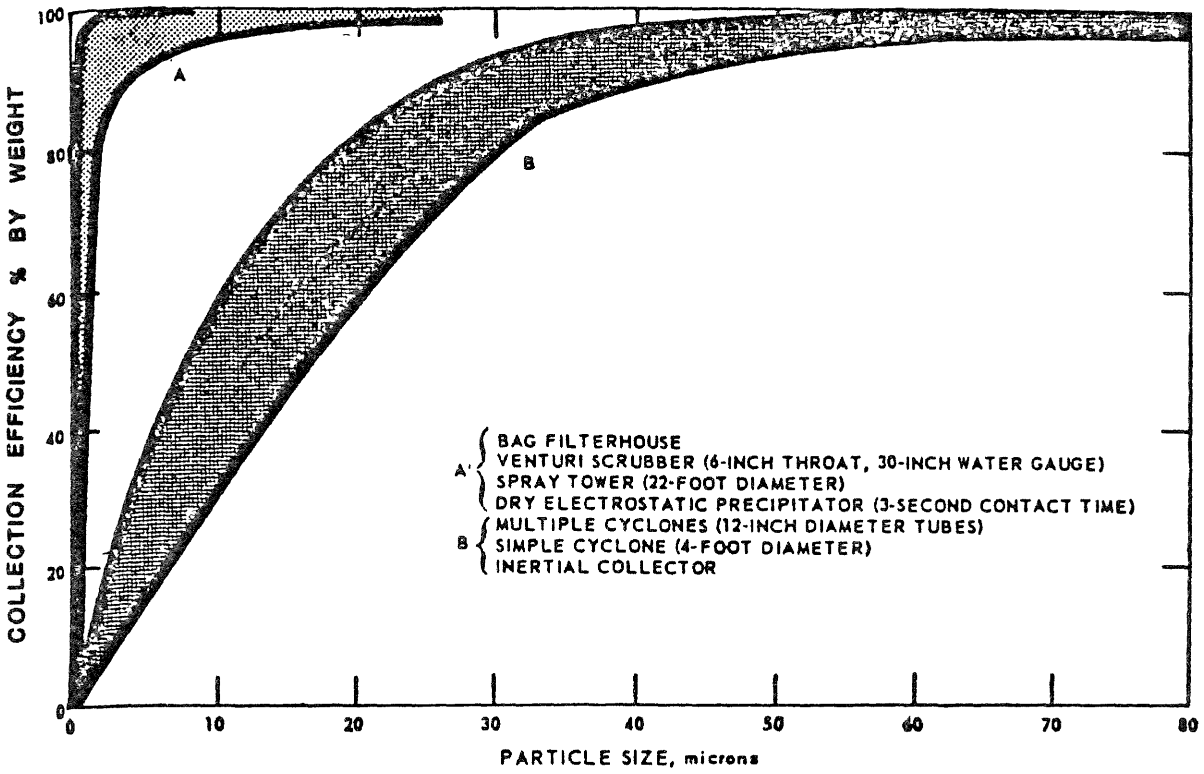
Fabric filtration is one of the oldest and most positive methods used for the collection of particles from gases. Fabric filters are typically used for high efficiency (99+%) particulate removal. Their principal limitation is temperature, with a maximum of approximately 500°F. Fabric filters for cleaning smelter gases are of both the bag and envelope types. A wide range of filtering materials including woven or felted fabric and natural or synthetic materials is utilized.

The particulate matter is removed from the gas stream by impinging on or adhering to the filter fibers. These fibers are normally woven with relatively large open spaces, sometimes 100 microns in diameter or larger. Consequently, the filtering process is not one of simple fabric sieving, as evidenced by the

FIGURE 45

COMPOSITE GRADE (FRACTIONAL) EFFICIENCY CURVES BASED ON TEST SILICA DUST

(SOURCE: AMSDEN, 1974, ROSS, 1972)



fact that high collection efficiencies for dust particles of one micron or less have been achieved. Small particles are initially captured and retained on the fiber of the fabric by direct interception, inertial impaction, diffusion, electrostatic attraction, and gravitational settling. Once a mat or cake of dust is accumulated, further collection is accomplished by mat or cake sieving as well as by the above mechanisms. Periodically the accumulated dust is removed, but some residual dust remains and serves as an aid to further filtering.

In smelting operations a baghouse is normally chosen as the particulate removal device when SO_3 concentration and chloride content of the effluent gases are low. High SO_3 concentrations are known to produce corrosion and deterioration of both the baghouse structure and the filter fabric. Chlorides contained in feed materials will produce hygroscopic effects on fabric filters. The chloride compounds, such as copper, zinc, and lead chloride, contained in these gas streams act as dessicants and can produce a sticky material which tends to blind and eventually tear the filter fabric. Filtration temperatures must also be carefully maintained in order to assure that the filter fabrics are not damaged. With close control of inlet gas temperatures, the formation of potentially harmful chemical substances such as sulfuric acid mist and metal chlorides can be kept to acceptable levels.

Electrostatic precipitators constitute another important class of particulate control devices. Separation of suspended particulate matter from a gas stream by high voltage electrostatic precipitation requires three basic steps:

1) electrical charging of the suspended matter
2) collection of the charged particulate matter on a grounded surface
3) removal of the particulate matter to an external receptacle

A charge may be imparted to particulate matter prior to the electrostatic precipitator by flame ionization or friction. However, the bulk of the charge is applied by passing the suspended particles through a high voltage, direct current corona. The corona is established between an electrode maintained at high voltage and a grounded collecting surface. The particles thereby become highly charged within a fraction of a second and migrate toward the grounded collecting surfaces. After the particulate matter deposits on the grounded collecting surface, adhesive, cohesive, and primary electrical forces must be sufficient to resist any mechanical action or counter-electrical forces that would cause re-entrainment of the particulate matter. Free-flowing liquids are removed from the collecting surface by natural gravity forces. Particulate matter is dislodged from the collecting surfaces by mechanical means such as vibrating with rappers or by flushing with liquids. The collected materials fall to a hopper from which they are removed.

Electrostatic precipitators are normally used when the larger portion of the particulate matter to be collected is smaller than 20 microns in mean diameter. When particles are large, centrifugal collectors are sometimes employed as precleaners. Gas volumes handled are normally in the range of 50,000 to 2 X 10^6 cfm. Operating pressures range from slightly below atmospheric pressure to 150 psi gauge and air operating temperatures normally range from ambient to 750°F.

Electrostatic precipitation is an effective technique for removing both solid and liquid particles from gas streams. It has the advantage over most other control systems of permitting either dry or wet collection of small particles. Fabric filter baghouses might be considered the first choice for a solid particulate emission control system. However, as the process gas stream increases in temperature to the threshold of baghouse operation, electrostatic precipitators gain more acceptance. Currently, electrostatic precipitators are used on all the roasters, reverberatory furnaces, and converters of the primary domestic copper smelting industry.

Table 14 lists the efficiency, the corresponding area of collecting surface required per 1000 SCFM of gas, and the square feet required at each efficiency relative to 97% removal of particulates in an ESP. Table 15 translates these figures into estimates of installed capital costs for the various smelter off-gases assuming 2 models for a smelter (in 1977 dollars)(EPA 1975). These costs must be regarded as rough estimates; and can be considered accurate to ±50%.

Tables 14 & 15

Figure 46 generally summarizes the typical capital costs of the various pollution control equipment (Dryden et al. 1966; Parkinson et al. 1972). Costs are a function of capacity of throughput gases.

Figure 46

Table 16 summarizes the basic types and subtypes of particulate collectors.[53] Table 17 summarizes typical characteristics of the control equipment described in Table 16 (Ross 1972). Efficiency values are based on many factors, some of which directly correlate with the parameters and characteristics of the material being treated.

Tables 16 & 17

Table 14. Collecting surface versus efficiency for metallurgical hot electrostatic precipitators.

PARTICULATE REMOVAL EFFICIENCY	COLLECTING SURFACE AREA REQUIRED PER 1,000 SCFM GAS, ft^2	COLLECTING SURFACE AREA REQUIRED FOR 97% PARTICULATE REMOVAL, ft^2
90	152	0.655
95	200	0.862
97	232	1.000
98	259	1.116
99	301	1.297
99.5	350	1.509
99.7	381	1.642
99.9	460	1.983
99.95	502	2.164

SOURCE: Coleman 1978b.

Table 15. Estimated capital cost installed for removing particulates from model smelter gas streams.

GAS STREAM	GAS FLOW (10^3SCFM)	CAPITAL COST ($\$10^3$)[a] AT VARIOUS EFFICIENCY LEVELS (in percent)			
		97	99	99.5	99.9
Flash Furnace Model					
Dryer	60.0	417.6	541.8	630.0	828.0
Roaster	--	---	---	---	---
Smelting Furnace	47.0	327.1	424.4	493.5	648.6
Copper Converters	49.2	342.4	444.3	516.6	679.0
Nickel Converters	10.6	73.8	95.7	111.3	146.3
Weak SO_2 Gas[b]	178.3	1241.0	1610.0	1872.2	2460.5
Electric Furnace Model					
Dryer	--	---	---	---	---
Roaster	25.2	175.4	227.6	264.6	347.8
Smelting Furnace	12.3	85.6	111.1	129.2	169.7
Copper Converters	49.2	342.4	444.3	516.6	679.0
Nickel Converters	10.6	73.8	95.7	111.3	146.3
Weak SO_2 Gas[b]	109.7	763.5	990.6	1152.0	1513.9

SOURCE: Coleman 1978b.

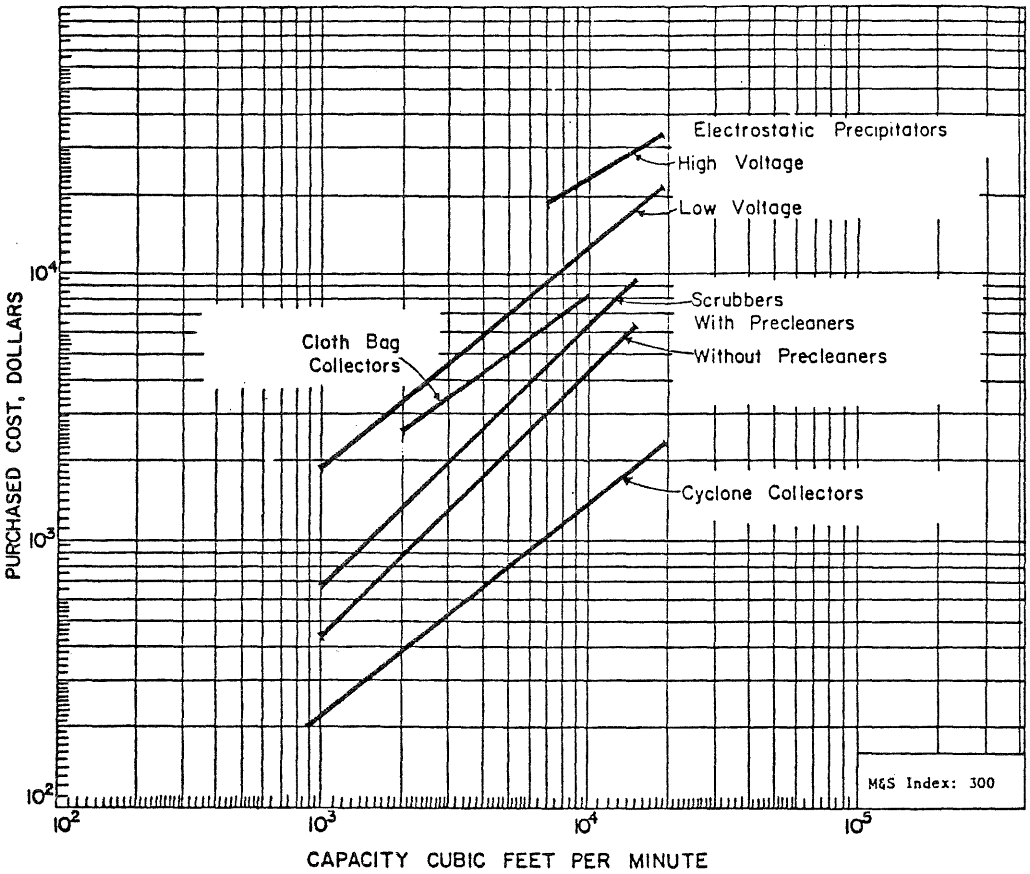
[a] At $30/ft^2 of collecting surface (installed);
[b] If particulate removal is not performed in SO_2 scrubber.

FIGURE 46

CAPITAL COST OF POLLUTION CONTROL EQUIPMENT*

(DUST COLLECTORS ONLY)

(SOURCE: PARKINSON, 1972)



* COST BASIS 1971 DOLLARS, M & S COST INDEX OF 300

Table 16. Fundamental operating characteristics of commercial particulate collectors.

BASIC TYPE	SPECIFIC TYPE	BASIC OPERATING FORCE	BASIC MEASURE AND UNIT OF CAPACITY	TYPICAL CAPACITY IN CFM OF GAS PER BASIC MEASURE OF CAPACITY	TYPICAL COLLECTION EFFICIENCY ON FINE DUST (%)	COST[a] TO PURCHASE FOB SHOP & INSTALL		COST[a] FOR MAINTENANCE AND POWER	
						fob shop	install	maint.	power
Mechanical Collectors	settling chamber	gravity	casing volume (ft^{3})	20	25	10	3	1	0.5
	baffle	inertia	inlet area (ft^{2})	1,200-3,600	40	13	4	2	1.3
	high efficiency cyclones	centrifugal	inlet area (ft^{2})	3,000-3,600	80	20	5	2	10
Fabric Filters	manual cleaning	filter cake filtration	fabric area (ft^{2})	1-4	99	35	20	7	10
	auto shaker cleaning	filter cake filtration	fabric area (ft^{2})	1-4	99	60	30	10	13
	auto reverse jet cleaning	felt fabric filtration	fabric area (ft^{2})	3-8	99	80	35	15	20
Wet Scrubbers	impingement baffle	liquid capture	baffle cross-sectional area (ft^{2})	500-600	80	30	15	7	10
	packed tower	liquid capture	bed cross-sectional area (ft^{2})	500-700	90	40	20	9	17
	venturi	liquid capture	throat area (ft^{2})	7,000-30,000	99	50	50	11	75
Electric Precipitators	single field	electric	collectrode area (ft^{2})	5	95	75	55	4	1.3
	multiple	electric	collectrode area (ft^{2})	3	99	100	70	5	1.3

SOURCE: Ross 1972.

[a] Cost in units of $1,000 (1970 dollars) for a collector to clean 100,000 CFM.

Table 17. Particulate control equipment characteristics.

CONTROL EQUIPMENT	OPTIMUM[a] SIZE PARTICLE (microns)	OPTIMUM CONCENTRATION (grains/ft^3)	TEMPERATURE LIMITATIONS (°F)	EFFICIENCY (%)	SOLID WASTE	LIQUID WASTE	COLLECTED POLLUTANT
Mechanical Collectors							
Settling chamber	50	5	700	50	X		dry dust
Cyclone	5-25	1	700	50-90	X		dry dust
Dynamic precipitator	10	1	700	80	X		dry dust
Impingement separator	10	1	700	80	X		dry dust
Bag Filter	1	0.1	500	99	X		dry dust
Wet Collectors							
Spray tower	25	1	40-700[b]	80		X	liquid
Cyclonic	5	1	40-700[b]	80		X	liquid
Impingement	5	1	40-700[b]	80		X	liquid
Venturi	1	0.1	40-700[b]	99		X	liquid
Electrostatic precipitator	1	0.1	1000	95-99	X		dry or wet dust

SOURCE: Ross 1972.

[a] Minimum particle size collected at approximately 90% efficiency under usual operating conditions.
[b] Limited by materials of construction when sprays are not in operation.

Table 17 continued.

CONTROL EQUIPMENT	COMMENTS
Mechanical Collectors	
Settling chamber	Good as precleaner
Cyclone	Low initial cost
Dynamic precipitator	
Impingement separator	
Bag filter	Bags sensitive to humidity, filter velocity and temperature
Wet Collectors	
Spray tower	Waste treatment required
Cyclonic	Visible plum possible
Impingement	Corrosion
Venturi	High-temperature operation possible
Electrostatic Precipitator	Sensitive to varying conditions and particle properties

Smelter Models--To illustrate the control effects of these devices on the particulate emissions from a smelter, the particulate source models given earlier (Figure 39) are used to feed control devices. The devices modeled are electrostatic precipitators, operating at a 97% removal efficiency. The sulfuric acid plant is also shown, with a high (99.9%) particulate removal efficiency. The models do not assume any wet scrubbing. These devices will be considered in the discussion of SO_2 control in the weak gas stream. Note that no attempt is made to specifically model the costs associated with these precipitators since the particulate source model does not assign specific particulate concentrations to the gas flows from the various sources within the smelter. However, ESPs would likely be installed on the gas streams from dryers, roasters, smelting furnaces, and copper converters. The figure of 97% removal efficiency is used for modeling purposes. However, Table 15 indicates that removal efficiencies of 99.9% are technologically achievable, but at considerably higher costs.

The particulate emission models discussed above are shown in Figure 47. Note particularly the effect of the acid plant on particulates in the strong gas stream. This high degree of removal is a necessary byproduct of the SO_2 control provided by the acid plant. From the viewpoint of optimizing particulate removal, this is an incentive to select source devices which produce strong SO_2 concentrations in any exit gas stream with necessarily high dust loadings. This certainly is not desirable from the viewpoint of an acid plant operator, but proven technology does exist to clean acid plant feed gas. It is reasonable to conclude that the technology is most likely to be optimally operated and maintained if the operation of the acid plant is at stake. For comparison, the dryer gases, part of the weak gas stream, do not qualify for treatment by the acid plant. Consequently, with no further particulate control, modeled emissions from this gas stream are 1,000 times greater than those from all the strong gas streams combined.

Figure 47

The constituents of this stack particulate emission can be modeled by assuming the particulates have the same composition as the initial smelter feed. Table 18 shows the results of this model for the particulates from the flash smelter installation. No attempt is made here to similarly model the composition of the electric smelter stack particulates. In this case, the assumption of a particulate composition comparable to the feed is a very poor one. This problem will be discussed further in section 4.7.4 on minor and trace metals.

Table 18

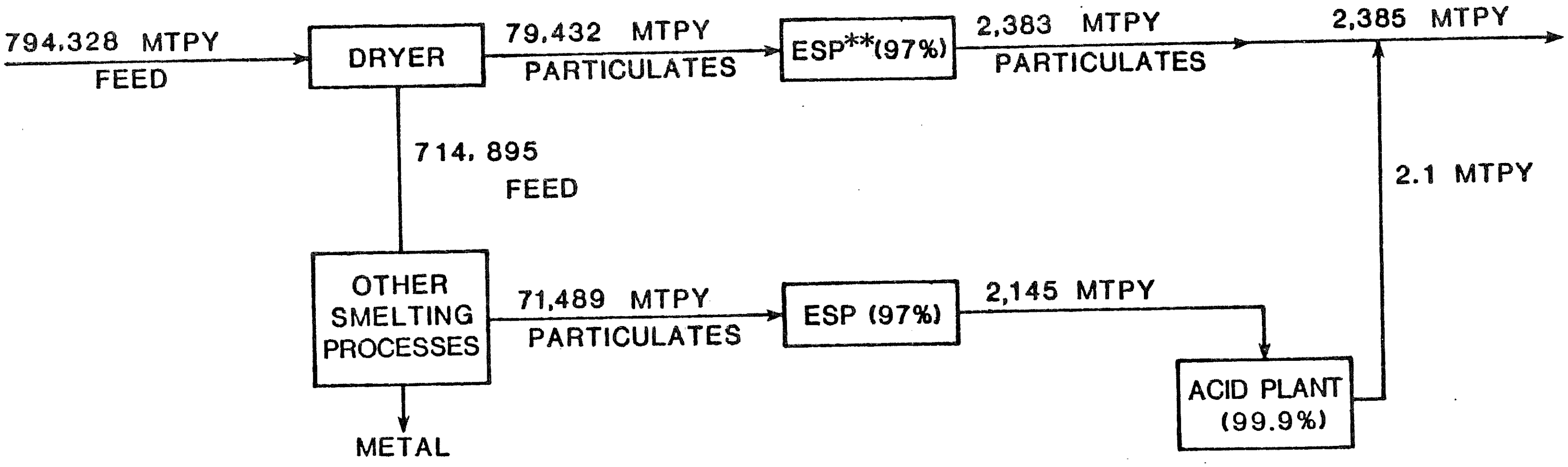
Upsets--Again, it must be realized that the model above assumes normal operating conditions. During upset conditions, emissions could be significantly higher. The emission implications of a breakdown of the electrostatic precipitators are clear from the model. Drier operation would likely be curtailed to prevent unacceptable losses of concentrate, as well as major particulate emissions. Similarly, smelter operations would likely be curtailed to prevent damage to the acid plant, in the event of an outage of the ESPs treating the strong gas stream.

4.7.3.2 Weak Gas Streams--Thus far the discussion of emission control devices has focused on control of constituents present in high concentrations. Central to the discussion has been the control of SO_2 and particulates in the strong gas streams, containing more than 3.5 to 4% SO_2, typically originating from

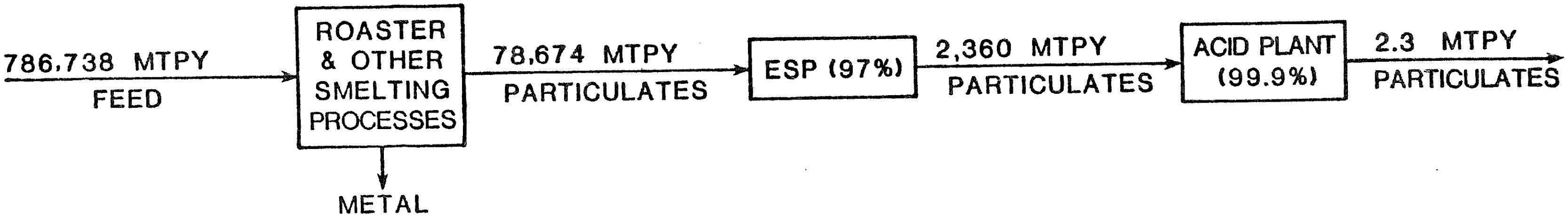
FIGURE 47

STACK PARTICULATE EMISSION MODELS* FOR TWO SMELTER CASES, EACH SMELTER PRODUCING 100,000 MTPY OF COPPER & NICKEL METAL

FLASH SMELTING CASE



ELECTRIC SMELTING CASE



*THE EXACT TONNAGES SHOWN IN THIS AND OTHER MODELS DO NOT REFLECT THE ACCURACY IMPLIED FOR THE MODEL, BUT SIMPLY THE FACT THAT THE STREAM SHOWN IS PART OF A MATERIAL BALANCE REQUIRING INTERNAL CONSISTENCY. THESE TWO MODELS ASSUME 10% OF DRYER FEED AND 10% OF FEED TO OTHER SMELTING PROCESSES (PRODUCING STRONG SO_2 GAS STREAMS) IS CARRIED OFF AS ENTRAINED PARTICULATES IN EXIT GASES . NORMAL OPERATING CONDITIONS ARE ASSUMED.

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Table 18. Model[a] for the constituents in the stack particulate emissions from a flash smelter facility processing 100,000 mtpy of copper and nickel metal.

CONSTITUENT	MTPY
Cu	263.5
Ni	50.45
S	496.63
As	27.44
Cd	1.84
Co	2.53
Be	0.02
Pb	9.8
Hg	0.07
Zn	23.82
Fe	581.67
Sb	0.003
Cl	0.39
F	0.02
S_iO_2	638.51
Al_2O_3	101.83
MgO	57.48
CaO	100.18
Other[b]	39
Total	2,385

[a] The model assumes the particulates will have the same composition as the smelter feed. Normal operating conditions are assumed.

[b] Includes oxides of Na, K, Ti, P, Mn, Cr, and Fe.

roasters, smelting furnaces, and copper converters. The one exception has been a discussion of the control of potentially high particulate levels in the gas exiting from a dryer, even though this is a weak gas stream in terms of SO_2 content. The discussion now focuses on control of gases emitted from the various sources containing such low concentrations of SO_2 and particulates that they are not of economic concern to the smelter operator. Such emissions, however, might not only create high ambient fugitive emissions when they leave the smelter building, but also create difficulties in the occupational environment within the smelter building. Consequently, the major weak gas stream control emphasis to date in the domestic industry has been to capture as much of this gas stream as possible using what is termed secondary hooding systems.

Secondary Hooding Systems--As noted above, the function of secondary hooding systems, with their associated fans and ducts, is to collect air emissions from various weak gas sources within the smelter before they enter the occupational environment and subsequently leave the building as low level fugitive emissions. The gases are instead typically diverted to a tall stack for emission to the air. The ambient effect of such devices is to reduce the high SO_2 concentrations which can be created by fugitive emissions in the vicinity of the smelter. This is discussed in detail in the air quality report, Volume 3-Chapter 3.

The principal elements of these systems typically include secondary hoods around the primary copper converter hoods, as well as hoods on smelter matte and slag taps and launders. Hoods might also be included on sources such as slag cleaning furnaces, nickel converters, anode furnaces, and open ladels of molten matte and slag. These gas streams, combined with any dryer gas streams, constitute the total contained weak gas stream. Gases escaping from these collection systems enter the occupational environment, and eventually leave the building as fugitive emissions.

No firm data has been found concerning the efficiency of this secondary hooding system. Nothing is available concerning the particulate collection efficiency of the hooding, but estimates have been made for the SO_2 collection efficiency. A draft document by the EPA (EPA 1977b) indicates that the system installed on the new Kennecott smelter at Garfield, Utah, will capture 67% of the SO_2 not contained in the strong gas stream. Based on observations at some 25 nonferrous smelters, an estimated efficiency of 90% was deemed reasonable for use in the smelter model for normal operating conditions (Coleman 1978b). It must be stressed that these values are not based on accurate measurements. They are useful, however, in understanding the relative quantities of emissions involved, and as such will be used in the emission models being developed.

The costs associated with the secondary hooding systems will of course vary widely depending on the specific sources to be controlled within the smelter. The EPA report noted above (EPA 1977b) estimates capital costs for collecting and venting converter aisle emissions of $\$19 \times 10^6$ (1977 dollars) for a smelter comparable in size to the model copper-nickel smelter being used here. Operating costs are estimated at almost $\$4 \times 10^6$ annually.

It is appropriate to add a cautionary note at this point concerning a tradeoff that may exist with the use of certain types of emission control devices. Control devices which capture pollutants at the source, such as the primary hooding used on copper converters, serve to improve both the occupational environment and the ambient environment. However, controls which capture pollutants at some distance from the sources listed previously may improve one of the environments (occupational or ambient) at the expense of the other. This is the case, for example, when the smelter building itself is used as part of the control system. If powerful vent fans are used to protect the occupational environment by rapidly evacuating fugitive emissions present in the building, the resulting pressure drop may actually increase these emissions which are then released to the ambient environment. The net result of the control system is an improved occupational environment at the expense of a degraded ambient environment. An example of the opposite tradeoff is provided by the ASARCO smelter in El Paso, Texas (Billings 1977b). A building ventilation system was installed there to capture emissions from the smelter building and duct them through a baghouse to a stack for discharge. The objective of the control system, to improve the ambient environment by reducing fugitive emissions, was achieved. However, due to inadequate draft in the collection system conditions of higher temperatures, reduced visibility, and higher SO_2 concentrations were created within the building, degrading the occupational environment.

With this cautionary note in mind, it should be possible to design and operate control systems in such a manner that tradeoffs of this type do not occur, or at least are minimized. If some tradeoff is inevitable, a careful risk assessment should be made to balance the potential advantages and disadvantages of a proposed control system. For example, a system which reduces ambient fugitive particulate emissions at the expense of higher particulate levels in the occupational environment requires that the occupational health implications for the workers be considered. Such particulates would most certainly contain constituents such as nickel, a known carcinogen (Volume 5-Chapter 2), requiring that particulate control systems receive especially thorough risk analyses before the optimum system is selected.

Smelter Model--As noted, insufficient information exists to make the modeling of particulate control by secondary hooding systems meaningful. However, it is useful to model the SO_2 control effectiveness of this system. For this purpose, a collection efficiency of 90% of the SO_2 in the weak gas stream is assumed. The resulting sulfur balance for the model copper-nickel flash smelter is shown in Figure 48. When compared to Figure 44, shown earlier, it is seen that reducing the fugitive emissions by 90% does not reduce overall sulfur release to the atmosphere, but merely redistributes the emissions. The system does, however, greatly reduce occupational concentrations and ambient concentrations near the smelter.

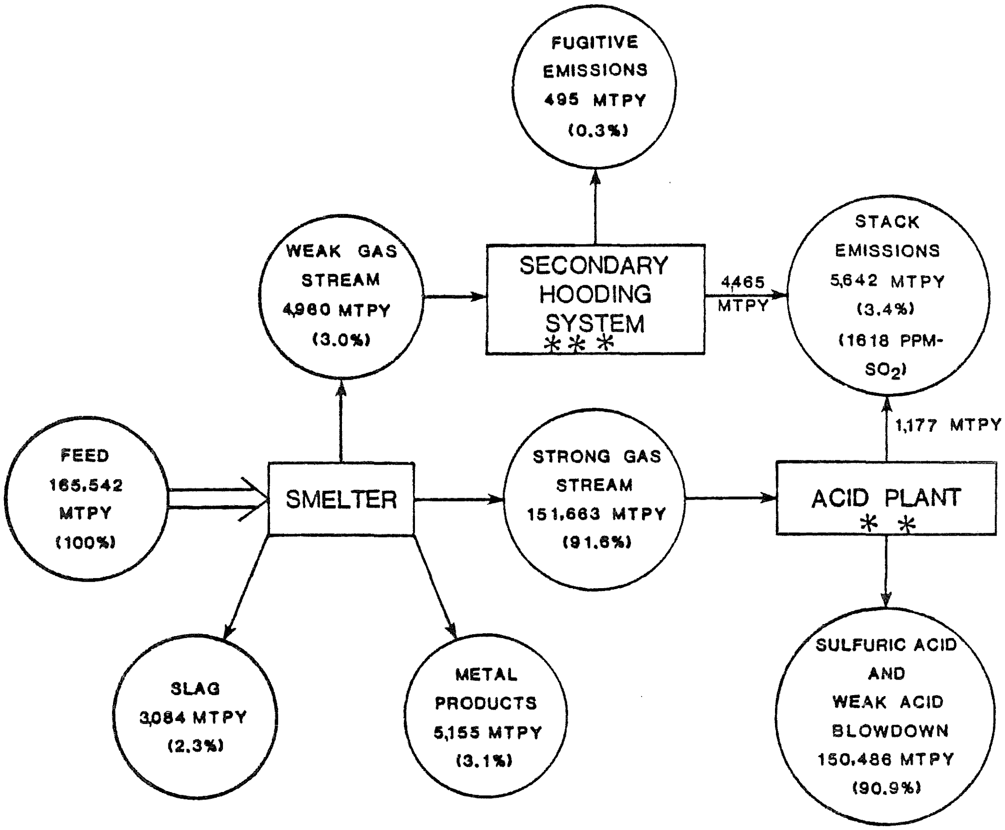
Figure 48

The use of secondary hooding control systems represents the most advanced technology currently widely accepted and in general use in the United States. The two newest copper smelters in the U.S., the Phelps Dodge Hidalgo flash smelter and the Kennecott Garfield Noranda smelter, both employ sulfuric acid plants and secondary hooding systems.

With the creation of a defined weak gas stream by means of a secondary hooding system, the possibility arises for treatment of that stream to remove a portion of the low SO_2 and particulate concentrations it contains prior to exhausting the stream out of a tall stack. The term "low concentration" here implies that the control is motivated principally to prevent air emissions, rather than to recover economically important quantities of material which would otherwise be lost. The actual concentrations at which economic recovery no longer is possible depend on many variables, including the composition of the particulates involved, as well as the gas volumes flowing from the sources.

FIGURE 48

SULFUR BALANCE* FOR A MODEL FLASH SMELTER
UTILIZING AN ACID PLANT AND
A SECONDARY HOODING SYSTEM,
PRODUCING 100,000 MTPY OF CU & NI METAL



* THE EXACT TONNAGES SHOWN IN THIS AN OTHER MODELS DO NOT REFLECT THE ACCURACY IMPLIED FOR THIS MODEL, BUT SIMPLY THE FACT THAT THE STREAM SHOWN IS PART OF A MATERIAL BALANCE REQUIRING INTERNAL CONSISTENCY.
DATA IS GIVEN IN METRIC TONS OF SULFUR.
NORMAL OPERATING CONDITIONS ARE ASSUMED.

** SO_2 REMOVAL EFFICIENCY OF 99.22%, 88,852 SCFM OF TAIL GAS AT 650 PPM SO_2

*** HOODING SO_2 COLLECTION EFFICIENCY OF 90%, 81,600 SCFM GAS FLOW AT 2,672 PPM OF SO_2

Weak Gas Stream SO_2 Removal Devices--The removal of SO_2 from weak gas streams is a relatively new problem for the metallurgical industry. As noted, the motivation to accomplish this removal is generally attributable to environmental concerns, rather than to the recovery of a constituent at a profit. In fact, the U.S. Environmental Protection Agency has found that, to date, the costs of controlling the SO_2 content in weak gas streams, typically less than 3.5% SO_2, at existing primary copper smelters in the U.S., is unreasonable using the various scrubbing systems currently available (EPA 1976a). This judgement is manifested in the fact that weak stream treatment technology is not used either by the new Phelps Dodge flash smelter at Hidalgo, New Mexico, or the Kennecott Noranda reactor at Garfield, Utah. Nevertheless, various treatment systems have been developed, are in commercial operation, notably in Japan (Rosenbaum et al. 1976), and appear to be feasible technologically. The approach utilized to control SO_2 in such cases has been to employ scrubbing systems to chemically react the SO_2 with liquid phase absorbents to yield sulfur compounds that can either be discarded, reprocessed, or sold directly as obtained for use in other industries. Table 19 lists several smelters employing scrubbing systems, and gives an estimate of their SO_2 removal efficiencies.

Table 19

The nature of metallurgical process off-gases is somewhat unique in that a wide variety of contaminants are included in the effluent stream along with sulfur dioxide. The presence of high concentrations of oxygen (relative to fossil-fuel-fired power generating plants), particulates, acid gases, metallic fumes, and high gas temperatures could cause chemical or mechanical problems with cyclic absorption systems, in which the scrubbing liquor is recycled.

Table 19. Smelters employing scrubbing systems.

SMELTER	SCRUBBER SO_2 REMOVAL EFFICIENCY[a]
Kosaka: Dowa Mining Co. JAPAN	84%
Onahama: Onahama Smelting & Refining Co. JAPAN	98%
Saganoseki: Nippon Mining Co. JAPAN	32%
Toyo: Sumitomo Metal Mining Co. JAPAN	90%

SOURCE: Rosenbaum et al. 1976.

[a] The values shown were calculated from sulfur balance data available in the literature and involve interpretations which require that the results be viewed as indicative of the range of actual experience, rather than firm specifications of performance.

Consequently, in most cyclic systems, pretreatment of the process off-gases would be required prior to absorption of the SO_2 in the scrubbing media. This is parallel to the problem seen in sulfuric acid plants, which require significant pretreatment of inlet gases to remove particulates.

During the past 40 years, over 50 process schemes utilizing various types of absorbents as scrubbing media have been investigated on a bench-scale, pilot-plant, or prototype basis in an effort to perfect the optimum control for low concentrations of SO_2 in process off-gases. As a result of these efforts, at least 2 processes have emerged as worthy of commercial application in the control of low concentrations of SO_2 in process off-gases from primary copper, lead, and zinc smelters. These are the Cominco ammonia adsorption process and the ASARCO DMA process, discussed earlier. Two other processes that have had commercial application in the control of SO_2 from either fossil-fuel-fired power plants, sulfur recovery plants, or sulfuric acid plants and are considered to have high potential in the control of low concentrations of SO_2 from smelter processes are calcium-based absorption systems and sodium sulfite-bisulfite absorption systems.

Brief discussions of the three above-noted sulfur dioxide absorption systems and their applicability to metallurgical processes follow. See section 4.7.3.1, the discussion of strong gas treatment technology, for a discussion of the DMA process.

<u>Ammonia Scrubbing Systems</u>--Ammonia scrubbing systems have received considerable attention in the history of SO_2 removal from process off-gases. The reasons for this include the relatively high affinity of ammonia solutions for SO_2 and the ability of such solutions to keep all the compounds involved in solution,

thereby avoiding scaling and silting problems in scrubbers. One viable system has been developed by the Consolidated Mining and Smelting Company of Canada, Ltd. (Cominco), and is capable of treating properly cleaned and conditioned smelter off-gases that have SO_2 concentrations in the range of 0.5 to 6.0%.

Briefly, hot smelter off-gas is treated and conditioned prior to introduction into the first scrubbing tower (Figure 49). The gases are cooled, fine solids are washed out, and SO_3 is absorbed to form weak sulfuric acid. The cooled off-gases then pass to the bottom of a scrubbing tower where they are contacted with a counter-current flow of ammonium sulfite-bisulfite solution. The solution in the first scrubber is maintained at low pH (approximately 4.6) and high salt concentration. Sulfur dioxide is absorbed to form additional ammonium bisulfite. A portion of the solution is recycled back through the tower, and a portion of the solution from the tower is sent to the stripper.

Figure 49

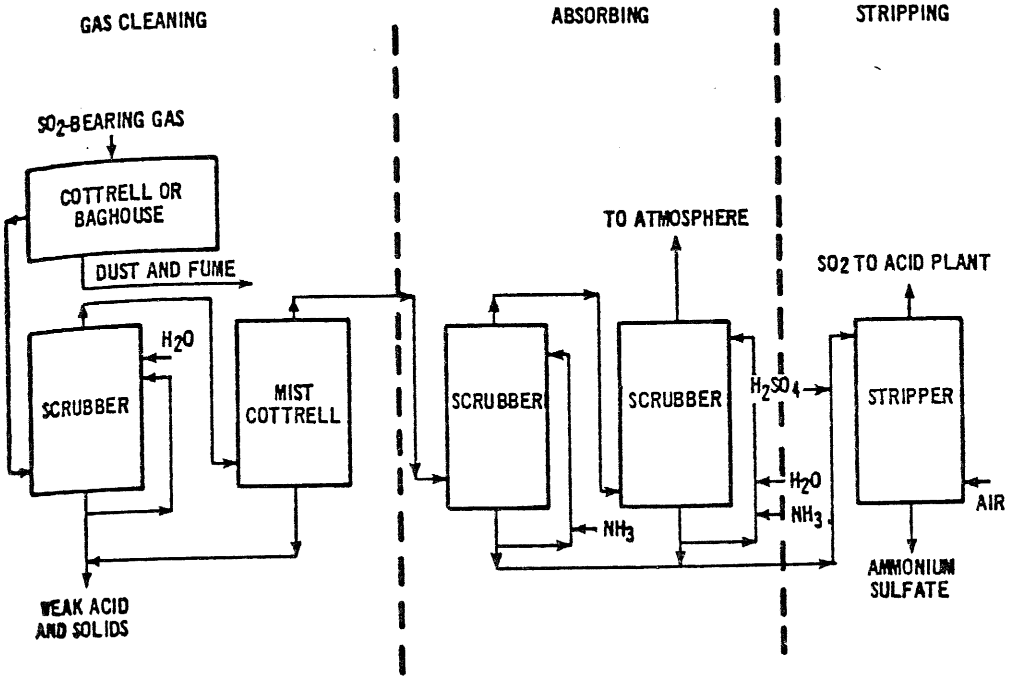
The partially cleaned gases then pass to a second scrubber where additional sulfur dioxide is removed by contact with an ammonium sulfite-bisulfite solution that is at a high pH (approximately 5.4) and has a low salt concentration. A portion of the scrubbing solution is recycled through the scrubber, and a portion of the solution from the tower is sent to the stripper. The off-gas from the scrubber passes to the atmosphere.

The bisulfite solution diverted to the stripper is acidified with sulfuric acid and stripped with air to produce about a 25% sulfur dioxide gas stream, and a solution of ammonium sulfate containing about 10% of the feed sulfur. The ammonium sulfate is then crystallized out and utilized as a fertilizer.

FIGURE 49

COMINCO AMMONIA SCRUBBING PROCESS

(SOURCE: AMSDEN, 1974)



If the consumption of sulfuric acid and ammonia and the production of ammonium sulfate are not economically favorable, the SO_2 can be removed from the ammonium bisulfite solution by stripping with steam.

A brief summary of operating problems that could affect the operation or the SO_2 removal efficiency of Cominco scrubbing systems is as follows:

1) Precleaning of process off-gases - If smelter process off-gases were not precleaned prior to introduction into the scrubber, problems could arise from fouling of cooler lines, etc., but there would be no effect on absorption rates. The particulates would have to be removed by settling and filtering the bisulfite scrubbing solutions prior to acid treatment, as they would interfere with the springing of the SO_2 from solution.

2) Visible emissions - A disadvantage of the ammonia SO_2 absorption system is the formation of a fume from the absorber outlet. Temperature and pH of the absorbent can affect plume formation. Reducing the SO_2 concentrations of the absorber outlet reportedly intensifies the visible emission problem.

The Cominco system has been used successfully not only by Cominco itself, but by the Allied Chemical Corporation at a sulfur acid production facility, and by the Olin Chemical Corporation, on sulfur recovery plant tail gases. Reported SO_2 removal efficiencies range from 75 to 98% (Amsden 1974).

Sodium Sulfite-Bisulfite Scrubbing--A number of domestic and foreign sodium sulfite-bisulfite scrubbing systems control tail gas emissions from sulfur recovery plants, sulfuric acid plants, and oil fired steam generators (Amsden 1974). Input concentrations of SO_2 range from 2,100 ppm to 13,000 ppm (1.3%). Reported removal efficiencies range from 88% to greater than 99%. Notably, the new Toyo smelter in Japan uses the system to treat acid plant tail gas. Their system reportedly removes 99.88% of the input sulfur, producing exhaust gas at only 3 ppm SO_2 (Ogura 1976). This approach is also used at the Saganoseki and Onahama smelters. In the United States, most of the development work on sodium sulfite-bisulfite scrubbing has been conducted by Davy Power Gas (formerly Wellman-Lord). A simplified flow diagram for the Davy Power Gas scrubbing system is shown in Figure 50.

Figure 50

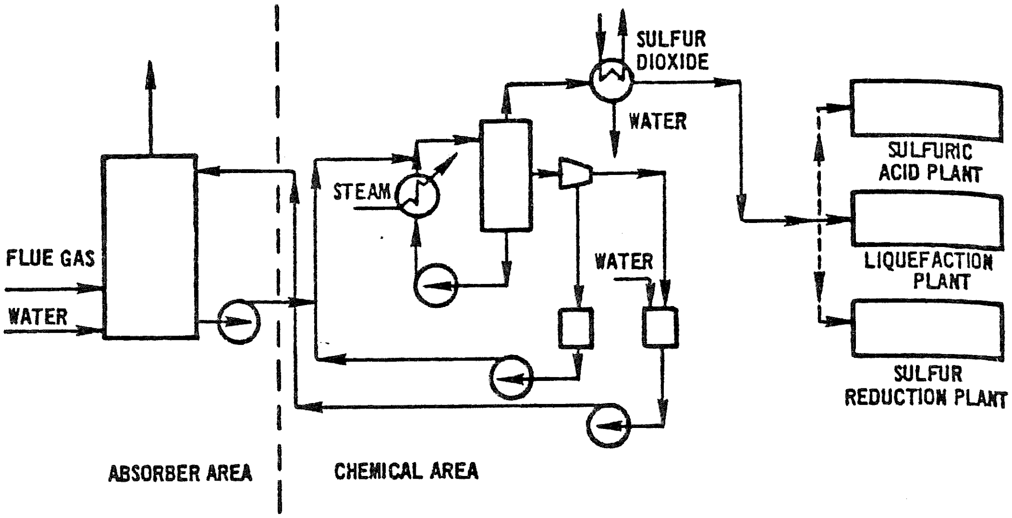
As with most cyclic-regenerative absorption systems, pretreatment is required if it is necessary to cool the process off gases and to remove particulates and acid gases that may interfere with the absorption process or cause problems such as corrosion and plugging or fouling of the system. This pretreatment step must be studied on a case-by-case basis to insure the selection of the optimum design in relation to the overall facility.

The system description is essentially as follows. Pretreated SO_2-laden process off-gases are introduced into a scrubber where they are absorbed in a counter-current flow of a solution of sodium sulfite-bisulfite. The rich absorbent from the bottom of the scrubber is pumped to an evaporator crystallizer system where it is heated by indirect heat exchange with low-pressure steam. As a result of the regeneration step, steam and SO_2 are driven off; and sodium sulfite crystals are formed in the liquid. The wet SO_2 gases are run through a condenser where the bulk of the steam is removed. The concentrated SO_2 stream can be utilized in a sulfuric acid plant, a sulfur recovery plant, or some other appropriate SO_2 process scheme.

FIGURE 50

DAVY POWER GAS SCRUBBING PROCESS

(SOURCE: AMSDEN, 1974)



The liquid phase from the evaporator crystallizer is sent to a centrifugal separator where the crystals of sodium sulfite are removed. These crystals are added to the water that was condensed from the SO_2 stream, and the solution thus formed is recycled to the scrubber. The clarified liquor from the centrifugal separator is recirculated to the evaporator. A portion of the clarified liquor is purged from the system in order to prevent a build-up of sodium sulfate in the system. The amount of sodium sulfate in the feed to the scrubber is controlled at about 5% by weight.

The advantage of the Davy Power Gas scrubbing system is the simplicity of its unit operations and the avoidance of steam stripping of the absorbent, thus substantially reducing steam requirements.

It is recommended that the process off-gas be as free as possible from dust, fume, and vapor or gaseous contaminants such as arsenic trioxide, hydrogen chloride, hydrogen fluoride, and sulfur trioxide. Solid particles in the absorbent solution may produce mechanical problems such as plugging or erosion while acidic gases and vapors will consume absorbent or cause chemical problems such as corrosion.

Smelter effluents in many cases could also cause problems with the system due to the presence of high concentrations of oxygen in the process off-gas and the possibility of introducing potential oxidation catalysts into the absorbent. In both cases, a build-up of an excessive sodium sulfate concentration in the absorbent could result.

In the required purging of sodium sulfate from the absorption system, a portion of the SO_2 is lost because of purging of associated sodium sulfite and sodium bisulfite. Total sodium sulfate formation directly affects the quantity of sodium hydroxide required as makeup to the system.

Calcium-Based Scrubbing Systems--Calcium-based scrubbing systems may be of the non-cyclic type or of the cyclic-nonregenerative type and are capable of SO_2 removal efficiencies ranging from 75-99% (Amsden 1974). In the non-cyclic system, the absorbent passes through the scrubber on a once-through basis. This type of system has inherent water pollution problems in some situations that could preclude its usage on a wide scale unless adequate water treatment systems are included. This problem has largely been bypassed since, in the 1930s, technology was developed on cyclic-nonregenerative scrubbing systems. The system is currently in use to treat metallurgical process gas streams with SO_2 concentrations ranging from 2,000 to 6,000 ppm, and appears likely to work successfully for weak gas streams in the range of 5,000 to 30,000 ppm (Amsden 1974).

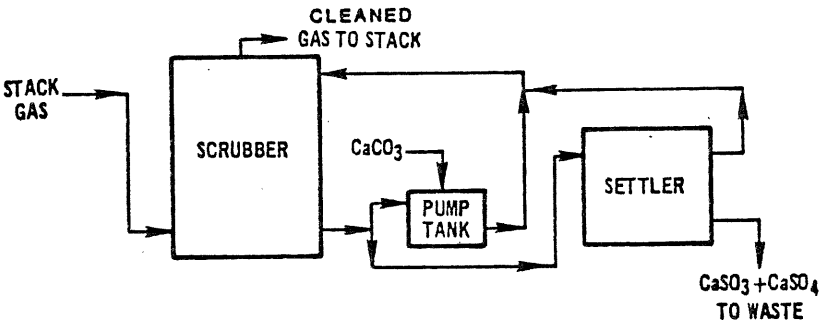
A large number of process varients have been developed for calcium-based scrubbing systems. The 2 most popular variants are the ones that employ either; 1) calcium carbonate or limestone, or 2) calcium hydroxide or slaked lime. A simplified flow diagram for a limestone slurry scrubbing system is depicted in Figure 51. The process description is essentially as follows. The SO_2-laden process off-gases vent to a scrubber where they are scrubbed counter-currently with a limestone slurry. Off-gases from the scrubber vent to the atmosphere. The SO_2-laden slurry from the scrubber is split with a portion going to the pump tank and a portion going to the settler. Calcium carbonate is added to the pump tank as make-up, and effluent from both the pump tank and the settler are recycled to the scrubber. Solids in the loaded absorbent ($CaSO_3$ + $CaSO_4$) are removed in the settler and pass to disposal.

Figure 51

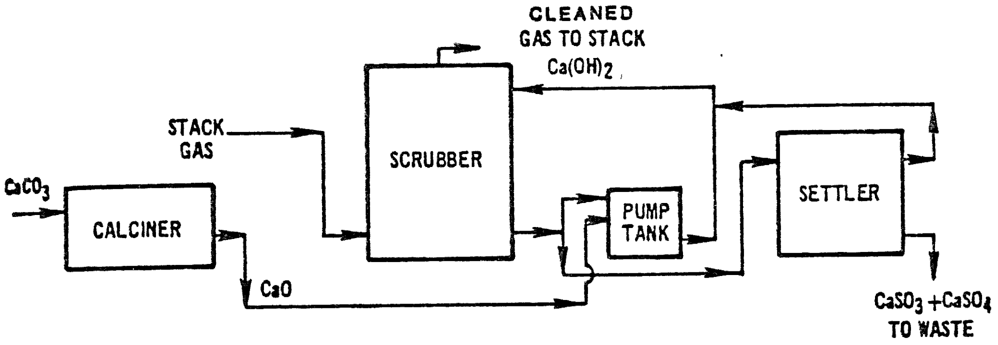
FIGURE 51

LIMESTONE/LIME SCRUBBING PROCESSES

(SOURCE: AMSDEN, 1974)



Scrubber addition of limestone.



Scrubber addition of lime

A lime slurry scrubbing system is also depicted in Figure 51. This system is essentially the same as the limestone scrubbing system except that limestone is calcined to calcium oxide prior to introduction into the scrubber slurry feed system.

The use of pulverized limestone as a reactant is the simplest approach in SO_2 scrubbing; however, the main problem with this system is that limestone is not as reactive as lime, and consequently more limestone is necessary on a stoichiometric basis, a larger scrubber is required and more slurry must be recirculated. For fixed scrubber parameters, lime scrubbing, though increasing scrubbing efficiency, necessitates calcining of the limestone with resulting increased costs.

A brief summary of scrubber parameters that could affect the operation or the sulfur dioxide removal efficiency of limestone scrubbing systems is as follows:

1) Scrubber design - The design of the scrubber is critical in limestone scrubbing systems. Mass transfer relationships and the scaling problem resulting from the formation of calcium sulfate ($CaSO_4$) must be considered. Optimum design would optimize the following requirements: large holdup; high relative velocity between the gas and liquid phase; maximum liquid surface; a minimum of internal parts; and minimum pressure drop.

2) Type of limestone - The ability of carbonate stones to chemisorb SO_2 varies greatly. An evaluation of 10 different stones from quarries in Ontario, Canada, indicated that calcite-type stones maintain a high efficiency for SO_2 removal until nearly exhausted, and dolomite stones consistently gave poor performance compared to the calcites.

3) Limestone particulate size - The efficiency of SO_2 removal and the effective utilization of the stone are both affected by the degree to which limestone is ground.

4) Liquid to gas flow ratio - The ratio of liquid to gas flow is important presumably because of its effect on decreasing gas phase resistance to SO_2 mass transfer and for scale control.

5) Slurry pH - An important consideration in the scrubber operation is the slurry pH, especially in regard to changes in pH that may occur in the scrubber circuit. The main concern with pH is its effect on scaling, corrosion, and blinding of reactive surfaces. The efficiency of SO_2 removal is not appreciably affected until the pH drops to about 4.8, after which the efficiency falls off rapidly. Mild steel cannot be used at pH less than 6.2 without risking severe corrosion problems. Rapid decrease in pH caused by absorption of SO_2 followed by rapid increase in pH caused by the addition of limestone can cause sulfite precipitation on the limestone slurry particles, thus blinding them and making the calcium carbonate inside unavailable for further reaction.

6) Inlet gas temperature - A significant variable in calcium-based scrubbing systems is the temperature of the inlet gas stream. Test data indicate that the SO_2 removal efficiency decreases linearly as the temperature of the gas increases. Warm incoming gas could strip SO_2 from the absorbent slurry. Humidification cooling is probably all that is required to prevent stripping. Scaling problems at the wet-dry interface caused by evaporation of water from the solution or slurry may also result from high inlet gas temperature.

7) Slurry solids loading - High slurry solids loadings provide improved rates of solubility for calcium, thus providing more effective replenishment of the

calcium ion. In addition, there is a beneficial effect of minimizing scaling and plugging by increasing the rate of desupersaturation--particularly with respect to sulfate--thus helping to confine precipitation to the holding tanks and avoiding excessive scale deposits in the process equipment and process lines. The most efficient SO_2 removal has consistently been obtained with slurry solids loadings of 12 to 15% by weight. Higher loadings cause silting out problems. It is pointed out that high solids loadings are extremely abrasive and may cause increased operating problems.

Technically, there are no known problems that would be insurmountable in the application of a calcium-based scrubbing system to control SO_2 from all smelter effluents; however, it would appear that its usage would be primarily applicable to weak streams from smelter processes, again because of economics. Scrubbers of this type are in operation in the U.S. treating effluent gases from coal-fired power plants, and are also being operated successfully on primary metal smelters, notably in Japan at the Kosaka and Onahama smelters (Rosenbaum et al. 1976). Thus, the basic technology has been reasonably proven in the field.

The operating problems associated with any type of scrubbing system can be divided into categories related to either chemical or mechanical operating problems. The chemical problems relate to SO_2 absorption, scaling, and corrosion. For example, the mechanical problems related to calcium-based scrubbing systems are similar to those inherent with any chemical process that involves pumping of slurries and abrasive and corrosive mixtures. The chemical industry has successfully handled these problems for many years.

Mechanical problems in many instances may relate to: 1) poor piping design resulting in plugging or erosion of lines; 2) the improper design, use, and operation of fans, pumps, and motors; 3) the use of improper materials of construction that can result in corrosion of equipment handling basic or acidic solutions; 4) improper scrubber or demister design that can cause plugging problems in the demister; and 5) lack of spare pumps, motors, and scrubbers that may necessitate shutting down or by-passing control facilities.

In summary, a variety of processes are available for SO_2 removal of weak gas streams. Little or no economic data is available on the various processes. However, with the present emphasis on minimizing atmospheric emissions, development work in this field is rapidly expanding both the technology, and the availability of cost and performance data. Again, the most up-to-date data must be obtained to adequately assess the effectiveness of any proposed weak gas control system.

Particulate Removal Devices--The removal of particulates from weak SO_2 gas streams must be briefly mentioned. As noted earlier, the weak gas stream from a device such as a spray dryer may contain significant concentrations of particulates (see section 4.7.2.1). These streams would certainly be cleaned by control devices such as cyclones, electrostatic precipitators, and baghouse filters. Beyond this, further particulate control is not likely unless required to prevent excessive air emissions, or to meet the pre-treatment requirements of any weak gas SO_2 removal systems. The devices applicable here such as wet gas scrubbers have already been discussed in the section on particulate control in the strong SO_2 gas stream, section 4.7.3.1.

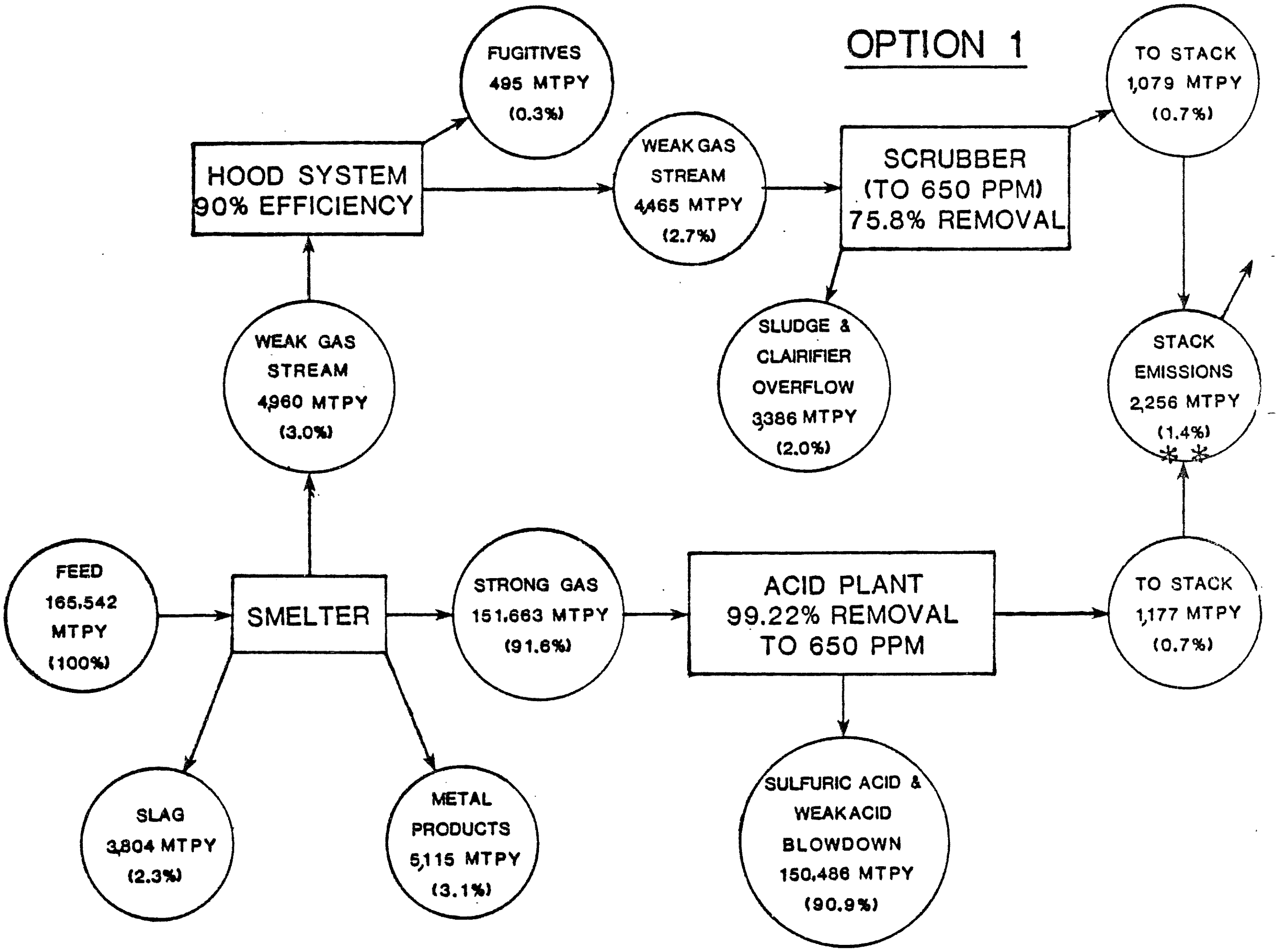
Smelter Models--Consistent with the emission models given earlier, 100,000 mtpy flash smelter models were developed to illustrate the general range of emissions that might be expected from a modern smelter installation utilizing weak gas control devices. For purposes of illustration, a limestone scrubbing system with a venturi prescrubber for particulate removal are assumed (Coleman 1978b). Two separate cases are modeled for weak gas SO_2 control. Option 1 assumes that the acid plant tail gas is not scrubbed, but is released via a tall stack at 650 ppm SO_2. The scrubber treats only the weak gas streams to an exit concentration of 650 ppm, and the gas then combines with the acid plant tail gas as a stack emission. The model corresponds to an SO_2 removal efficiency of approximately 76% in the limestone scrubber. This case is termed the new source performance standard ("NSPS") model since it reflects exit gas SO_2 concentrations specified in present new source performance standards for primary copper smelting furnaces (EPA 1976a). Figure 52 indicates the overall sulfur balance for this "NSPS" case. It must be stressed here that use of the term "NSPS" merely indicates that this model was designed using emission values given in existing federal regulations. There is no intent to imply that any actual facility using the approach indicated in this model would in fact meet applicable emission standards for a new smelter and/or refinery operation. Such a determination can only be made by appropriate state and/or federal agencies.

Option 2 is intended to represent the best state-of-the-art control technology currently in use. Here, the acid plant removal efficiency is assumed to increase to 99.64%, with a resulting tail gas concentration of 300 ppm SO_2. The scrubber now treats both the weak gas stream and the acid plant tail gas with an SO_2 removal efficiency of 90%. The resulting stack gas, at a flow of approximately 170,000 SCFM, contains residual SO_2 at a concentration of 143 ppm. The sulfur balance for this case is given in Figure 53.

Figures 52 & 53

FIGURE 52

SULFUR BALANCE* FOR A MODEL FLASH SMELTER USING SECONDARY SO_2 REMOVAL TO PRODUCE EXIT GAS CONCENTRATION OF 650 PPM SO_2

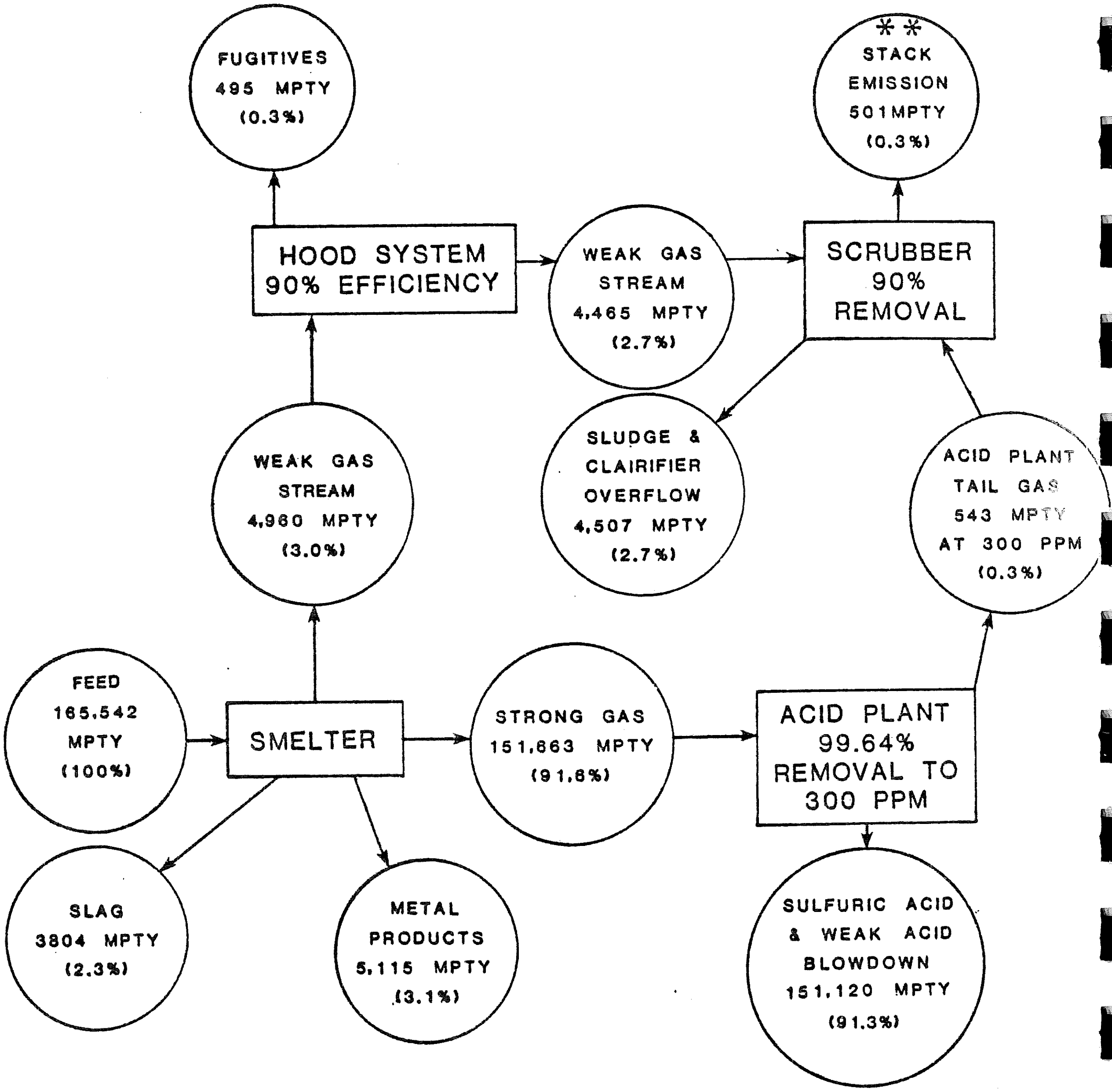


* THE EXACT TONNAGES IN THIS AND OTHER MODELS DO NOT REFLECT THE ACCURACY IMPLIED FOR THE MODEL, BUT SIMPLY THE FACT THAT THE STREAM IS PART OF A MATERIAL BALANCE REQUIRING INTERNAL CONSISTENCY.
DATA IS GIVEN IN METRIC TONS OF SULFUR PER YEAR, AND % OF IMPUT SULFUR
NORMAL OPERATING CONDITIONS ARE ASSUMED,
WITH PRODUCTION OF 100,000 MTPY OF CU & NI METAL

** APPROXIMATELY 170,000 SCFM AT 650 PPM SO_2

FIGURE 53

SULFUR BALANCE* FOR A MODEL FLASH SMELTER USING SECONDARY SO_2 REMOVAL WITH EFFICIENIES REPRESENTATIVE OF STATE-OF-THE-ART CONTROL TECHNOLOGY (OPTION 2)



* THE EXACT TONNAGES SHOWN IN THIS AND OTHER MODELS DO NOT REFLECT THE ACCURACY IMPLIED FOR THE MODEL, BUT SIMPLY THE FACT THAT THE STREAM IS PART OF A MATERIAL BALANCE REQUIRING INTERNAL CONSISTENCY. DATA IS GIVEN BOTH AS METRIC TONS OF SULFUR PER YEAR, AND % OF IMPUT SULFUR. NORMAL OPERATING CONDITIONS ARE ASSUM WITH PRODUCTION OF 100,000 MTPY OF CU & NI METAL.

** APPROXIMATELY 170,000 SC M AT 143 PPM SO_2

Cost estimates for the model scrubbers in the 2 cases were prepared and are shown in Table 20. The results indicate that the "NSPS" case would reduce stack emissions from the earlier modeled value of 5,642 mtpy sulfur in the absence of any weak gas stream removal equipment, to 2,256 mtpy. This 60% reduction comes at an estimated capital cost of $\$4.6 \times 10^6$, with an annual operating cost of $\$2.0 \times 10^6$. Case 2, the state-of-the-art case, reduces the emissions a further 78% to 501 mtpy. The cost estimates show this added control is achieved at a 30% increase in both capital and operating costs, to $\$6 \times 10^6$ and $\$2.6 \times 10^6$ per year, respectively.

Table 20

Models have also been developed for particulate emissions from a hypothetical smelter installation employing scrubbers to treat the acid plant tail gas and the weak gas stream (Coleman 1978b). For the models, a venturi prescrubber is assumed to treat the weak gas stream prior to entry into the scrubber. The venturi prescrubber is assumed to operate with a particulate removal efficiency of 70%. In addition, the fact that the SO_2 scrubber itself acts to removal particles from the inlet gas stream is recognized by assigning it a 50% particulate removal efficiency. Insufficient information is available to allow modeling of different removal efficiencies to be meaningful, unlike the case for SO_2 in which "NSPS" and state-of-the-art cases were modeled. However, it is useful to present not only the flash smelter model, but also an electric smelter model to point out the particulate emission implications of a dryer. Figure 54 presents these models. Note the significantly lower overall emissions from the electric smelting case, due principally to the absence of a gas stream from a dryer which by-passes the acid plant. The overall feed to the electric furnace is lower

Table 20. Estimated costs[a] for limestone slurry scrubbing of gases from a model flash smelting installation.

	CASE 1	CASE 2
System Description	Scrubber treats only weak gas streams. Both acid plant and scrubber exist gases are at 650 ppm. Acid plant removal=99.22% Scrubber removal=75.8%	Scrubber treats both weak gas stream and acid plant tail gas. Both acid plant and scrubber work at SO_2 removal efficiencies representive of best available technology. Acid plant removal=99.64% Scrubber removal=90%
Total capital costs, $\$10^6$	4.6	6.0
Total annual operating costs, $\$10^6$	2.0	2.6
Resulting annual stack emissions, sulfur, mtpy	2,256	501

SOURCE: Coleman 1978b.

[a] 1977 dollars.

than to the flash furnace due to the absence of coal.

Figure 54

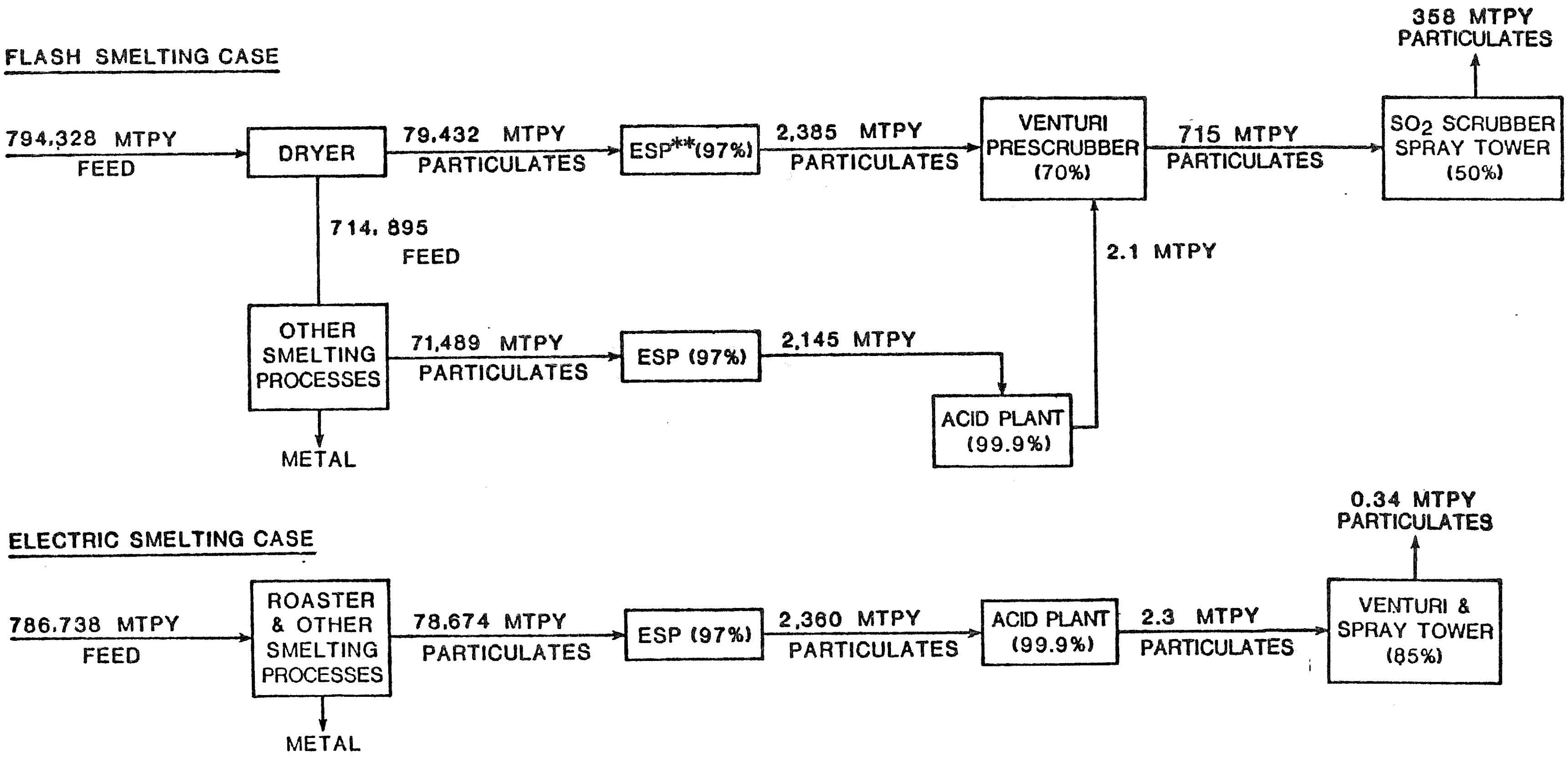
The composition of these particulate emissions have also been modeled for the flash smelter case by assuming the composition would be the same as that for the input feed (see Figure 54). The results are given in Table 21. This is a reasonable assumption for the flash smelting case, in which the dryer is the principal source of particulates. The assumption is expected to be quite poor for the electric smelting case since the high temperatures present in the principal particulate sources could significantly alter the composition of particulates emitted. This is particularly true if high levels of volatile elements are present. Elements such as arsenic may leave the smelting furnace as a hot gas, thus escaping removal by the electrostatic precipitators. Subsequent cooling causes these gases to condense and be emitted as particulates, including aerosols. For this reason, no model is presented for the emission composition in this case. This is discussed further in the next section.

Table 21

Upsets--Previous comments concerning upset conditions apply here as well. Clearly, all the devices discussed for control of weak gas streams are subject to failures for a variety of reasons. Scrubbers might be expected to be particularly uncertain in terms of expected operational reliability due to their relative newness in metallurgical applications, with corresponding lack of performance data. Further, devices of this type tested elsewhere may perform quite differently when exposed to the rigors of the climate in northeastern Minnesota.

FIGURE 54

STACK PARTICULATE EMISSION MODELS* FOR TWO SMELTER CASES, EACH SMELTER PRODUCING 100,000 MTPY OF COPPER & NICKEL METAL



*MODELS ASSUME 10% OF DRYER FEED AND 10% OF FEED TO OTHER SMELTING PROCESSES (PRODUCING STRONG SO_2 GAS STREAMS) IS CARRIED OFF AS ENTRAINED PARTICULATES IN EXIT GASES. NORMAL OPERATING CONDITIONS ARE ASSUMED.TOTAL PARTICULATES ARE GIVEN IN METRIC TONS/YEAR. THE EXACT VALUES SHOWN IN THE MODELS DO NOT REFLECT THE ACCURACY IMPLIED FOR THE MODELS. BUT SIMPLY THE FACT THAT THE STREAMS SHOWN ARE PART OF A MATERIAL BALANCE REQUIRING INTERNAL CONSISTENCY.

**NUMBERS IN PARENTHESIS INDICATE PARTICULATE REMOVAL EFFICIENCIES.

Table 21. Model[a] for the constituents in the stack particulate emissions from a flash smelter facility producing 100,000 mtpy of Cu and Ni metal.

CONSTITUENT	MTPY
Cu	39.53
Ni	7.57
S	74.50
As	0.01
Cd	0.01
Co	0.38
Be	0.00007
Pb	0.02
Hg	0.00006
Zn	0.33
Fe	87.26
Sb	0.0005
Cl	0.06
F	0.003
SiO_2	95.79
Al_2O_3	15.28
MgO	8.62
CaO	15.03
Other[b]	14
TOTAL	358

[a] The model assumes the particulates will have the same composition as the smelter feed. Normal operating conditions are assumed.

[b] Includes oxides of Na, K, Ti, P, Mn, Cr, and Fe.

Upon failure of these control devices, they could be bypassed, if so designed. In this event, emissions would be expected to approximate those modeled earlier without secondary control devices.

4.7.3.3 Summary, SO_2 and Particulate Emission Models--It is useful to summarize the various levels of SO_2 and total stack particulate emissions discussed in the several models presented in this section. It is also helpful to place these emissions in perspective by listing emissions from a variety of other sources for comparison. Figures 55 and 56 summarize this information for SO_2 and total particulates, respectively.

Figures 55 & 56

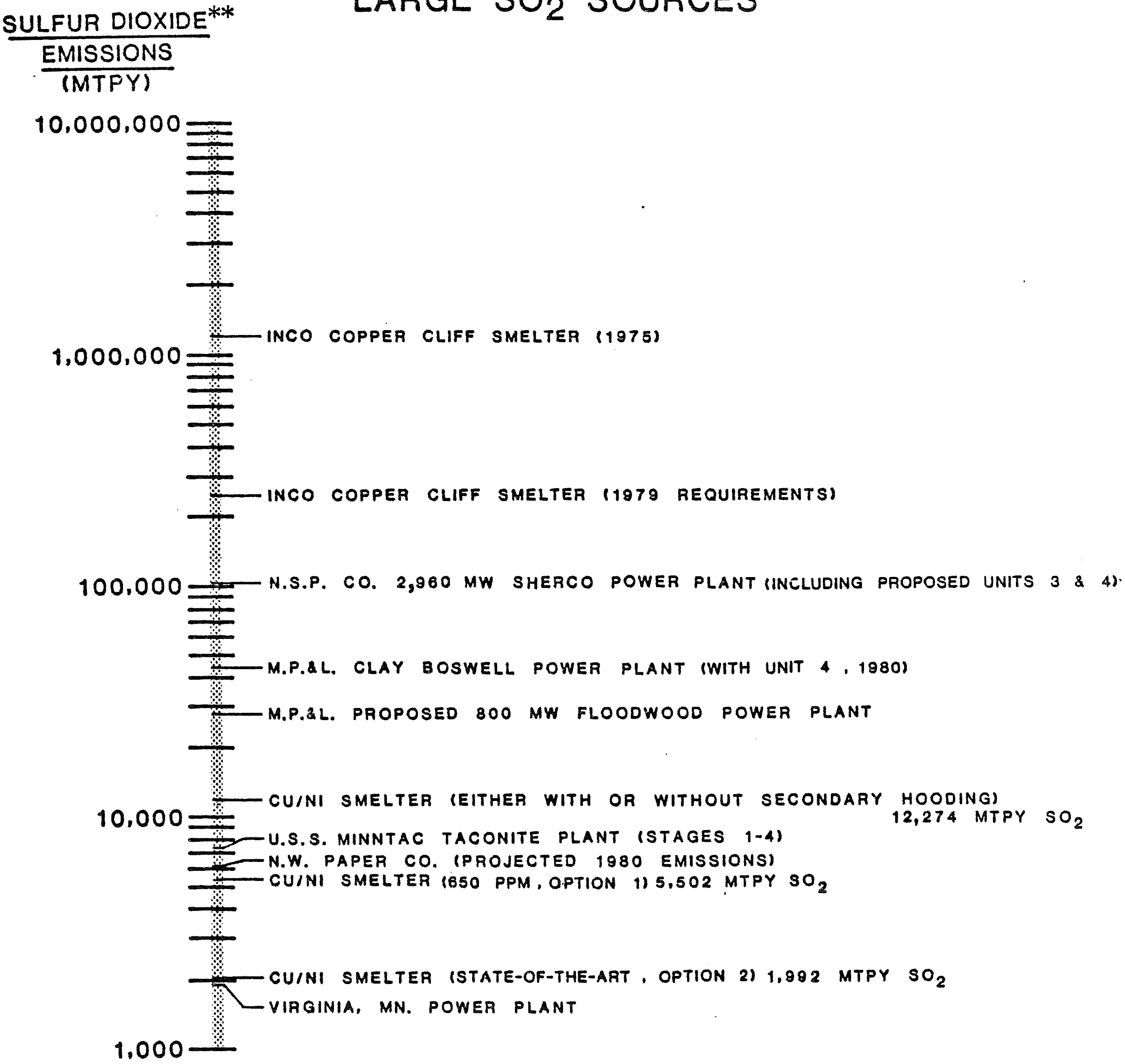
4.7.4 Smelter Minor and Trace Element Emissions

The concentrate feed to a smelter may contain a variety of minor and trace elements which might pose a number of problems including operating difficulties for the smelter, as well as occupational and environmental health difficulties created by emissions of these impurities. These emissions may take the form not only of air emissions, but also of water and solid wastes as well. However, past concern in this area has focused on atmospheric emissions of elements such as arsenic, lead, and mercury. Thus, it is appropriate to include this discussion as a special topic in this section on atmospheric emissions. A report on this topic was prepared by Radian Corporation for the Regional Copper-Nickel Study (Coleman 1978a), and the findings are included in the following discussion.

As discussed in the mineral resource chapter, Volume 3-Chapter 2, extensive studies were undertaken at the University of Minnesota in which a variety of poten-

FIGURE 55

SUMMARY OF MODELED FLASH SMELTER SO_2 EMISSIONS* AND EMISSIONS FROM OTHER LARGE SO_2 SOURCES



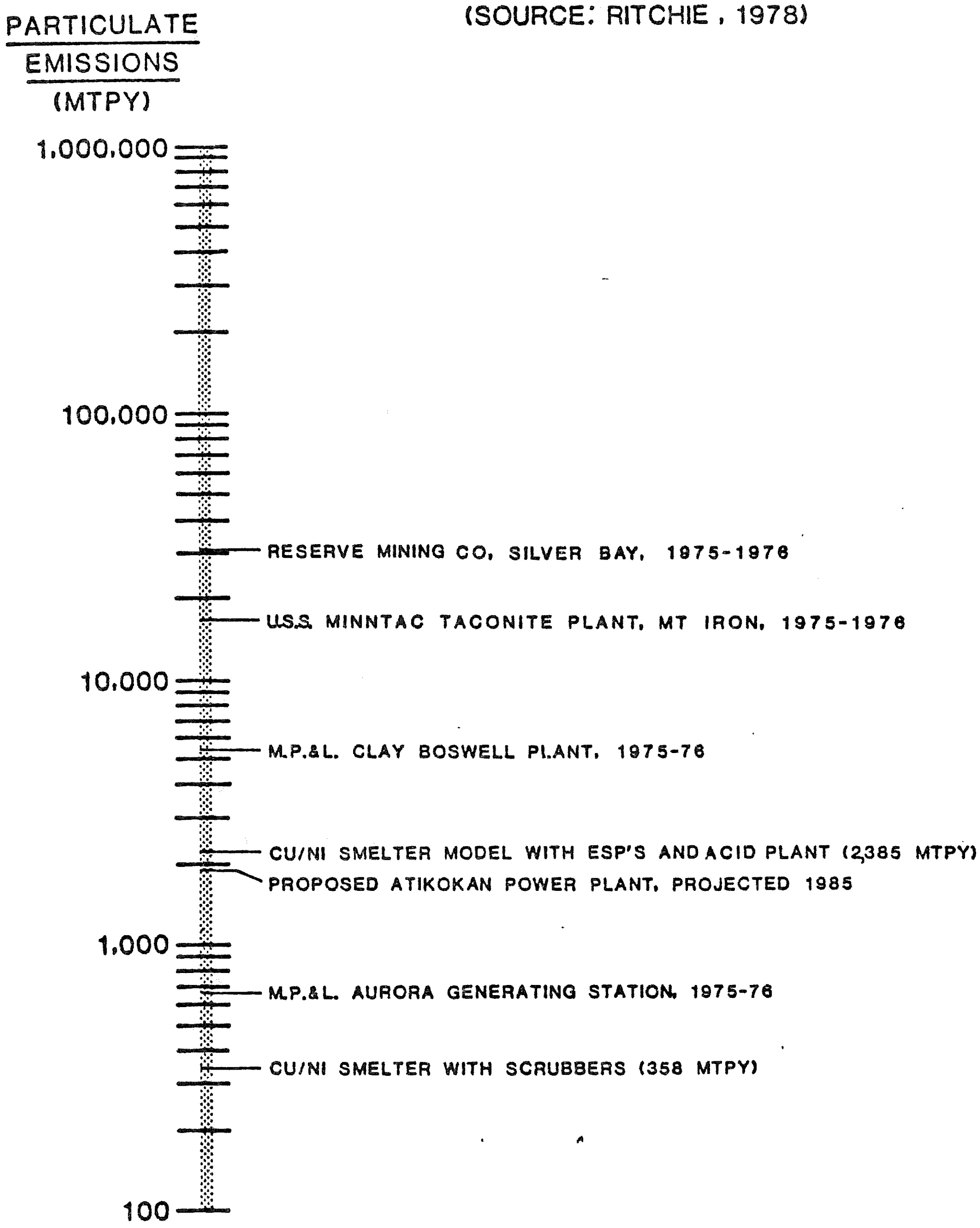
*VALUES INCLUDE STACK PLUS FUGITIVE EMISSIONS

**VALUES SHOWN ARE MTPY OF SO_2 ;WHICH IS TWICE THE AMOUNT OF SULFUR

FIGURE 56

SUMMARY OF MODELED FLASH SMELTER STACK PARTICULATE EMISSIONS AND EMISSIONS FROM OTHER LARGE PARTICULATE SOURCES

(SOURCE: RITCHIE , 1978)



tial gabbro ore samples were subjected to bench-scale processing tests to create concentrate samples. These concentrates were analyzed to determine their chemical and mineral compositions. All of the resulting data was synthesized to produce a model of a concentrate, given in Table 22. Of course, specific mine sites would be expected to yield concentrates whose actual compositions would certainly vary from the model. However, viewed as a representative regional model, this analysis provides a basic summary of all information available to date on the general composition to be expected. For many of the trace constituents of concern, an order of magnitude estimate for their concentration is all that is needed, and the model adequately provides this information.

Table 22

Elements not shown in the concentrate model are, within the limits of the available information, not expected to be present in any significant concentrations. However, these include several constituents traditionally of concern in smelting operations, such as antimony and bismuth, and thus deserve mention. Limited data was available for many of these constituents, explaining their exclusion from the concentrate model. However, as discussed in the geology chapter, Volume 3-Chapter 1, available information has been compiled and yields the estimates shown in Table 23, as a supplementary list to the constituents included in the concentrate model.

Table 23

It must be stressed that these estimates are based on considerably less systematic data than are those used for the model concentrate, and might be expected to vary by as much as one or 2 orders of magnitude in practice.

Table 22. Chemistry of model copper-nickel concentrate.

ELEMENT	DISSEMINATED[a] MODEL CONCENTRATE	UNITS
$Si(SiO_2)$	7.25(15.53)	PCT
$Al(Al_2O)_3$	1.81(3.43)	PCT
Fe(FeO)	2.53(3.26)	PCT
Mg(MgO)	1.55(2.57)	PCT
Ca(CaO)	1.14(1.61)	PCT
$Na(Na_2O)$	0.39(0.53)	PCT
$K(K_2O)$	0.08(0.10)	PCT
$Ti(TiO_2)$	0.10(0.17)	PCT
$P(P_2O_5)$	0.01(0.03)	PCT
Mn(MnO)	0.03(0.04)	PCT
$Cr(Cr_2O_3)$	0.04(0.06)	PCT
B	310.1	PPM
Ba	129.6	PPM
Be	0.06	PPM
Sr	50.2	PPM
V	85.5	PPM
Th	3.0	PPM
Zr	25.7	PPM
S	25.870	PCT
Cu	13.825	PCT
Ni	2.647	PCT
Fe	30.001	PCT
Co	0.132	PCT
Zn	2 137.0	PPM
Pb	60.7	PPM
Ag	34.3	PPM
As	31	PPM
Hg	174.3	PPB
Mo	28.1	PPM
Cd	40	PPM

[a] Values in parenthesis are for compositions of oxides. All concentrations are by weight. The exact values shown in this model do not reflect the accuracy implied for the model, but simply the fact that this stream is part of a material balance requiring internal consistency.

Table 23. Estimate of concentration of trace elements in a Minnesota copper-nickel concentrate, supplemental list.[a]

ELEMENT	CONCENTRATION
Ag	26.8 PPM
Au	0.90 PPM
Rh	15.8 PPM
Pt	1.00 PPM
Pd	2.93 PPM
Sb	1.7 PPM
Sn	less than 740 PPM
W	less than 900 PPB
Bi	100 PPM
F	3.2 PPM
Cl	111.6 PPM
Se	less than 4 PPM
Te	less than 3.3 PPM

[a] See geology report, Volume 3-Chapter 2. Values shown are concentrations by weight.

It is useful to put these concentration estimates into perspective by examining the composition of other copper-containing concentrates smelted at existing U.S. operations. Table 24 (EPA 1976b) lists the ranges of minor element content in the concentrates of several U.S. copper smelters along with the model concentrate discussed above for comparison. Table 25 defines the concentration range designations used. The minor elements shown are those which have been and are of concern principally from the point of view of human health. Comparing this information with the compositional information presented for Minnesota copper-nickel concentrations, all the constituents shown are seen to be present in "low" concentrations except nickel and manganese. Manganese is present in medium concentrations, while of course nickel is in high concentrations by the nature of the deposit. Nickel is a constituent of particular concern as a possible atmospheric pollutant, as is discussed in Volume 5-Chapter 2 on human health. It is important to note that high aresenic levels, such as those experienced at the Asarco Tacoma smelter, are not expected to occur at an installation processing a Minnesota concentrate, based on all available data. Similarly, problems encountered elsewhere with mercury and lead do not appear to exist here.

Tables 24 & 25

All of the constituents discussed above, with the exception of nickel, will be present in what is termed minor or trace amounts. Certain of these, notably the precious metals such as gold, silver, platinum, and paladium will be recovered in the refinery process as valuable by-products. The others are considered as minor or trace impurities, to be eliminated. Impurities in the concentrate are eliminated in the smelting processes either by volatilization or by slagging.

Table 24. Quantities of nine elements in copper smelter ore concentrates.

FACILITY	QUANTITIES OF ELEMENTS IN ORE CONCENTRATES[a] (See Table 25) As	Hg	Cd	Pb	Ni	Mn	Zn	Sb	Se
Asarco-Tacoma, Wash.	H	H	M	M	H	H	M	H	—
Anaconda-Anaconda, Montana	H	L	M	M	M	M	M	M	M
Kennecott-McGill, Nevada	L	M	L	L	H	M	L	M	M
Kennecott, Garfield, Utah	M	L	L	M	H	M	L	H	M
Asarco-El Paso, Texas[b]	L	L	L	H	H	M	L	L	—
Kennecott-Hurley, New Mexico	L	L	L	L	H	M	L	M	M
Asarco-Hayden, Arizona	L	M	M	M	H	M	M	L	—
Phelps Dodge-Morenci, Arizona	L	M	L	L	M	M	L	L	M
Phelps Dodge-Douglas, Arizona	L	M	M	M	M	M	M	M	M
Hypothetical Smelter Treating a Model Minnesota Cu-Ni Concentrate	L	L	L	L	H	M	L	L	L

SOURCE: EPA 1976b.

[a] L = low, M = medium, H = high

[b] Also a Pb smelter.

Table 25. Definition[a] of ranges of element concentrations[b] in copper smelter ore concentrations.

ELEMENT	LOW (L) (less than)	MEDIUM (M)	HIGH (H) (greater than)
As	200	200 - 999	1000
Hg	1	1 - 9.9	10
Cd	100	100 - 999	1000
Pb	1000	1000 - 9,999	1%
Ni	20	20 - 99	100
Mn	100	100 - 999	1000
Zn	1%	1% - 29.9%	30%
Sb	100	100 - 999	1000
Se	5	5 - 99	100

SOURCE: EPA 1976b.

[a] See Table 24.
[b] All values are in ppm by weight unless otherwise indicated.

The path of the major impurities through the smelting circuit is well defined. Sulfur exits as SO_2 in the process off-gases and iron, silicon, and aluminum exit as either slag or tailing from a slag flotation process. The paths of minor or trace elements through the smelter are less well defined and depend greatly on the type of smelting furnaces used and the ways in which they are operated.

At this time, it is clearly not possible to predict exactly the distribution of minor elements for any smelting scheme used to treat the Duluth Gabbro ore. The variations in concentrate composition make predictions impractical. However, it is certainly possible to make reasonable estimates based on the model concentrate analysis and existing thermodynamic and smelter operating data in order to pinpoint the major potential environmental problems.

The approach taken here is designed to make and justify these types of estimates. The elements presenting the greatest potential hazard are prioritized based on both chemical and process considerations. This prioritization identifies the key elements in the Duluth Gabbro ore body which may pose operational and environmental pollution problems if they are processed in a primary copper/nickel smelter. It is based on the model concentrate and trace elemental values just presented. The various constituents of concern are placed into one of 2 groups, priority 1 or priority 2, as follows:

1) <u>Priority 1</u> includes elements which may be present in sufficient amounts to pose either operating problems with potential engineering and/or economic consequences to the company, or environmental problems with potential human health, air pollution, water pollution, or solid waste pollution implications.

2) Priority 2 includes elements traditionally of concern which do not appear to be present in sufficient concentrations to pose the hazards of concern under the Priority 1 list.

The criteria used for placing an element in Priority 1 were:

1) quantity of element present in the concentrate,
2) toxicity to either human health or the environment, and
3) likelihood of release into the environment.

Existing smelter data was used in each case to apply these criteria to the elements present in the Duluth Gabbro Complex. For the first criterion, comparisons were made between the analyses of the model concentrate produced from the Duluth Gabbro Complex and other ores, mainly copper ore. Expected problems based on the similarities or differences between the ore compositions were noted.

Assuming that the concentrate would be processed by a flash or electric smelting facility, Table 26 lists the elements grouped into the priority 1 category and indicates the reason for their inclusion in this group. Each of the elements will be briefly discussed in turn.

Table 26

Arsenic is a known carcinogen and has been identified both as being a serious health hazard and presenting a difficult control problem at most U.S. primary copper smelters. Arsenolite (As_2O_3) has been identified as the predominant crystalline form of arsenic emitted by copper smelters. It is volatile, toxic, and soluble in water. Based on available data, the model concentrate contains only minor quantities of arsenic (31 ppm). However, large fluctuations in the arsenic concentration of smelting furnace feeds are known to occur. This is due to changes in both ore composition and flue dust recycle rate.

Table 26. Priority 1 pollutants associated with copper-nickel concentrate smelting.[a]

ELEMENT	AIR EMISSION	WATER EFFLUENT	SOLID WASTE
Arsenic	V, T	S, T	L, T
Cadmium	V, T	S, T	L, T
Cobalt	V[b], T	S, T	L, T
Copper	V[b], T	S, T	L, T
Nickel		S, T	L, T

[a] Based on analysis of model concentrate.

[b] Metal oxide is volatile at furnace temperature. Volatile metal chlorides and metal fluorides have not been considered at this time.

V = volatile at furnace temperature,
T = toxic,
S = soluble in acidic solution,
L = leachable by acidic solution

Cadmium is recognized as being a toxic material and presenting a significant environmental threat. There is evidence that cadmium stored in the body may accumulate over a period of years. It is more volatile than arsenic at furnace temperatures and is likely to escape as cadmium metal fume or CdO dust during either upset conditions or operations such as tapping, pouring, dust handling and furnace repair.

Cobalt is a major component in the Duluth Gabbro Complex and will likely be a by-product from the copper/nickel smelter. The toxicity of cobalt dust and fume is nearly the same as that of cadmium but it is far less volatile. However, it is likely to be a major contaminant in the acidic wastewater generated by either the copper/nickel smelter or the cobalt refinery.

Copper dust and fume is slightly less toxic than either cobalt or cadmium but more toxic than arsenic. It is likely to be emitted as fume and dust from tapping, pouring, dust handling, and furnace repair operations. Copper also should be a major contaminant in acidic smelter wastewaters.

Nickel dusts and fume have a toxicity similar to that for copper. Nickel carbonyl, $Ni(CO)_4$, is extremely toxic and could pose a serious occupational hazard if present. Nickel can also be expected to be a major contaminant in smelter and refinery wastewaters.

All of the remaining elements in the concentrate are included in the Priority 2 list as being either present in sufficiently small amounts, having a low toxicity, or being unlikely to be released to the environment. The various prioritization criteria, along with the Priority 1 elemental concentrations in the concentrate are summarized in Figure 57. Also included are those Priority 2 elements which are of serious concern at existing smelters and would pose problems if present in higher concentrations.

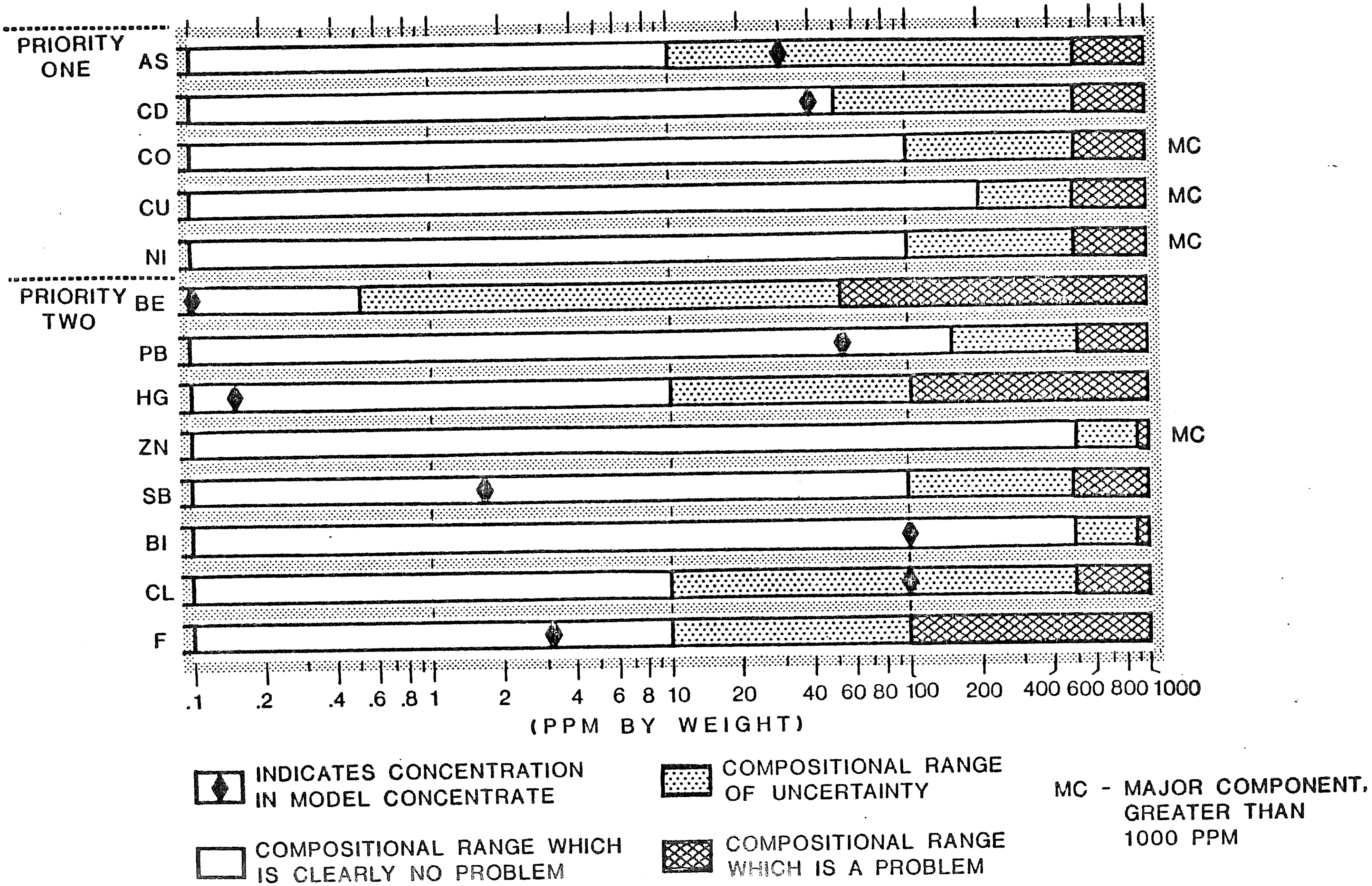
Figure 57

A few comments are appropriate. Chlorine appears to be present in amounts sufficient to qualify it as a priority 1 element. However, the value shown is not from the concentrate model, but from the supplemental list of trace elements. It is not based on any actual concentrate analyses, but rather on a conservative extrapolation of data from the analysis of feed material (ore) to the processing tests. The actual value might be considerably lower since chlorine (and fluorine) are not expected to be associated with the sulfide minerals and thus might be reasonably well separated from the concentrate during processing. This constituent should be monitored particularly carefully in any actual development to resolve this uncertainty. Further, zinc is not rated as priority 1 due to its low toxicity, but would again clearly require close watching in any actual development.

Smelter Model--No attempt was made to specifically model the annual material balance for trace elements in a hypothetical smelter as was done for sulfur. The reason is the large, often order of magnitude uncertainty attached to the various model trace elemental compositions of the concentrate. However, the general relative distribution of elements in the smelter was modeled (Coleman 1978a) in an attempt to illustrate the principal distribution patterns expected for the priority 1 elements and the priority 2 elements traditionally of concern. Two balances were generated, one for a flash smelter and one for an electric smelter. The smelters were assumed to employ acid plants and scrubbers on the weak gas streams and acid plant tailgas, with scrubber effluents being separated in a clarifier into a sludge component and a clarifier overflow com-

FIGURE 57

CONCENTRATE COMPOSITION RANGES USED AS PART OF PRIORITIZATION CRITERIA



ponent. In addition, the buildup of a non-recyclable dust component is also indicated.

The basic assumptions made in order to complete the material balances are as follows:

1) The behavior of minor elements in the Duluth Gabbro Complex ore will not differ significantly from the behavior observed for other ores.

2) Data collected from copper reverberatory furnaces is applicable, at least for an order-of-magnitude approximation, to the electric and flash smelting cases considered.

3) All furnace electrostatic precipitators (ESP) operate at 316°C (600°F).

4) Fugitive emissions are not accounted for as part of the steady-state material balances.

5) Emissions due to process upsets are not considered.

6) No distinction has been made between gaseous and particulate emissions in gas streams. The data required to make that type of estimate is not available at this time.

The resulting distributions are shown in Tables 27 and 28 for the flash and electric cases, respectively.

Tables 27 & 28

It is interesting to note that aside from minor redistributions, most of the elements modeled behave similarly in either type of smelter. In the presence of

Table 27. Preliminary material balance for priority 1, and 2 elements--copper-nickel flash smelter.

	DISTRIBUTION OF ELEMENTS IN SMELTER EXIT STREAMS[a] (given as a percentage of element in the concentrate)								
ELEMENT	STACK GAS	ACID	CLARIFIER OVERFLOW	SLUDGE	METAL-LIC DUST	ANODE COPPER	CU-NI MATTE	DISCARD SLAG	ESTIMATED ACCURACY[b] (%)
Priority 1									
Arsenic	0	TR[c]	1	77	9	TR	1	12	20
Cadmium	0	TR	TR	7	93	TR	TR	TR	20
Cobalt	0	0	TR	TR	TR	1	49	50	20
Copper	0	0	TR	TR	TR	76	22	1	10
Nickel	0	0	TR	TR	TR	1	97	2	10
Priority 2									
Beryllium	0	0	1	13	1	0	1	84	25
Lead	0	TR	2	21	30	TR	2	45	15
Mercury	30	12	28	28	2	0	0	0	20
Zinc	0	TR	TR	3	41	TR	6	50	15
Antimony[d]	0	TR	1	11	72	TR	TR	16	20
Bismuth[d]	0	TR	TR	6	93	TR	TR	1	10
Chlorine[d]	1	TR	1	11	86	0	0	1	25
Fluorine[d]	1	TR	1	11	86	0	0	1	25

[a] Fugitive Emissions not included.
[b] Percentage of total element flow which may be improperly distributed.
[c] TR = present as a trace element, less than 100 ppm.
[d] Elements assumed to be present in trace quantities.

Table 28. Preliminary material balance for priority 1, and 2 elements--copper-nickel electric smelter.

	DISTRIBUTION OF ELEMENTS IN SMELTER EXIT STREAMS[a] (given as a percentage of element in the concentrate)								
ELEMENT	STACK GAS	ACID	CLARIFIER OVERFLOW	SLUDGE	METAL-LIC DUST	ANODE COPPER	CU-NI MATTE	DISCARD SLAG	ESTIMATED ACCURACY[b] (%)
Priority 1									
Arsenic	0	TR[c]	1	84	9	TR	1	5	20
Cadmium	0	TR	1	9	94	0	0	TR	20
Cobalt	0	0	TR	TR	TR	1	49	50	20
Copper	0	0	TR	TR	1	76	22	1	10
Nickel	0	0	TR	TR	TR	1	97	2	10
Priority 2									
Beryllium	0	0	2	16	2	0	1	79	25
Lead	0	TR	1	10	37	0	2	50	20
Mercury	12	25	6	55	2	0	0	0	20
Zinc	0	TR	1	10	37	0	2	50	20
Antimony[d]	0	TR	1	11	74	TR	TR	14	20
Bismuth[d]	0	0	TR	5	94	TR	TR	1	15
Chlorine[d]	TR	TR	1	10	88	0	0	1	25
Fluorine[d]	TR	TR	1	10	88	0	0	1	25

[a] Fugitive Emissions not included.

[b] Percentage of total element flow which may be improperly distributed.

[c] Tr = present as a trace element, less than 100 ppm.

[d] Elements assumed to be present in trace quantities.

a scrubber, none of the elements have a significant fraction of their distribution to the stack gas except mercury. In the case of mercury, the stack component is more than twice as large in the flash case as in the electric case. If a scrubber is not used, and both sludge and clarifier overflow components are assumed to join the stack gas component, then in addition to mercury arsenic immediately stands out with 85% and 78% of input arsenic being emitted to the atmosphere from the two models, emphasizing the reason for concern over the arsenic levels in the concentrate.

4.7.5 Fugitive Emissions

As discussed earlier, fugitive emissions are those air emissions which escape collection by control devices, or leak from ducts and other openings following collection, and subsequently escape from building vents and other openings. The smelting complex represents a principal source for fugitive emissions, both gaseous and particulate. These will each be briefly discussed in turn.

4.7.5.1 Gaseous Fugitives--Once again, the focus of interest here is SO_2. Earlier discussions have detailed the various sources of SO_2, as well as applicable control devices and their removal efficiencies. It was noted that the weak SO_2 gas stream is the source of fugitive SO_2 emissions. The use of a secondary hooding system to collect a portion of these gases for treatment and/or release up a tall stack acts to reduce these emissions. The flash smelter models presented earlier estimated 9,920 mtpy of SO_2 would be emitted as fugitives in the absence of a secondary loading system, with a reduction to 990 with hooding at 90% collection efficiency.

Since a secondary hooding system has become essentially standard on new smelting installations; it is useful to focus on this type of system, and to briefly discuss the origins of the fugitive SO_2, as reflected by the 990 mtpy in the model. In terms of SO_2 sources in the smelter building, clearly, the smelting furnace and copper converters, as major SO_2 sources, are correspondingly major contributors to the fugitive SO_2 leaving the site. Again, no data exists to document the distribution of fugitive SO_2 among the various sources in the smelter. However, using the estimates made by Radian Corporation (Coleman 1978b), a distribution was modeled for the hypothetical flash smelter installation, and is shown in Table 29. This breakdown is useful since it indicates that the smelter and copper converters are of principal concern here, and should be the focus for improved control if it is desired to reduce overall SO_2 fugitive emissions. The converters are of particular concern since their emission contributions occur over fairly short time intervals, and thus at higher concentrations, than the continuously operating smelting furnace. Thus, the copper converters would rate as top priority sources to receive improved control technology in any effort to reduce overall SO_2 fugitive emissions. The Hoboken converter, currently in use at the Inspiration smelter in Arizona, is a good example of the type of new technological developments that must be explored if major reductions in fugitive emissions are desired. See section 4.2.4 for a discussion of the Hoboken converter.

Table 29

As discussed earlier, the weak SO_2 gas stream is generally expected to account for approximately 1-3% of the input sulfur to a modern smelter. This implies that even in the absence of secondary hooding, fugitives would not exceed 3% of the input sulfur. This is a far cry from smelting practices of the past, in which, for example, open roasting of concentrates with subsequent release of a

Table 29. Model for distribution of Fugitive SO_2 among various sources in a model flash smelter installation producing 100,000 mtpy Cu and Ni metal.[a]

SO_2 SOURCE	MODELED ANNUAL FUGITIVE EMISSIONS MTPY SO_2	CONTRIBUTION TO SO_2 FUGITIVE EMISSIONS
Flash furnace	330	33.5%
Copper converters	330	33.5%
Slag cleaning furnaces	200	20.0%
Nickel converter	98	10.0%
Anode furnace	32	3.0%
TOTAL	990	100%

[a] Normal operating conditions are assumed, with 90% collection efficiency of secondary hooding systems.

major fraction of the input sulfur as fugitives created wastelands such as that surrounding the Cities Service smelter at Copper Hill, Tennessee. By comparison, the new Kennecott Garfield smelter is estimated to lose only 0.36% of the input sulfur as fugitives (EPA 1977b), and only 0.6% of input sulfur attributed to fugitives is reportedly required to close the sulfur balance of the Sumitomo Toyo smelter at Niihama City, Japan (Ogura 1976). Of course, a great deal of unavailable documentation would be required to verify these figures, and the performance during startups, shutdowns, and upset conditions is not reported. A great deal of monitoring and development work is clearly required before the issue of fugitive SO_2 emissions is finally well understood. However, both in the U.S. and abroad a great deal of effort is being focused on this problem and new data should be available constantly. It is important that these developments be followed closely so that the most up-to-date information will be used when any specific development decisions are made in Minnesota.

4.7.5.2 Particulate Fugitives--As already mentioned, reliable data quantifying the amount and composition of fugitive particulates escaping from the various sources within a smelter is not available at this time. However, the principal particulate sources have been recognized and discussed in the literature. A recent study conducted for the EPA (EPA 1977a) summarized the available information. The following discussion briefly summarizes the findings of that study which are relevant to consideration of a new facility processing copper-nickel concentrate.

It is useful to list the various potential sources of particulate fugitives on the smelter site. These emissions principally originate from:

1) transfer and conveying of material, including

    unloading and handling of concentrate, limestone/lime, coal, and silica flux

- loading into piles
- vehicular traffic
- loading out
- wind erosion

2) storage piles for concentrate, coal, limestone/lime, and silica flux

3) drying operations (roasting operations)
   - charging
   - leakage

4) smelter furnace operations
   - charging furnace
   - tapping furnace
   - smelting furnace leakage

5) copper and nickel converting stages
   - converter charging
   - converter leakage
   - slag tapping from converter
   - blister copper tapping

6) waste disposal sites

Material transfer and conveying operations are a major potential source for fugitive emissions. Loss of materials is primarily at the feeding, transfer, and discharge points and occurs due to spillage or wind erosion. The majority of particulate emissions are generally from spillage and mechanical agitation of the material at transfer points. Emissions from inadequately enclosed systems can also be quite extensive. Emissions from transfer and conveying generally have the same chemical characteristics as the materials being processed.

Mechanically generated dust is a function of material particle size and machinery speed. Generally, mechanically generated dust may be controlled by convering or hooding the area emitting the dust, applying a negative pressure to the hooded area with subsequent treatment of the exhausted air by control equipment. Enclosures also protect conveyor systems and transfer points from wind erosion losses. Enclosures can either be complete or partial.

Control by wet suppression methods can also be effective, and includes the application of water, chemicals, or foam. Typical points of application are conveyor feed and discharge points, with some applications at conveyor transfer points. Wet suppression with water only is a relatively inexpensive technique, but has the inherent disadvantage of being short-lived. Control with chemicals, added to water for improved wetting, or foam is longer lasting but more expensive than water alone.

Open or partially enclosed storage piles are often used for bulk materials not affected by precipitation or slight contamination, such as coal and silica flux. The material may be stored for a short time with a high turnover rate to accommodate surges in daily or weekly rates of sequential processes, or may provide a long term reserve for emergency supply or to meet cyclical seasonal demands.

Most dust arises from stockpile areas as the material is dumped from the conveyor or chute onto the pile and as bulldozers move the pile. During periods with high wind speeds or low moisture, wind erosion of a non-weathered surface may also cause emissions. Emission rates are dependent on the particle size distribution of the pile, turnover rate for the pile, methods for adding and removing material, and the pile configuration. Also, the amount of wind erosion affects emission rates by affecting the particle size distribution at the surface of the pile.

Enclosing materials in storage sheds or bins is generally the most effective means of reducing emissions from this source category because it prevents or reduces wind exposure, as well as allowing any emissions to be captured. This method would likely be used for concentrate storage. However, storage bins or silos may be very expensive. Storage buildings must be designed to withstand wind and snow loads and to meet requirements for interior working conditions. For material with a wide range of particle sizes, one alternative to enclosure is to screen the material prior to storage, sending the oversize material to open storage and the fines to silos. Certain materials, such as lime, must be stored in a covered area to protect it from moisture. In such cases, silos or bins would be required.

Wind screens, or partial enclosure of storage piles, can reduce wind erosion losses but do not permit capture of the remaining storage pile fugitive emissions. Earthen berms, vegetation, or existing structures can serve as wind screens.

Telescoping chutes, flexible chute extensions, and traveling booms are used to minimize the free fall of material onto piles and thus reduce resulting emissions. Similarly, emissions due to loadout can be reduced by reclaiming the material from the bottom of the pile with a mechanical plow or hopper system. The use of telescoping chutes and flexible chute extensions for piles with high material flow rates may require closer control of operations because of the possibility of jamming. Traveling or adjustable booms can handle high flow rates, but have greater operating costs.

Wetting agents or foam which are sprayed onto the material during processing or at transfer points retain their effectiveness in subsequent storage operations. Wetting agents retain surface moisture for extended periods, thereby preventing dusting. Spraying of the material prior to storage may not be possible in cases where product contamination could result or where the material is water soluble. However, such materials are generally not placed in open storage anyway. Steam has also been found to be an effective dust suppressant for some short term storage operations.

A method to reduce fugitive particulate emissions from roasters, if roasting is used, is to increase the draft of air through the roaster. The discharge of calcine from the roaster can be enclosed and vented to control equipment. Roaster charging can be controlled by hood systems. Fabric filters or electrostatic precipitators can be used as removal equipment.

Hood systems can be used to control smelting furnace slag and metal tapping operations. Smelting furnace leakage can be reduced by a comprehensive maintenance program. Increasing the flow rate of the primary system will decrease leaks but may also reduce the sulfur dioxide concentration in the gas stream. This is a disadvantage if a flue gas desulfurization system is used.

During converter roll out for charging and tapping, the primary hood system can be vented directly to a control device such as a baghouse filter or electrostatic precipitator, bypassing the acid plant. However, during this roll out period, the stationary hood and vent system's fume capture efficiency is very low, since the converter opening is not under the hood.

Secondary hoods which capture the fumes during the roll out operating mode would decrease fugitive particulate emissions. The hood would be elevated sufficiently to minimize interference with converter operation yet low enough to capture emissions during charging. All of the hoods would be connected to a common duct leading to a fabric filter system equipped with an induced draft fan, filter cleaning device, and dust hoppers. The hoods would be equipped with dampers geared to open at converter roll out. The secondary hood system would have the advantage of obviating the need for general building ventilation. Also, better control of operating parameters and procedures, such as control of the converter blast air flow, can reduce fugitive particulate emissions as the converter is tilted. The fire refining and slag cleaning furnaces can also be hooded and ducted to particulate control devices.

Typically, *slag pile dumping* emissions are currently uncontrolled. An intermediate dumping site could be partially hooded and the fumes vented through a fabric filter or scrubbing system. Then the cooled slag would be conveyed to the long term slag disposal site. However, at large facilities, this may require extremely large hoods and air flow rates, making such a system impractical.

Fugitive dust can occur anywhere dusty *waste material* is dumped for disposal. For a smelter this may include non-recyclable metallic dust catch from air pollution control equipment, process overload discharges, building demolition wastes, contaminated products, etc. Like open storage, emissions come from dumping and from wind erosion across unprotected surfaces. Since waste piles are generally not disturbed after dumping, there are no emissions from an activity comparable to loading out of the storage pile. However, there may be emissions from transporting the waste material on site if it is dry when it is produced or from a reclamation process such as landfill covering associated with the waste disposal operation. If the surface of the waste material does not include a compound that provides cementation upon weathering or if the surface is not compacted or is in an area of very little rainfall, wind erosion of fines can occur with winds greater than about 13 mph.

Small volume wastes that are especially dusty, such as metallic dust or street sweepings, are best handled as a slurry or wetted in order to prevent dust losses. If the waste material must be kept dry to eliminate corrosion or chemical reactivity problems, it should be handled with the same care as process material to minimize fugitive dust emissions. Fugitive dust from waste disposal operations is sometimes a problem through oversight or lack of interest. After spending hundreds of thousands of dollars to remove particulate air pollutants with highly efficient electrostatic precipitators or baghouses, it is foolish not to take such precautions as covering the material removed from the collection equipment while hauling it to a dumpsite. Reasonable environmental policies would also indicate advisability of covering these wastes with earth and reclaiming the land by planting a vegetative cover.

For wastes such as scrubber sludges which are pumped to a disposal site and subsequently leave a dry, exposed surface, complete crusting of the surface material can reduce emissions. Further emission reductions can be achieved by either chemical or vegetative stabilization of the surface.

Fugitive particulate control technology options for copper-nickel smelting sources are summarized in Table 30 (EPA 1977a).

<u>Table 30</u>

TABLE 30

CONTROL TECHNIQUES FOR PRIMARY COPPER SMELTING FUGITIVE PARTICULATE EMISSION SOURCES

◆ TYPICAL CONTROL TECHNIQUES.

○ IN USE (BUT NOT TYPICAL) CONTROL TECHNIQUE.

■ TECHNICALLY FEASIBLE CONTROL TECHNIQUE.

		FUGITIVE EMISSIONS CAPTURE AND CONTROL METHODS											
		Preventative Procedures and Operating Changes						Capture Methods			Removal Equipment		
	Source typically uncontrolled	Wet suppression (water and/or chemical)	Confinement by enclosure	Better control of raw material and quality	Better control of operating parameters & procedures	Improved maintenance and/or construction program	Increase exhaust rate of primary control system	Fixed hoods, curtains, partitions, covers, etc.	Movable hoods with flexible ducts	Closed buildings with evacuation	Fabric filter	Scrubber	ESP
1. Unloading and handling of ore concentrations		○	○										
2. Ore concentration storage		○	○										
3. Limestone and flux unloading and handling			○										
4. Limestone flux storage			○										
5. Roaster or dryer charging								■		■	○		○
6. Roaster or dryer leakage						○	○			■	○		○
7. Calcine transfer			○					○	○	■	○		○
8. Charging smelting furnace	✓							○	○	■	○		○
9. Tapping of smelter	✓							○	○	■	○		○
10. Smelter furnace leakage	✓					■		○	○	■	○		○
11. Slag tapping	✓							○	○	■	○		○
12. Converter charging	✓				○			■	■	■	■		
13. Converter leakage							◆	■	■	■	■		
14. Slag tapping from converter	✓				○			■	■	■	■	■	■
15. Blister copper tapping	✓				○			■	■	■	■		
16. Blister copper transfer	✓							■	■	■	■		
17. Charging blister coppter to fire refining furnace	✓								■	■	■		
18. Copper tapping and casting	✓								■	■	■		
19. Slag tapping and handling	✓								■	■	■		
20. Slag pile dumping and cooling	✓							■	■		■	■	

4.8 SOLID WASTE PRODUCTION AND CONTROL

In addition to particulate and gaseous emissions to the atmosphere, pollutants whose discharge quantities are a function of equipment selection, certain solid wastes exist from the various processes used in smelting and refining of the concentrates and associated air pollution control equipment which must either be recycled or safely discarded following appropriate treatment. These materials consist principally of discard slag, and a variety of sludges.

4.8.1 Slag

Slag is a principal solid waste product of the smelting operation. Regardless of smelter location or siting the quantity of slag produced will be fairly fixed and predictable, a direct function of the quantity of feed and flux input to the smelter at any particular constant matte grade produced. For example, a 100,000 mtpy metal operation would generate between 550,000 and 650,000 mtpy of disposable slag. In land-use planning for the smelter, provisions will have to be made for disposal of the non-usable portion of the discardable slag, regardless of site selection. When the slag is discarded as a liquid to solidify in place, provision must be made for on land disposal of all slag produced. Slag cooled in place is considered to be a relatively inert material and not subject to significant leaching or decomposition. Slag granulation is another possible treatment. This is accomplished by pouring the molten slag through water jets into a launder. The launder is an inclined channel, lined with refractory material, for the conveyance and/or treatment of molten material from the smelting furnace. Following this, the granulated slag can be used in several ways if the smelter is adjacent to the mine and mill operation, i.e. as an "onsite" operation:

1) potential backfill in underground mining operations
2) mine road construction material
3) tailing dam construction material
4) aggregate
5) solid waste discharge

For "offsite," or remote smelter, operations where slag granulation is the preferred treatment, slag can be used as: ,

1) aggregate
2) solid waste discharge

Slag typically contains some 30-45% Fe by weight, and it might be thought that this iron has potential as an economic byproduct. However, the iron is present in a solid solution, principally with silica in the form FeO SiO_2, with silica accounting for 30-40% of the slag. As a result, it is not possible to concentrate the iron oxide by any economic means to produce an iron-rich product suitable for use in the iron industry. At present, there are no indications that particular elemental constituents of discard slag can be profitably recovered.

When disposed of on site, slag, as well as other solid residues, is typically open dumped on piles conveniently located by the smelter. Granulated slag is not generally considered to be as inert as liquid slag which has solidified in place; therefore, it is subject, with time, to bashing, deterioration, and degregation if not properly treated and discarded so that it is protected from the forces of wind and water. This could be achieved, for example, by stabilizing the surface of a completed pile by convering with overburden and revegetating. For reference, the slag pile resulting from 25 to 30 years of operation of a 100,000 mtpy smelter might occupy 25 acres and be 200 to 300 ft high.

4.8.2 Sludge

As was pointed out earlier, sulfuric acid plants, both single and double contact, are often used to convert the SO_2 in waste gas streams into H_2SO_4. However, as was discussed earlier, in many cases the concentration of SO_2 in the acid plant exhaust, or tail gas when combined with other low SO_2 content gases of the smelter may contain on the order of 0.1% SO_2. This weak gas stream may be further cleaned of SO_2 by scrubbing with chemical solutions. The products derived from these scrubbing systems consist of small quantities of sulfates ($CaSO_4$, $MgSO_4$, Na_2SO_4, etc.) which are water soluble and consequently may pose problems as viable forms for permanent sulfur storage. They can, however, be recycled to the smelting furnace after drying to keep this part of the sulfur stream in a closed circuit. In instances where discharges of this nature are not recycled, and the smelter/refinery location is distant from the milling complex, special lagoons and/or discharge basins will be required. These basins will be much smaller than basins required for mill tailing. The quantity of solid waste will be a function of the quantity of input feed to the smelter, and variables such as the type and number of scrubbers, chemical precipitators, etc., which result in solid waste discharges. For "onsite" operations smelter/refinery discharges of this type might be combined with the mill discharges and disposed of in the tailing basin.

The use of chemical scrubbers thus reduces stack or air discharges at the expense of creating solid waste and possibly water discharges. It is estimated that 10% of the land-disposed waste from the U.S. smelting and refining industries results from control of air and water pollution with about equal percentages (5%) coming from each. The remaining 90% is comprised of manufacturing process residuals, including furnace slags, furnace linings and refractories, sands, and miscellaneous sludges.

The predominant practices used in the primary metal smelting and refining industries for disposal of residuals originating from the overflow of smelting and refining thickeners are lagooning and open dumping. Scrubwater from wet emissions control and process wastewater with or without lime treatment is generally routed to unlined settling pits or to unlined lagoons. Settled sludge is often dredged from pits or lagoons and stored or disposed of on land. Industries which produce small quantities of sludge will often leave sludges permanently in lagoons. The use of unlined settling pits and lagoons is the predominant practice.

The principal potentially hazardous constituents found in primary and secondary smelting residuals are heavy metals, including arsenic, cadmium, lead, zinc, copper, chromium, antimony, nickel, and mercury.

Average factors for estimating the generation of disposal sludges may be departed from significantly at individual plants for the following reasons:

1) Sludges stemming from slurries generated by operations such as acid plant blowdown, contact cooling, and washdown, appear to vary widely in amount and disposition.

2) Acid effluent generation and neutralization practices are currently in a state of very rapid change.

Sludges from smelters and fire refineries are generated at a much higher rate than those from electrolytic refineries mainly as a result of the need to scrub sulfur dioxide from emissions of smelters. Electrolytic refineries produce relatively little sludge.

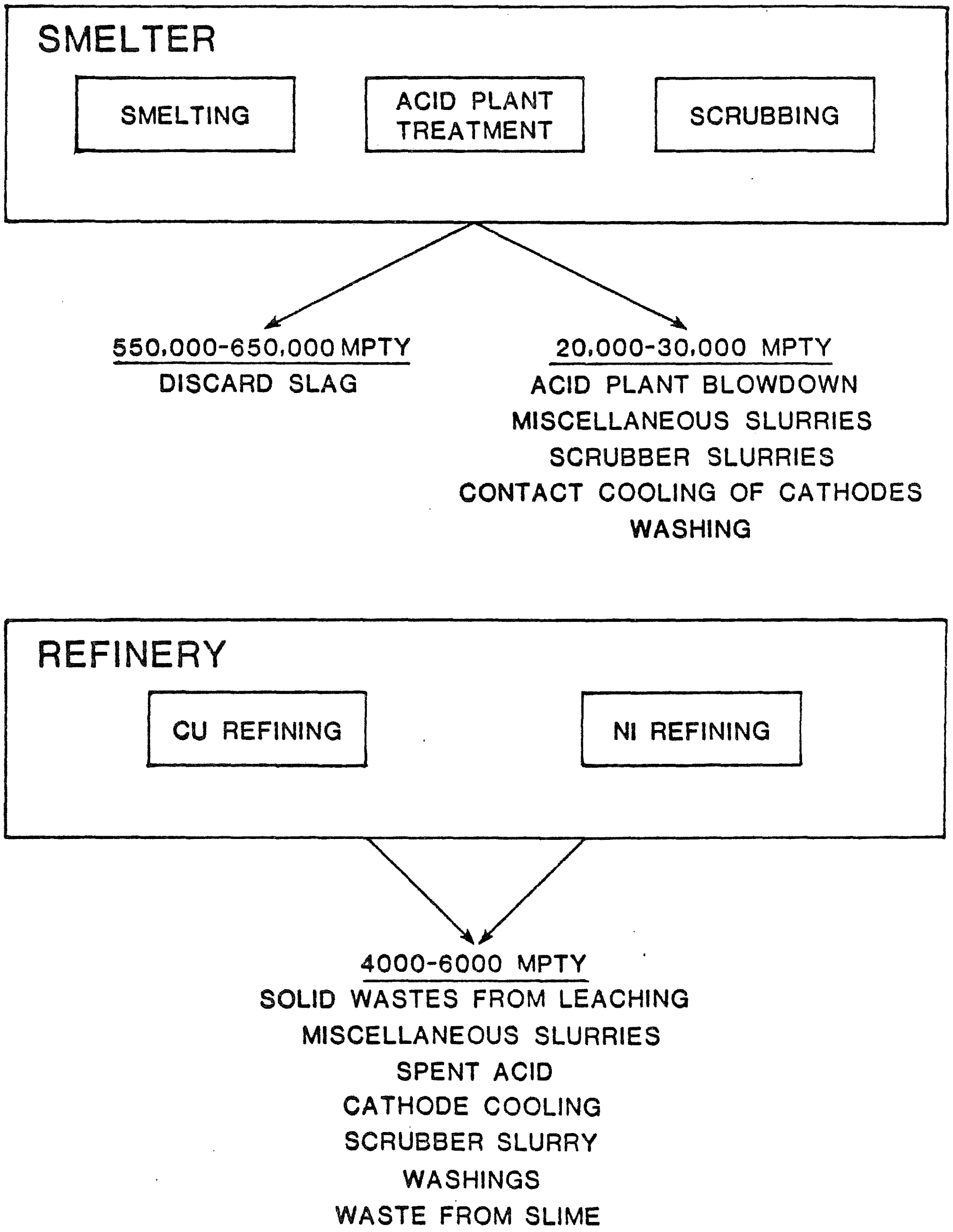
For a smelter/refinery complex which might be anticipated for the treatment of Minnesota copper-nickel ores, 13,500-36,000 mtpy of waste residual might be generated. For an integrated operation with state-of-the-art emission control devices, this could consist of 9,500-15,500 mtpy of sludge generated from acid plant treatment of the strong SO_2 gases, 10,500-14,500 mtpy of sludge generated from the treatment of weak SO_2 gases if such treatment is used, and 4,000-6,000 mtpy of sludge generated from the copper and nickel refineries. Figure 58 summarizes these discharges, along with the slag produced. A large portion of this sludge material can be immediately separated by thickening and recycled, if desired, back to the smelting operation, so it need not be considered a true waste material.

Figure 58

Total land or acreage encumbered by a lagoon capable of handling the above residual waste material ranges from 7-17 acres at a depth not exceeding 10 ft. In certain instances it may be more desirable to construct many lagoons of relatively small capacity than to construct one large lagoon. In some cases it may be advantageous to separate certain wastes in order to maintain chemical quality control on potentially recyclable sludge material.

Present treatment and disposal technology used in major smelter and smelter/refinery complexes consists of dredging from settling lagoons the sludge resulting from acid plant blowdown, miscellaneous slurries from scrubbers, contact cooling of anodes, washings, etc., with storage on land before eventual recycle. Overflow from acid plant settling lagoons is sent to the mill tailing ponds. Miscellaneous slurries from electrolytic refineries (spent acid, cooling water blowdown, scrubber water, and washings) are also settled in lagoons or

FIGURE 58 SOLID WASTE DISCHARGES



tailing ponds. Settled sludges may either be dredged and disposed of on land, recycled for use, or left permanently in tailing ponds.

In the event of potentially significant leaching of hazardous constituents, the use of lined lagoons for the storage or permanent disposal of sludges is usually considered environmentally adequate. Leachable sludges which are dredged or pumped from lagoons or settling pits and dumped on land can be chemically fixed so that leaching of heavy metals may be prevented. Alternatively, sealing of soil in disposal areas with bentonite or other low permeability material should reduce or prevent leachate percolation.

For those slags or other land-disposed or stored solid residues which have been shown to leach significantly in solubility tests, soil treatment at disposal or storage areas would be needed. Collection of run-off from disposal dumps containing slags, sludges, or dusts with leachable heavy metals or other potentially hazardous constituents is advisable. Collected runoff may require treatment before discharge, or retention and evaporation in lagoons.

4.9 WATER REQUIREMENTS AND DISCHARGES

4.9.1 Water Quantity Requirements

Water is required in all segments of smelting and refining operations. Hence, liquid waste discharges are expected when treatment occurs. The principal sources for water discharges in the smelter are:

1) slag granulation water
2) anode contact cooling water
3) acid plant bleed water
4) non-contact cooling water

Principal copper and nickel refinery discharges include:

1) cathode contact cooling water
2) product casting cooling water
3) others (including electrolytic bleed, scrap anode rinse waters, scrubber water bleed, barometric condensor)

For purposes of environmental impact analysis, the above water uses can be divided into two types:

1) process or contact water
2) cooling or non-contact water

Process water is subject to contamination due to contact with products throughout the complex, both from the quality standpoint and thermally. Non-contact cooling water, however, is subject only to thermal impact and does not experience quality changes other than those caused by concentration of constituents due to evaporation in subsequent cooling treatment. Figure 59 presents 2 extreme water balance models which provide an indication of the range in water discharge to be expected depending on design and operation of the smelter/refinery complex. The larger discharges reflect once-through use of water, while the smaller values indicate maximum use of internal recycling. Also shown is a breakdown of discharges by major use of the water within the smelter/refinery operation.

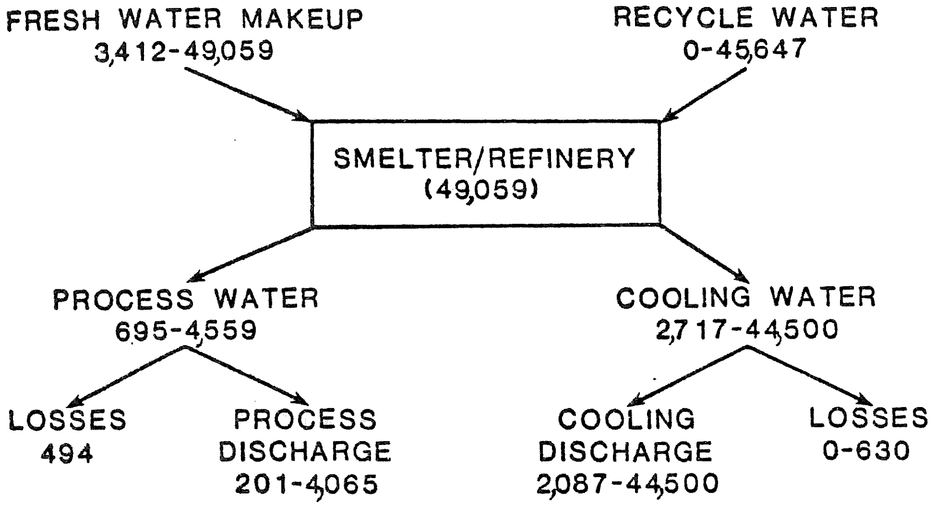
Figure 59

The data sources and assumptions used to arrive at water use model values will be commented on briefly. For the smelter, typical water use data for the different process functions were taken from a 1975 EPA report (EPA 1975) and scaled for the 100,000 mtpy smelter model. For anode cooling, a capacity of 67,000 mtpy copper was assumed, with the balance of the copper being produced by electrowinning in the nickel refinery. Where consumption values were given in units of metal produced, such as for slag granulation, the combined tonnage of copper plus nickel was used. Cooling water requirements for the smelter were scaled from a water balance presented for a proposed copper smelter (AMAX 1977d), with evporative losses calculated thermodynamically to provide sufficient cooling to return the recycled water to the initial input temperature. The water requirements for the copper refinery were again based on EPA data (EPA 1975) as well as data from a Battelle study,[64] and scaled to a refinery processing 67,000 mtpy of anodes. Evporative losses during cooling of product castings were assumed to equal the losses during anode cooling of the same amount of metal.

FIGURE 59

WATER DISCHARGES FROM A MODEL SMELTER/REFINERY COMPLEX PROCESSING 100,000 MTPY OF CU & NI METAL

(IN GALLONS/MINUTE)



PROCESS WATER DISCHARGE COMPONENTS, GPM	
SMELTER	
ANODE CASTING	0-275
SLAG GRANULATION	0-2,600
ACID PLANT BLOWDOWN	0-770
POTABLE WATER	0-30
CU REFINERY	71-260
NI REFINERY	130
TOTAL	201-4,065

NON-CONTACT COOLING WATER DISCHARGE COMPONENTS, GPM	
SMELTER	
PROCESS COOLING	616-10,201
TURBINE CONDENSER COOLING	644-10,864
ACID PLANT COOLING	760-15,000
CU REFINERY	0
NI REFINERY	67-8,435
TOTAL	2,087-44,500

Very little information was available on the water requirements of a nickel refinery processing a Ni-Cu matte. Information based on the AMAX Port Nickel refinery (AMAX 1978e) was used in the absence of more applicable information. As with other parameters modeled for the nickel refinery, the resulting values must be used with caution since other processes might be employed, with significantly different requirements. Using the chemically complex Port Nickel as a model, and scaling for a combined copper plus nickel capacity of some 36,000 mtpy, process and cooling water requirements were modeled. Once-through cooling requirements were derived by simply assuming that the evaporative losses given for Port Nickel reflect cooling from temperatures comparable to those in the smelter cooling water systems. The total modeled flow without the use of cooling towers was then obtained by scaling from the once-through requirements of the smelter.

These figures are again based on a hypothetical smelter/refinery model and are intended merely to represent typical values, since actual requirements depend critically on the specific processes and equipment selected. Nevertheless, it can be seen that process flow requirements are of the order of a few thousand gpm; while cooling requirements are in the range of tens of thousands of gpm. Notably, use of closed cycle systems can reduce both of these discharges by more than an order of magnitude, with corresponding reductions in the make-up requirements to the facility.

The actual water make-up requirement for a facility is the sum of the discharges and the losses for a variety of uses within the facility. Table 31 gives an example indicating the water losses, and the operations in which these losses occur. Of the 494 gpm modeled as process water losses, about 10% is accounted for in the manufacture of sulfuric acid and water retained in granulated slag.

The balance is lost to evaporation during contact cooling processes. Similarly, the 630 gpm loss represents evaporation from a cooling tower or pond with a closed-cycle non-contact cooling system. Near-zero losses occur here only if the system is operated using once-through cooling, with a discharge of the heated effluent.

Table 31

Combining losses and discharges, a picture is obtained of the overall water balance for the complex. Figures 60 and 61 show the model operation in the two extreme water management schemes:

Figures 60 & 61

Case 1: once-through use, no internal recycling. This case should not be considered as realistic for northeastern Minnesota since water resources are not unlimited in the area. It does, however, emphasize the basic flow requirements of the system, as well as the magnitude of the temperature raise in the non-contact cooling water system.

Case 2: maximum use of cooling towers/ponds and internal recycling of water. This case is likely to be much more representative of actual practice in a modern facility, operating under present-day water discharge regulations and in an area of limited water resources. Note that, even though the bulk of the make-up requirements are to offset actual losses in the operation, a portion is still required to offset discharges. It is important to recognize that some water might be discharged from the facility to prevent the buildup of undesirable constituents in certain water systems. For example, the discharge of

Table 31. Water losses in a model smelter/refinery complex producing 100,000 mtpy of Cu and Ni metal.

PROCESS WATER LOSSES		NON-CONTACT COOLING WATER LOSSES	
Smelter	gpm	Smelter	gpm
Anode casting	33	Process cooling	0-154
Slag granulation	220	Turbine condenser cooling	0-161
Acid plant blowdown	47	Acid plant cooling	0-190
Potable	0		
Cu Refinery	33	Cu Refinery	0
Ni Refinery	161	Ni Refinery	0-125
TOTAL	494	TOTAL	0-630

FIGURE 60

WATER BALANCE FOR 100,000 MTPY METAL MODEL SMELTER/REFINERY COMPLEX ASSUMING NO INTERNAL RECYCLE. (FLOWS SHOWN IN GPM WATER)

CASE 1

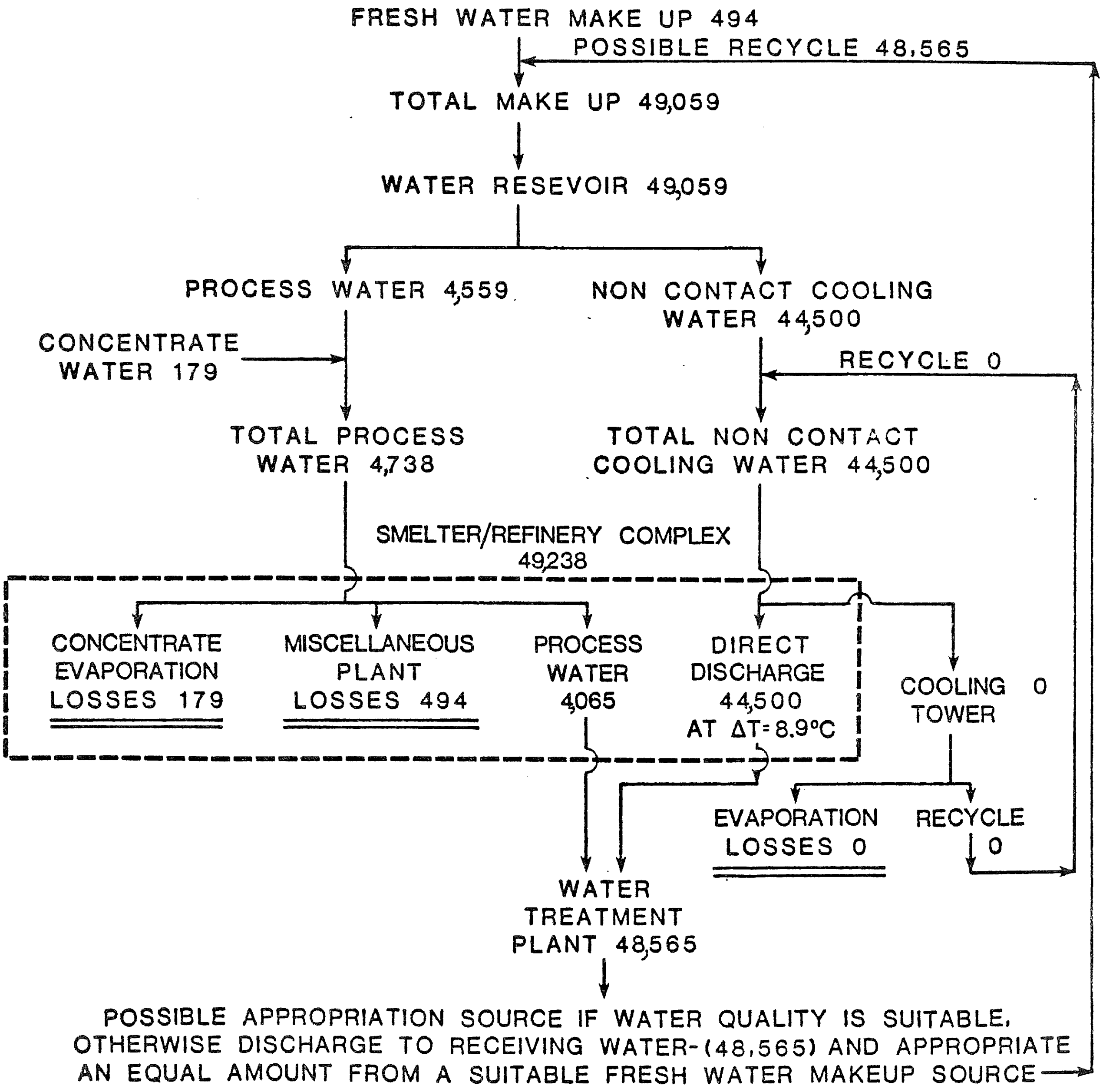
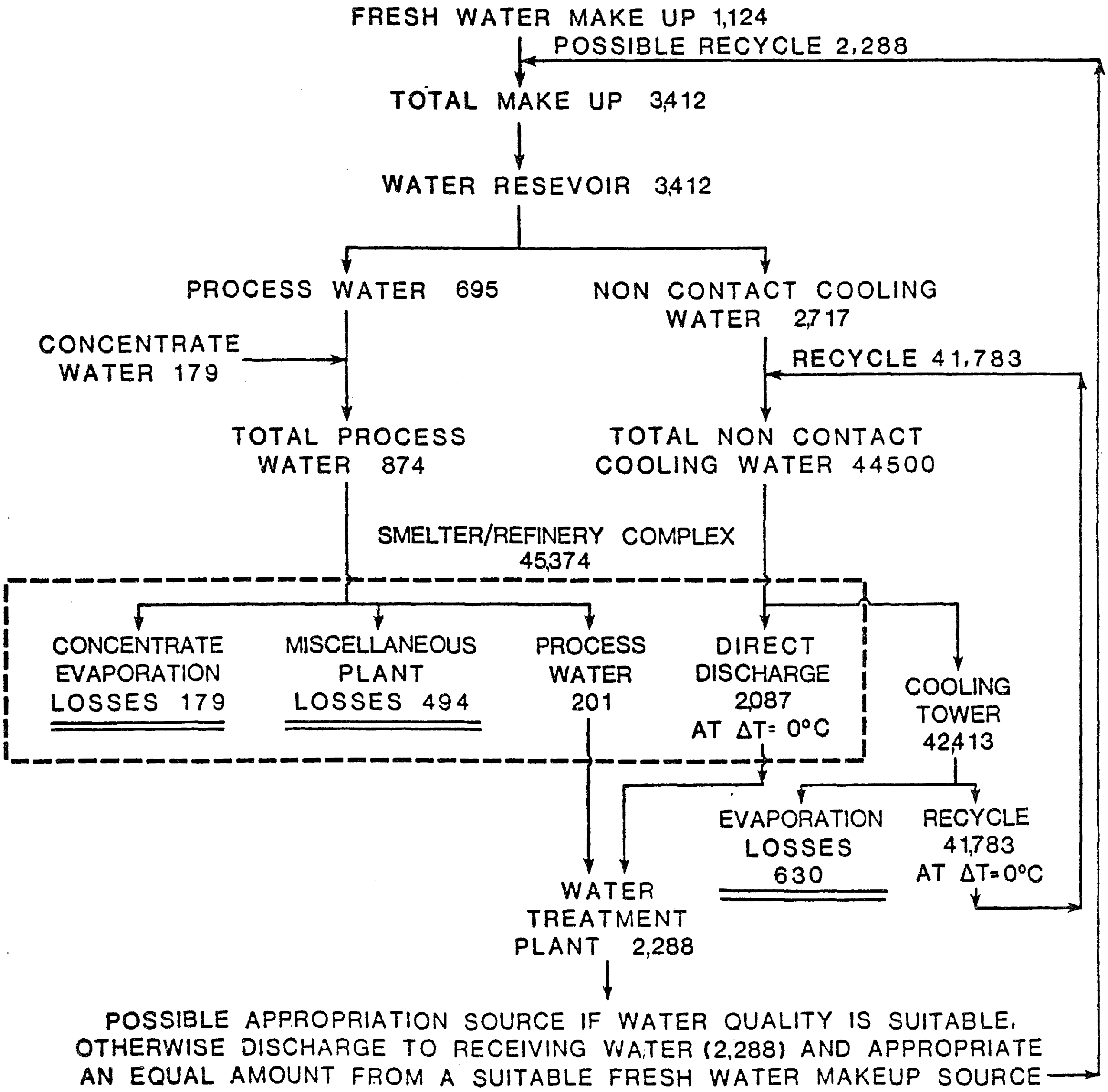


FIGURE 61

WATER BALANCE FOR 100,000 MTPY MODEL SMELTER/REFINERY COMPLEX ASSUMING MAXIMUM INTERNAL RECYCLE, (FLOWS SHOWN IN GPM WATER)

CASE 2



2,087 gpm from the cooling water system reflects the need to prevent the buildup of dissolved solids, with subsequent scaling, in the cooling system. The value shown is extremely conservative, reflecting a situation which would only arise, for example, if the make-up water were of very poor quality. If the make-up is of high quality, the discharge requirement might be as low as 60 gpm or less.

It must be understood that, given sufficient treatment, all discharges could in principal be eliminated. However, given the unknown nature of specific water chemistry problems that might arise, and the often prohibitive costs of sophisticated water treatment facilities, it would be a mistake not to recognize that the facility may be designed so that some type of discharge is necessary.

In summary, for the example being used, and depending upon the location and the potential sources for available water, the present model indicates that from 3,412 to 49,059 gpm of water will be required as intake to the smelter/refinery complex. Discharges range from 2,288 to 48,565 gpm while consumption figures range from 494 to 1,124 gpm for the complex, exclusive of water contained in the incoming concentrate and lost to evaporation in the drying process.

4.9.2 Water Quality

The previous discussion has dealt with the principal uses of water in a smelter/refinery complex and the general quantities needed to meet these requirements. A specific model was generated as a device to illustrate the comparative quantity requirements for the uses discussed. This approach will now be extended to the question of the water quality that might be expected for the various process water streams. As noted earlier, the cooling water stream is a non-contact stream and any discharge should not be contaminated by any material from the operation. There would be an enhancement of the concentration of the constituents naturally present in the intake water as a result of any evaporative loss in the cooling system, and certain chemicals might be added, for example to prevent algal buildup in a closed cycle cooling system. However, the model presented earlier is quite conservative in showing an extremely high blowdown for the closed cycle case (case 2). Here, as in the open cycle of case 1, the increased concentration of natural constituents would be negligible, and special additives should not be needed. Thus, the question of the quality of this stream will not be discussed further. It is important for any specific proposed operation, that the quality of this stream be assessed accurately in terms of the specific design criteria used in order to determine the blowdown requirements, as well as any chemical additives to be used in the cooling water system.

To reiterate the various process streams and modeled flows for these streams, this discussion will deal with:

Process Stream	Modeled Flow, gpm
1) anode casting water	275
2) slag granulation water	2,600
3) acid plant blowdown	770
4) potable water	30
5) copper refinery water	260
6) nickel refinery water	130
Total	4,065

The requirements shown are those from the case 1 model with no internal recycling. This is the appropriate model to use in examining the potential release of various water quality constituents, since the use of internal recycling would not eliminate these constituents but might simply concentrate them into a few streams. An example would be the use of anode casting and acid plant blowdown water for slag granulation. Any constituents carried by these streams would be present in the water retained in the granulated slag, and could be discharged along with any runoff from this operation.

Unlike the case of the possible composition of ore, concentrate, tailing, and water running from waste rock/lean ore piles, it was not possible to simulate waters from the various process streams of interest in order to determine their qualities. Rather, this discussion must rely heavily on information available in the literature, which deals principally with the domestic copper industry. One such study, conducted for the U.S. Environmental Protection Agency (EPA 1975), is relied on heavily. This information naturally reflects problems present at certain domestic copper operations which are not likely to occur with a Minnesota development, notably involving arsenic. Similarly, parameters of particular concern in Minnesota are nickel and cobalt, which are not present or occur at low levels at most domestic copper operations. In addition, no data on the quality of water from a nickel refinery have been found. These points are discussed further in the following sections.

For comparative purposes, it is useful to present here information on the water quality found in streams in the Study Area presently minimally disturbed by human activities, as well as the highest concentrations observed for various water quality parameters of interest. This latter reference is provided by a worst case model of the leachate from a waste rock/lean ore pile. Table 32 presents the mean concen-trations for a variety of water quality parameters measured in the relatively undisturbed streams in the Study Region (see Volume 3-Chapter 4 for further details). Table 33 presents the worst case model for the constituents in a waste rock/lean ore pile leachate. These values are representative of the highest concentrations observed during the course of field monitoring work of the runoff from Duluth Gabbro stockpiles (see Volume 3-Chapter 4 for further details).

Tables 32 & 33

Each of the various smelter/refinery process water streams is briefly discussed.

1) Anode casting water--Data from sampling at 2 domestic smelters indicates increased levels of suspended and dissolved solids in this stream, and elevated levels of some metals, especially copper. Table 34 lists the resulting data, as well as the average for the two plants.

2) Slag granulation water--Values for samples taken from 3 domestic smelters are shown in Table 35, along with an average value. Here values for lead, zinc, and arsenic are notably high. The pH was found to be just above the neutral point.

3) Acid Plant Blowdown--Again, the data for 3 domestic smelters is shown in Table 36, with an average. As expected, sulfate is elevated and pH depressed. Arsenic, cadmium, iron, lead, and zinc values are also elevated.

4) Potable Water--Specific data are not available for this stream, but it is not expected to be the source of significant amounts of dissolved metals. The stream is principally composed of the sewage effluents from the sanitation facilities serving project personnel. As such it would be treated by a small sewage treatment facility, and poses no water quality problems unique to a

Table 32. Mean values of various water quality parameters in relatively undisturbed streams in the Study Area.

PARAMETERS	MEAN STREAM VALUE
Al (ug/l)	112
As (ug/l)	.82
Ca (mg/l)	6.8
Cd (ug/l)	.046
Cl (mg/l)	2.4
Co (ug/l)	.59
Cu (ug/l)	4.2
Fe (ug/l)	723
F (mg/l)	.158
Hg (ug/l)	.126
K (mg/l)	.61
Mg (mg/l)	3.8
Mn (ug/l)	77.8
Na (mg/l)	17.2
Ni (ug/l)	3.5
Pb (ug/l)	.76
Zn (ug/l)	3.2
Alkalinity (mg/l)($CaCO_3$)	25
TOC (mg/l)	16.9
P-total (ug/l)	22
No_2 No_3 (ug/l)	121
TDS (mg/l)	87
SO_4 (mg/l)	7.1
pH	6.7
Specific conductance (umhos/cm)(25°C)	65
Suspended solids (mg/l)	3.4
Color (Pt-Co)	114
Silica (mg/l)	7.2

Table 33. Extreme values of various water quality parameters observed in waste rock/lean ore leachate (values in mg/l unless noted).

PARAMETER	VALUE
TEMP (°C)	1.8
DOC	18.8
ALK ($CaCO_3$)	79.5
pH (pH units)	6.98
SC (umho/cm)	3250
SO_4	2600
Ni (T[a])	39.8
Cu (T)	1.71
Zn (T)	2.40
Co (T)	2.40
Fe (T)	7.20
Ca (T)	346
Mg (T)	268
Cl	56.7
Mn (T)	11.2
Cr	0.123

[a] T = total metal concentration.

smelting/refining installation. The amount involved is also quite small relative to the other streams being considered. Therefore, with the assumption that this stream will be adequately treated by a sewage plant, it will not be discussed further.

5) Copper Refinery Water--Water quality data for effluent water from eight domestic copper refineries are given in Table 37. No significant treatment was being used at these refineries, so the average shown is considered to represent the raw waste streams. Values for several metals, such as zinc, iron, copper, lead, and nickel are high, as is the value for $SO_4^{=}$.

6) Nickel Refinery Water--No data were found for the water quality of effluents from a nickel refinery. A variety of processes are available for treating the nickel-copper matte likely to be produced from a smelter treating a Minnesota concentrate. Some of these processes, such as that utilized at the Amax Port Nickel refinery in Louisiana are chemically quite complex. This makes it particularly difficult to estimate in general what the composition of effluents from such a refinery might be. It is clearly quite important that reliable data on such effluents be obtained in the event that a specific refinery installation is proposed to treat a Minnesota copper-nickel matte.

Tables 34-37

Water Quality Model--Consistent with the smelter/refinery water quantity models already presented, it is appropriate to apply the foregoing information to develop a model for the water quality of the combined process water effluents from the model copper-nickel smelter/refinery complex. Such a model is useful as an indicator of the range of constituent concentrations which might be expected,

Table 34. Raw waste characterization: anode casting water.

PARAMETER	UNITS	PLANT 1	PLANT 2	AVERAGE
pH	pH	7.4-8.4	7.5	7.8
TDS	10^3ppm	--	17.7	17.7
TSS	"	--	0.33	0.33
$SO_4^=$	"	--	0.23	0.33
Cn^-	"	--	--	
As	"	0.0	0.001	0.0005
Cd	"	0.0	0.0	0.0
Cu	"	0.001	0.022	0.011
Fe	"	0.0	0.001	0.0005
Pb	"	0.001	0.005	0.003
Hg	"	0.0	0.0	0.0
Ni	"	--	--	--
Se	"	0.0	0.002	0.001
Te	"	--	--	--
Zn	"	0.0	0.0	0.0

SOURCE: EPA 1975.

Table 35. Raw waste characterization: slag granulation water.

PARAMETER	UNITS	PLANT 1	PLANT 2	PLANT 3	AVERAGE
pH	ph	6.4-7.6	7.7	8.1	7.6
TDS	10^3ppm	--	10.0	91.2	50.
TSS	"	--	0.48	3.6	2.0
$SO_4^=$	"	--	4.44	7.44	5.9
Cn^-	"	0.0016	0.0004	0.0012	0.0010
As	"	0.300	0.265	0.0011	0.187
Cd	"	0.0022	0.0001	0.0000	0.0007
Cu	"	0.032	0.009	0.0012	0.014
Fe	"	--	0.003	0.0072	0.005
Pb	"	0.389	0.003	0.0016	0.130
Hg	"	0.00001	0.00001	0.0000	0.00001
Ni	"	0.0084	0.0001	0.0014	0.0033
Se	"	0.0021	0.0001	0.0129	0.0050
Te	"	0.0053	0.0001	--	0.0027
Zn	"	1.89	0.032	0.0005	0.64

SOURCE: EPA 1975.

Table 36. Raw waste characterization: acid plant blowdown.

PARAMETER	UNITS	PLANT 1	PLANT 2	PLANT 3	AVERAGE
pH	pH	2.0-2.5	1.8	2.0	2.0
TDS	10^3ppm	--	78.5	410	244
TSS	"	--	0.102	3.74	1.92
$SO_4^=$	"	--	7.69	64.0	36.0
Cn^-	"	0.0000	0.0000	0.0024	0.0008
As	"	0.044	0.129	0.004	0.059
Cd	"	0.0002	0.0014	0.0276	0.0097
Cu	"	0.0001	0.0018	--	0.0010
Fe	"	0.0014	0.0015	0.1116	0.0382
Pb	"	0.0051	0.0142	0.2501	0.0898
Hg	"	0.0000	0.0000	0.0002	0.0001
Ni	"	0.0000	0.0000	0.0030	0.0010
Se	"	0.0001	0.0000	0.0268	0.0090
Te	"	0.0000	0.0000	--	0.0000
Zn	"	0.0017	0.215	0.436	0.218

SOURCE: EPA 1975.

Table 37. Effluent loadings of selected constituents from selected U.S. copper refineries.

	EFFLUENT LOADINGS (10^3ppm) -- PLANT NUMBER								
PARAMETER	1	2	3	4	5	6	7	8	Average
Alkalinity	0.04	0.45			0.02			0.044	0.14
COD	0.21	0.40		0.7	0.30		0.125	0.472	0.37
Total Solids	7.1	0.88		6.9			0.384	3.40	3.7
Dissolved Solids	6.5	0.67		1.7	0.94		0.241	1.63	1.9
Suspended Solids	0.54	0.21		0.81	0.10		0.143	1.00	0.47
Oil and Grease			0.003		0.05				0.03
Sulfate (as S)	28	0.046	16.1	1.0			0.091	0.066	7.55
Chloride	1.8				0.22	0.14	0.37	1.14	0.67
Cyanide									
Aluminum	0.037		0.004		0.01	0.0006		0.0004	0.01
Arsenic	0.026	0.0003	0.174	0.00047		0.0002	0.003	0.0001	0.03
Cadmium								0.0001	0.0001
Calcium	0.27		0.0002		0.06		0.040	0.28	0.13
Chromium					0.0001				0.0001
Copper	0.04	0.0002	0.43	0.03	0.002	0.032	0.001	0.0005	0.07
Iron	0.44	0.04		0.006	0.0006	0.0001	0.028	0.0003	0.07
Lead	0.026		0.005		0.0001		0.0002		0.01
Magnesium				0.19			0.0064	0.115	0.10
Mercury			0.0001		0.0001				0.0001
Molybdenum								4.72	4.72
Nickel	0.04				0.001		0.0064	0.0001	0.01
Potassium	I.0			0.03				0.013	0.35
Selenium	0.022		0.042				0.0006	0.0001	0.02
Silver			0.0001					0.0001	0.0001
Sodium	3.7							0.91	2.31
Tellurium	0.040		0.052						0.050
Zinc	0.005	0.013	0.008	0.14	0.0001	0.0001	0.0032		0.02
pH[a]	7.3	6.9	7.0	8.2	6.4	6.2	5.6	7.6	6.9

SOURCE: EPA 1975.

[a] Values represent arithmetic averages where more than one effluent stream leaves a plant.

and to highlight those parameters which should receive particular attention if it is necessary to employ water treatment technology to protect the quality of receiving waters. As discussed earlier, the relevant quantity model is that for case 1, which best reflects overall potential mass flows of the various constituents of interest. Based on the available data, only selected parameters have been modeled, for comparison to data gathered in the Regional Study area. In view of the lack of data for a nickel refinery, the data for electrolytic copper refineries are used for the nickel refinery. This clearly represents a major weakness in the model, and the results must therefore be interpreted with extreme caution. Further, it is necessary to acknowledge the presence of high Ni and Co values in the smelter feed. This is done by substituting the Ni concentration from the worst case waste rock/lean ore pile leachate model (Table 33) in place of the values given for existing domestic operations since those values are consistently below the 39.8 mg/l in the leachate model. Further, since no data are available for cobalt, the value of 2.40 mg/l from the leachate model will be assumed. Once again, any use of this model must keep these assumptions in mind. Table 38 presents the parameters to be modeled, and a summary of the available data in the form of average concentrations in the various process flow streams from domestic copper operations sampled along with the modeled flow value assigned to each stream. As noted earlier, the potable water stream is omitted.

Table 38

A single smelter/refinery effluent water quality model was generated by combining the models given for the various streams. All constituents shown are assumed to behave conservatively, so that their final concentrations may be com-

Table 38. Water quality data summary for process water streams.

PARAMETER	ANODE CASTING WATER	SLAG GRANULATION WATER	ACID PLANT BLOWDOWN	Cu REFINERY WATER	Ni REFINERY WATER[a]
PH	7.8	7.6	2.0	6.9	6.9
TDS (mg/l)	17,770	50,000	244,000	3700	1900
SO_4=(mg/l)	230	5,900	36,000	22,650	22,650
As (mg/l)	0.5	187	59	30	30
Cd (mg/l)	0	0.7	9.7	0.1	0.1
Co (mg/l)[b]	2.4	2.4	2.4	2.4	2.4
Cu (mg/l)	11	14	1.0	70	70
Fe (mg/l)	0.5	5	38.2	70	70
Hg (mg/l)	0	0.01	0.1	0.1	0.1
Ni (mg/l)[b]	39.8	39.8	39.8	39.8	39.8
Pb (mg/l)	3	130	89.8	10	10
Zn (mg/l)	0	640	218	20	20
Modeled flow (gpm)	275	2600	770	260	130
Percent of total process water flow	7	64	19	6	3

[a] Assumed to be the same as the copper refinery water.

[b] Value based on worst case model of waste rock/lean ore leachate.

puted as a weighted average. To complete the balance, the small potable water contribution is included assuming the concentration of each parameter modeled is zero. No significant error is expected from this assumption. Table 39 gives the overall smelter/refinery water quality model, derived by the methods discussed above. In addition, Table 40 indicates the annual constituent mass loadings implied by this model at the assumed flow rate, and the percent of the overall constituent input accounted for by the model. Some clarifying comments must be made at this point.

Tables 39 & 40

Internal Consistency--As a consistency check, the weighted average concentration for each parameter was expressed as an annual mass loading and compared to the annual input as simulated by the smelter feed model presented earlier (Table 12). As expected, the weighted average concentrations for arsenic, mercury, and lead in existing domestic operations implied a source for these constituents considerably larger than is expected in the smelter feed using a Minnesota concentrate. Accordingly, the concentrations of the above elements in the process water effluent model were adjused downward to reflect 100% recovery for these constituents in the effluent water. This clearly represents an extreme worst case for these constituents, since portions of each are expected to experience other fates such as being bound into the discard slag or released as an air emission. However, given the quite general nature of the model for the concentrate composition, this assumption is reasonable here. The resultant value indicates the potential order-of-magnitude concentration which might occur in the processs water effluent, and emphasizes the fact that arsenic, mercury, and lead, as well as zinc, cobalt, nickel, and copper may result in significantly elevated effluent water concentrations if they are present in the feed.

Table 39. Integrated water quality model for a smelter/refinery process water effluent stream.[a]

PARAMETER	MODELED VALUE
Flow (gpm)	4,065
pH	2.7
TDS (mg/l)	79,700
$SO_4^=$ (mg/l)	12,800
As (mg/l)	3.0[c]
Cd (mg/l)	2.3
Co (mg/l)	2.40[a]
Cu (mg/l)	16.6
Fe (mg/l)	17.2
Hg (mg/l)	0.017[b]
Ni (mg/l)	39.8[a]
Pb (mg/l)	5.2[c]
Zn (mg/l)	450

[a] Value based on worst case model of waste rock/lean ore leachate.

[b] Unless otherwise noted, model values are based on data from selected domestic operations (EPA 1975).

[c] Values adjusted downward to reflect 100% of the constituent present in the modeled smelter feed.

Table 40. Mass loadings and recovery of constituents implied by the smelter/refinery process water quality model.[a]

PARAMETER	MASS LOADING (mt/yr)	PORTION OF INPUT ACCOUNTED FOR
$SO_4^{=}$	33,000 (as S)	20% (as S)
As	22	100%[b]
Cd	18	70%
Co	19	2%[c]
Cu	130	0.1%
Fe	130	0.07%
Hg	0.13	100%[b]
Ni	310	2%[c]
Pb	40	100%[b]
Zn	350	50%

[a] See Table 39.

[b] 100% recovery assumed (see discussion).

[c] Based on value from worst case waste rock/lean ore leachate model.

Scrubber Systems--No specific water quality model has been prepared to deal with the effluent from a weak gas scrubber. However, the elements most affected by the use of a scrubber, as seen in the material balance shown in Table 27 discussed earlier, are arsenic, mercury, and lead. As just noted, the present water quality model reflects 100% recovery of these constituents into the process water effluent stream, so the mass flows are accounted for. The effect of a scrubber would be to add a small quantity of additional water, diluting the modeled concentrations slightly. However, as with the potable water, the amount is expected to be small and any resulting error from its emission is not significant in the context of the generalizations already present in the model.

pH--The low pH predicted for the model is the result of the weak acid blowdown from the sulfuric acid plant. In reality, this stream would most certainly be neutralized prior to combining it with the other process streams to prevent this acidification of the overall process effluent stream.

TDS and $SO_4^=$--The model values for these parameters are quite high. In fact, the $SO_4^=$ value accounts for some 20% of the overall input sulfur. Care must be used in interpreting these results since they are elevated as a result of a few high values recorded at domestic operations. These values would indicate the consumption of a significant amount of sulfuric acid in the refining processes, as well as recovery of sulfur in the weak acid blowdown from the acid plant. The fate of a great portion of these constituents would no doubt be the sludge that would accumulate in settling ponds prior to any discharge to receiving waters.

A variety of treatment technologies exist for reducing the concentrations of heavy metals and other constituents in process waste waters. These technologies vary from simple lime and settling methods, to more sophisticated approaches such as reverse osmosis and vapor-compression evaporation. See Volume 3-Chapter 4 for a discussion of these treatment technologies and their efficiences.

It must be noted that due to the variety of possible approaches that may be utilized, particularly in the nickel refinery, no attempt has been made to model the process water quality in so far as any chemical additives are concerned. Rather, it is simply pointed out that a large number of additives might be used somewhere in the overall smelter/refinery operation, and these must be clearly identified in any actual proposed operation. The behavior of these chemicals must then be characterized, including their concentrations in any effluent streams, their breakdown products and decay rates, and the toxicity of any discharges. Only on this basis can the potential environmental impacts of such additives be reliably assessed.

When the smelter/refinery complex is situated in the vicinity of the mining and processing complex (i.e. an "onsite" location), process water discharge is generally combined with the mill tailing discharge and disposed of in the tailing basin. Since the smelter/refinery process water discharge is small relative to the processing water discharge, impacts from said pollutants may be minimal, as the impacts resulting from smelter/refinery discharges may be masked by the impacts resulting from processing discharge waters. In some cases, however, where a purification plant is required for treatment of certain process discharges smelter/refinery waters could also be treated if this proves to be desirable, prior to discharge. When the smelter/refinery complex is located away from the mining and processing complex, for example at an "offsite" location such as Duluth, some form of water treatment or purification will likely be necessary prior to any discharges of water. The presence of a purification system for water treatment will raise both capital and operating costs for the integrated operations where the final vertical treatment stages are separated by great distances.

Many variations of the water flow system shown in Figures 60 and 61 are possible, one of which is shown in Figure 62. In this example of an "onsite" facility, smelter/refinery non-contact cooling water is directly recycled after cooling to the intake temperature and the process water discharge is treated and recycled to the tailing basin. All processing water requirements other than water contained in the ore are supplied by recycle from the tailing basin, and the only fresh water is added to the smelter/refinery.

Figure 62

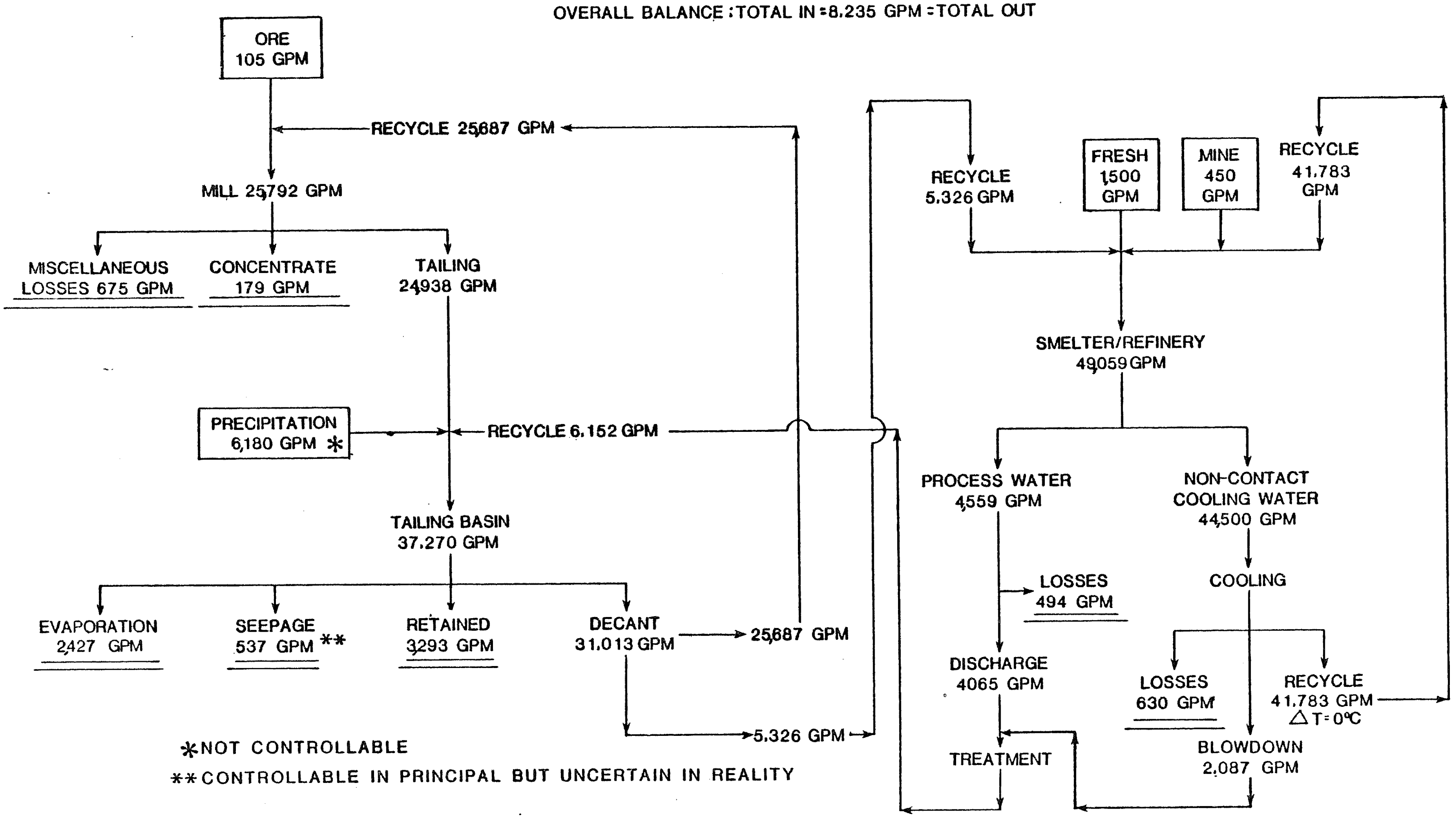
FIGURE 62

EXAMPLE OF TOTAL WATER BALANCE

20 X 10^6 MPTY ORE INTEGRATED OPERATION

(FLOW IN GPM WATER)

OVERALL BALANCE : TOTAL IN = 8.235 GPM = TOTAL OUT



*NOT CONTROLLABLE

**CONTROLLABLE IN PRINCIPAL BUT UNCERTAIN IN REALITY

4.10 UPSET CONDITIONS (Coleman 1978a,b)

Relatively small amounts of air emissions, aqueous effluents, and solid wastes are generated by a modern smelter on a continuous operating basis. However, it is likely that the pollutants generated during upset periods will constitute the major smelter pollution problem, especially as the smelter ages and equipment failures become more probable. This situation is much different than that for conventional reverberatory smelting where the major pollution problem is the reverberatory furnace off-gas, during normal operation.

Probability theory can be used in principal to predict the potential environmental impact of pollution caused by process upsets. The probability that a piece of equipment will be functioning at the end of a time period t, or that it can be repaired or maintained in time u and returned to functional status is given by the following equation:

$$P = \exp [- At\ e^{-Bu}]$$

where: A = the reciprocal of the mean time between full forced outages

t = time period to be considered

B = the reciprocal of the mean time to repair a forced outage

e = 2.718, the base of natural logarithms

u = time to return equipment to service, following outage

This implies that there is a finite probability that upsets will occur due to process equipment failures and that they will become more frequent as time progresses.

Unfortunately, smelter operating data is not available, as it is for the electric power utility industry, to calculate the values of A and B. As a result, neither the likelihood of occurrence nor the environmental impact of smelter process upsets can be explicitly calculated.

A qualitative evaluation can be made, however, which will identify the pollutants most likely to be generated during either upset conditions or during operations likely to produce fugitive emissions.

The actual pollution problems associated with a particular flowscheme depends more on the design and operation of the pollution control technology than on the process operation. Electrostatic precipitators, waste heat boilers, cyclones, hooding and ventilation systems, acid plants, tail gas scrubbers, and water treatment plants all experience outages due to equipment, power, and human failures. In addition, the control technology cannot be expected to perform effectively during either start-up or shutdown periods.

An analysis of all the potential failures in a smelter which would create an environmental impact is a large job in itself and is not attempted here. Rather, the framework for performing a detailed environmental impact analysis is described in terms of the following classes of failures:

1) catastrophic failure, e.g. loss of electric power or steam supply
2) loss of a particular pollution control device due to equipment failure
3) failure of a control device to perform due to overloads
4) failures due to inadequate maintenance

Ideally, the control technology used at the smelter should be designed to minimize the possibility of each of these types of failures. However, it is unlikely that any control technology will be designed to prevent emissions in the event of a catastrophic failure. This is the least likely but potentially most serious failure. The high SO_2 concentration furnace gases may have to be vented to the atmosphere when this type of failure occurs in order to prevent any potential poisoning of the V_2O_5 catalyst in the sulfuric acid plant. Without power, the electrostatic precipitators and process gas fans would not function. As a result, air emissions during this type of failure would consist of very high SO_2 concentration gases heavily laden with metal particulates and vapor. The emissions would likely occur at ground level since the gases could not be routed through the acid plant catalyst beds and out the stack. A duct bypassing the acid plant would allow the stack to be used and could eliminate the immediate danger to the workers in the smelter.

The likelihood of losing a particular pollution control device due to equipment failure can be minimized by providing equipment spares and by using the proper materials of construction. Equipment redundancy will increase the cost of the control technology but is essential, especially for the key pollution controls. The sulfuric acid plant will be the key pollution control device because all of the volatile elements of concern are contained in the process gases it treats in a hazardous form. Loss of the acid plant would, for example, have a much larger impact than the loss of a weak SO_2 gas scrubber. As a result, the acid plant should be designed, operated, and maintained in a fashion which will insure that outages due to equipment failure, process fluctuations, or inadequate maintenance are minimized.

This type of qualitative discussion could be continued for each of the control devices and each failure mode. However, the problem of assigning some quantitative value to the environmental impact of upsets or failures in smelter operation is not so easily addressed. It is clear, however, that of the elements of concern, sulfur is likely to be emitted in the largest quantities, and in the form of SO_2. Beyond this single generalization, there is clearly a possibility for the emission is quantities of metallic vapors and dust, particularly Cu, and Ni, in the event of certain types of upsets. The health and safety of workers is of principal concern in this context. Clearly, each individual facility must be examined in detail, and an acceptable design and procedure developed to handle all major upset possibilities. This is important both from the viewpoint of providing security for plant personnel, as well as safeguards against accidental, uncontrolled discharges to the environment.

4.11 SUMMARY-POLLUTION CONTROL TECHNOLOGY

As applied to smelting/refining, pollution control technology incorporates well-known and well-defined techniques and equipment. Examples include particulate control, SO_2 gas control, water chemistry control, and material containment during transportation, loading, and unloading. Each important potential pollution area is listed in Table 41 along with mitigating measures applicable to that particular instance. Effectiveness of each mitigation is also shown in qualitative terms.

Table 41

4.12 OTHER DEVELOPMENT CONSIDERATIONS

4.12.1 Transportation Variables

Both the location of the smelter/refinery complex with respect to the mine and the mill, and the degree of vertical integration, including the form and type of output product, will determine whether special transportation facilities and/or transportation corridors are needed for successful operation.

Table 41. Smelting/refining pollution potentials and mitigating measures.

SMELTING/ REFINING OPERATION	SOURCE POTENTIAL POLLUTION	MITIGATION MEASURES	EFFECTIVENESS OF MITIGATION*
Materials Handling	Fugitive Emissions Transfer & conveying of material Unloading & handling of ore concentrate Ore concentrate storage Loading onto piles Vehicular traffic Loading out Wind erosion Limestone flux unloading & handling Limestone flux storage Storage Piles Waste disposal sites	Fugitive Emissions Wet suppression (water and/or Confinement by enclosure) Better control of raw materials handling	Fair-Good
Smelting	Fugitive Emissions Drying operations (roasting operations) Charging Leakage Smelter furnace operations Charging furnace Tapping furnace Smelting furnace leakage Slag tapping Copper & nickel converting stages Converter charging Converter leakage Slag tapping from converter Blister copper tapping Blister copper transfer Anode furnace operations Charging anode furnace Copper tapping & casting Slag tapping & handling	Fugitive Emissions Confinement by enclosure Better control of operating parameters & procedures Improved maintenance and/or construction program Increase exhaust rate of primary control system Fixed hoods, curtains, partitions, covers, etc. Removable hoods with flexible ducts Closed buildings with evacuation Use of fabric filters, scrubbers, electrostatic precipitators	Poor-Fair

Table 41 continued.

SMELTING/ REFINING OPERATION	SOURCE POTENTIAL POLLUTION	MITIGATION MEASURES	EFFECTIVENESS OF MITIGATION
Smelting	Stack Emissions	Stack Emissions	
(contd.)	Drying	Use of acid plants and/or other	
	Flash furnace smelting	SO_2 conversion systems	Fair-Good
	Copper converting	Use of fabric filters, scrubbers,	
	Nickel converting	electrostatic precipitators	
	Solid Waste Discharges	Solid Waste Discharges	
	Discard slag	Slag granulation & byproduct sale	
	Acid plant blowdown	of discard slag for:	
	Miscellaneous slurries	Potential backfill in underground	
	Scrubber slurries	mining operations	Good
	Contact cooling of cathodes	Mine road construction material	
	Washings	Tailing dam construction material	
		Aggregate	
	Water Discharges	Storage in unlined lagoons and/or	
	Process water discharges	discharge basins	
	Anode casting water	Storage in tailing basins	
	Slag granulation water	Storage in lined lagoons and/or	
	Acid plant blowdown water	discharge basins	
	Potable water	Chemical fixation of leachable	
	Cooling water discharges	sludges	
	Process cooling (non-contact)		
	water	Water Discharges	
	Turbine condensor cooling	Water purification treatment	Fair-Good
	Acid plant cooling	Cooling towers/ponds	Good
Refining	Solid Waste Discharges	Solid Waste Discharges	
	Solid wastes from leaching	Storage in unlined lagoons and/or	
	Miscellaneous slurries	discharge basins	
	Spent acid	Storage in tailing basins	Fair-Good
	Cooling water	Storage in lined lagoons and/or	
	Scrubber slurry	discharge basins	
	Washings	Chemical fixation of leachable	
	Waste from slimes	sludges	

Table 41 continued.

SMELTING/ REFINING OPERATION	SOURCE POTENTIAL POLLUTION	MITIGATION MEASURES	EFFECTIVENESS OF MITIGATION
Refining (contd.)	Water Discharges Process water discharges Cooling water discharges	Water Discharges Water purification treatment	Fair-Good
General	Fugitive Emissions Dust lift off from plant area and roads	Fugitive Emissions Revegetate, water, and treat roads to prevent dust	Fair-Good
	Water Discharges Water runoff from plant area Sanitary facilities	Water Discharges Provide drainage collection, and contour to disipate water Provide sewage collection & treatment plant	Good
	Miscellaneous Oil & grease spills	Miscellaneous Oil & grease traps Proper maintenance	Good

[a] Key: Good-indicates proven effective control technology exists that is known to operate reliably in many installations.

Fair-indicates proven effective control technology exists or is in the demonstration stage at one or more installation.

Poor-indicates proven effective control technology has not been developed, or is not yet ready for full scale application.

Regardless of the location of the smelter/refinery, a transportation corridor will be required to transport all marketable products. For a fully integrated operation a transportation system, most probably rail transport, will be required to move one or more major output products. These products and the range of quantities typically involved are summarized in Table 42. Also included are comments on the properties of these products that require special handling considerations.

Table 42

For distances typically less than 20 to 30 mi, truck haulage in lieu of rail transport may be the preferable means of movement of refinery products such as cathodes, powders, and granulated material, as well as intermediate smelter products such as granulated mattes, granulated slag, and ingots, or sulfuric acid. This particular mode of transportation, which may be the sole method needed for product transportation, assumes that ready and available markets for the processing and/or sale of such products are located within the immediate vicinity.

In situations where the refinery or refineries are separated from the smelter by great distances, hundreds to thousands of miles, a water transportation system, typically utilizing barges or tankers, in combination with one or more of the above mentioned transportation systems may be utilized.

In addition to the transport of output products, various input materials will be required by the operation. For example, the principal input materials required by a smelter/refinery complex producing 100,000 mtpy of metal may include one or more of the following: coal; coke; limestone, lime, silica flux. Table 43 indicates the range of amounts typically involved in an operation of this size.

Table 42. Typical range of production for a modern smelter/refinery complex.
(Basis: 100,000 mtpy metal production)

ITEM	RANGE (mtpy)	PHYSICAL CONDITION	REMARKS
Cathode Copper	80,000- 90,000	Ingots (34x24x1 in.), 300 lb	
Cathode Nickel	10,000- 20,000	Ingots (34x24x1 in.), 140 lb	
Sulfuric Acid	400,000-500,000	Liquid	Spillage of acid during loading, hauling, and unloading may result in creating hazardous conditions
Bulk Cu-Ni Matte	120,000-150,000	1. Crushed aggregate (-1/4 in.) 2. Fine powder (80%-200M) 3. Ingots (38x24x2 in.), 550 lb	Fine powdered matte is susceptible to spillage and/or dusting during loading, hauling, and unloading situations
Ni-Cu Matte	30,000- 40,000	1. Crushed aggregate (-1/4 in.) 2. Fine powder (80%-200M) 3. Ingots (38x24x2 in.), 550 lb	Fine powdered matte is susceptible to spillage and/or dusting, loading, hauling, and unloading situations
Discard Slag (for sale)	0-630,000	Crushed aggregate (-1/4 in.)	

These items will likely be transported by rail.

Table 43

A transportation system with a capacity of moving the above marketable products will also have ample capacity to transport additional output products such as salable dusts, and cobaltic materials, as well as minor input materials to the operation such as electrodes, electrode pastes, refractories, and spare parts.

If the smelter is separated from the refinery by great distances, then a transportation corridor with a capacity to handle similar output quantities will be required between the smelter and refinery. In cases where the smelter/refinery complex is distant from the mine and mill, a transportation system with an additional capacity and capability will be required to move 600,000 to 700,000 mt of bulk copper-nickel concentrate annually. Comparable total tonnages are involved, even if selective or differential flotation is used to generate 2 separate concentrates. Special loading and unloading facilities will also be required, ultimately adding to the capital and operating costs.

4.12.2 Support Services and Facilities

4.12.2.1 Energy Facilities and Supplies--Many forms of energy are used in the smelting and refining of copper and nickel. Melting of the charge materials may be accomplished with assistance from fossil fuels such as natural gas, oil, or pulverized coal firing, or with electric-resistance heating. Electricity is used for electrolysis in recovering and purifying copper and nickel by plating from solution. Electricity is used to power motors for gas, liquid, and solid materials handling. Air pollution control has increased gas handling requirements and consequently electricity consumption.

Table 43. Typical range of major materials required for a modern smelter/refinery complex. (Basis: 100,000 mtpy metal production)

ITEM	RANGE, mtpy
Coal[a]	30,000 - 50,000
Limestone/lime[b]	20,000 - 100,000
Silica flux	100,000 - 150,000

[a] Coal is a possible fuel, depending on the type of smelting furnace chosen.

[b] Limestone (or lime) consumption will depend heavily on the types of air emission and water treatment control technologies employed.

Natural gas and electricity are the major or preferred forms of energy typically used throughout the nonferrous metals industry today. Where electric arc resistance furnaces are used, electricity becomes the major source of energy. Table 44 summarizes the modeled values of annual consumption of the various forms of energy to be anticipated in the production of 100,000 metric tons of metal from a flash smelting/refining operation.

Table 44

The energy model was derived from a variety of information sources. The smelter energy estimates are based on general information on a flash smelter provided by AMAX (AMAX 1978a). If these estimates are expressed as total energy requirements per pound of metal (copper plus nickel) produced, the result compares well (within 25%) with the total energy per pound of copper required by the domestic copper industry (Rosenkrantz 1976). The model values (2.3 X 10^4 BTU/lb of metal) are higher than the published values for copper, which appears reasonable in light of the more energy intensive requirements of nickel. The estimates for the copper refinery are based again on U.S. Bureau of Mines data for the domestic copper industry (Rosenkrantz 1976), assuming a refinery capacity of 67,000 mtpy of copper. The resulting total energy requirement is modeled as 6.1 X 10^3 BTU/lb of copper.

As with other variables, modeling the energy requirements of the nickel refinery was complicated by the lack of representative data. Published data (Dasher 1976) indicates that the energy required to refine a pound of nickel at various operations around the world ranges from __ to 5.3 kwH. An average value of 3.65 was selected for modeling purposes. Further, it was assumed that the copper recovered from the nickel-copper matte by electrowinning required as much energy as

Table 44. Model for the annual energy requirements for a flash smelter/refinery installation producing 100,000 mtpy of Cu and Ni metal.

TYPE OF FUEL	UNITS	SMELTER	CU REFINERY	NI REFINERY	TOTAL
Natural Gas	10^6 CF/y	0	0	222.0	222.0
	10^9 BTU/y	0	0	222.0	222.0
Coal	10^3 mt/y	40.0	0	0	40.0
	10^9 BTU/y	1060.0	0	0	1060.0
LPG	10^6 gal/y	0	0	1.0	1.0
	10^9 BTU/y	0	0	92.0	92.0
Gasoline	10^6 gal/y	0	0	0	0
	10^9 BTU/y	0	0	0	0
Diesel	10^6 gal/y	0	0	0	0
	10^9 BTU/y	0	0	0	0
Fuel Oil	10^6 gal/y	0	0	0	0
(except diesel)	10^9 BTU/y	0	0	0	0
Thermal	10^9 BTU/y	0	331.0	1300.0	1631.0
(independent of fuel type)	10^9 BTU/y	0	331.0	1300.0	1631.0
Electricity	10^6 kwH/hr	386.0	54.0	140.0	580.0
	10^9 BTU/y	4053.0	567.0	1470.0	6090.0
Peak Load Requirement	Mw	55.1	7.7	20.0	82.8
TOTAL	10^9 BTU/y	5113.0	898.0	3084.0	9095.0
Distribution	%	56%	10%	34%	100%

Conversion Factors:

Coal--2.65 X 10^6 BTU/mt
LPG--92,000 BTU/gal
Nat. Gas--1,000 BTU/CF
Electricity (prod.)--10,500 BTU/kwH
Gasoline-- 125,000 BTU/gal
Diesel--138,690 BTU/gal
Fuel Oil--149,690 BTU/gal

the nickel, so the refinery model was scaled by using a requirement of 3.65 kwH/lb of total metal, copper plus nickel. This would clearly overestimate the requirement if a less energy intensive method is used to recover the copper. An example is the cementation process used by Falconbridge at Kristiansand, Norway (Boldt 1967), in which the cement copper is recycled to the smelter, increasing the volume of metal treated in the copper refinery. Making the assumption noted above, the resulting total energy requirement was apportioned among the various fuel types based on the fuel distribution calculated for the AMAX Port Nickel refinery (AMAX 1978e). Again, given the rather unique and complex nature of the Port Nickel operation, this modeled division must be used with great caution. For example, propane and/or natural gas is needed at Port Nickel for the production of hydrogen required by the operation. Other processes (Boldt 1967) may not require these fuels at all. Nevertheless, the resulting model is useful in that it does illustrate the range of fuel types that may be required in a nickel refinery, depending on the process selected.

It should be noted that the conversion factor used for electrical energy here is 10,500 BTU/kwH. This means that the BTU energy requirements shown for electrical energy include the energy lost to waste heat in the central power plant which is generating the electricity. An 80% duty factor was used in estimating all peak electrical power requirements.

All forms of fossil fuel will likely be imported to the smelter/refinery site. Electricity will be purchased from public utility companies. Should new demand for electricity on the part of the copper-nickel operation exceed present supply, then the copper-nickel complex will have to consider building facilities to provide their own electrical needs, or arrange for extra generating and transmission capacity to be installed by local power companies. See Volume 5-

Chapter 11 for discussion of energy supplies and demands for the region and the facilities required to support copper-nickel development in northeastern Minnesota.

4.12.2.2 Manpower Requirements--Typical manpower requirements have been determined on the basis of a single model smelter/refinery complex and are as outlined in Table 45. The table indicates that approximately one-third of the total work force is associated with the smelter, and that the remaining two-thirds is associated with the two refineries. Total manpower needs for an "offsite" operation is expected to be slightly larger due to the increased need for people in the administrative and maintenance categories.

Table 45

4.12.2.3 Land Requirements--Chapter 5 lists all of the parameters of the Study models, one of which is land requirements. In a fully-integrated 20 X 10^6 mtpy open pit mining operation, over 7,300 acres of direct-use land is necessary, with an additional 40% as undisturbed but controlled land, for a total of over 10,200 acres. Of this, about 37% is occupied by mining, just over 60% by processing, and less than 2.5% by the smelting/refining operation. Specifically, of the land directly under use, the smelter needs 50 acres, the refineries need 100 acres, and the slag disposal pile occupies 25 acres for a total of 175 acres. The undisturbed area then is 70 acres for a grand total of 245 acres.

These values were based on interpretations of available information, as the literature is limited and no facilities such as are described here actually exist to serve as examples. A reasonably close analogue is shown in Figure 63,

Table 45. Typical manpower required to administer, operate, and maintain a 100,000 mtpy metal smelter/refinery operation.

	PERSONNEL FOR MODEL SMELTER/REFINERY OPERATION			
	Administrative & Salaried	Labor & Hourly	Total	TYPICAL RANGE OF TOTAL
"Onsite Operation"				
Smelter	32	180	212	200-275
Cu Refinery	16	66	82	80-135
Ni Refinery	65	262	327	300-375
TOTAL	113	508	621	580-785
"Offsite Operation"				
Smelter	33	187	220	208-285
Cu Refinery	17	70	87	88-143
Ni Refinery	68	272	340	312-390
TOTAL	118	529	647	605-818

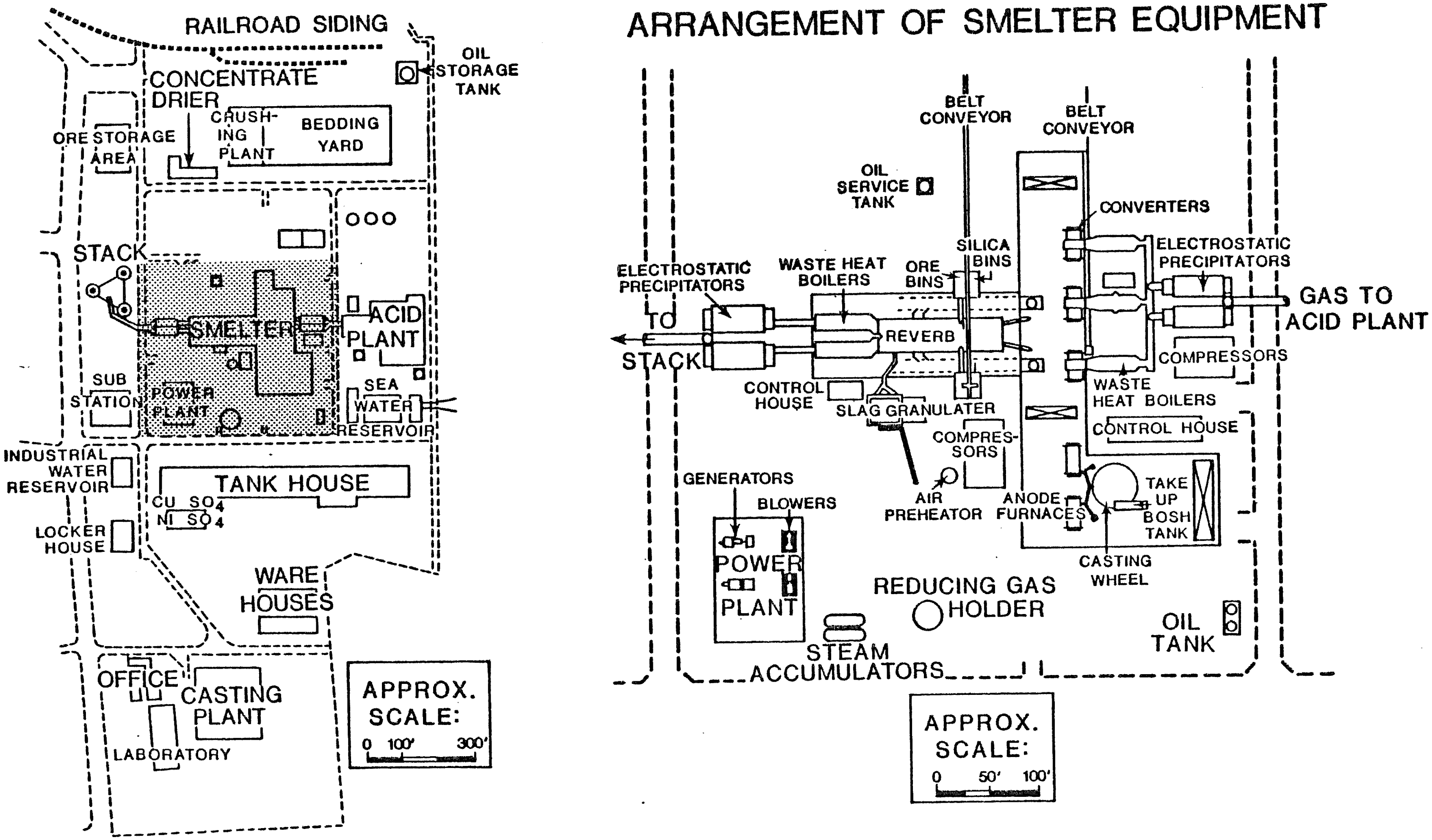
which illustrates the site layout of the Onahama copper smelter in Japan. This modern-day smelter/refinery complex occupies about 50 acres in total and is approximately the size of the model smelter facility. Note the relative scale and positions of the smelter building, refinery buildings, and plant, and concentrate unloading, storage, and handling facilities.

Figure 63

FIGURE 63

SITE LAYOUT OF THE ONAHAMA COPPER SMELTER IN JAPAN

(SOURCE: NAGANO ET AL. 1968)



PLANT AND BUILDING SITE PLAN

ARRANGEMENT OF SMELTER EQUIPMENT

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