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BACKGROUND INFORMATION DOCUMENT FOR REVISION OF NEW SOURCE PERFORMANCE STANDARDS FOR PRIMARY COPPER SMELTERS

DRAFT
CHAPTERS 3 THROUGH 6

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3. THE PRIMARY COPPER SMELTING INDUSTRY: PROCESSES AND POLLUTANT EMISSIONS

3.1 GENERAL

The primary copper smelting industry extracts copper from sulfide copper ores by the pyrometallurgical process of smelting. A major commodity metal, the refined copper ultimately produced is used in electrical wire, heat exchangers, pipes, coins, and as a component of the alloy brass.¹

The domestic smelting industry is comprised of seven companies that operate 15 smelters distributed throughout the country. The majority of plants are located in the southwest near large deposits of copper ore. Arizona, which has extensive ore deposits, has the greatest number of smelters, a total of seven. Two smelters are located in New Mexico, and a single smelter is located in each of the following States: Nevada, Texas, Utah, Tennessee, Michigan, and Washington. Domestic smelters range in production capacity from 13,600 Mg/year for the Cities Service Company smelter in Copperhill, Tennessee, to 254,000 Mg/year for the Kennecott Corporation smelter in Garfield, Utah. The 15 smelters, their locations, and capacities are presented in Table 3-1.

The basic raw material of copper, copper ore, is a mixture of copper-bearing minerals and copper-free minerals. The copper ores are distinguished generally as either sulfides, oxides, or native, depending upon the copper-bearing minerals they contain. Some 165 copper minerals are known, but only a few are commonly found in ore deposits.² Some of the more important sulfide and oxide minerals from which copper is extracted are listed with their chemical compositions in Table 3-2.

The sulfide ores account for 85 to 95 percent of domestic copper production,³ with the most common copper-bearing minerals contained in

TABLE 3-1. DOMESTIC PRIMARY COPPER SMELTERS, 1979

Company	Location	Annual capacity ^a	
		Mg	Tons
ASARCO, Incorporated	El Paso, Texas	91,000	100,000
	Hayden, Arizona	182,000	200,000
	Tacoma, Washington	91,000	100,000
Cities Service Company	Copperhill, Tennessee	13,600	15,000
Copper Range Company	White Pine, Michigan	52,000	57,000
Inspiration Consolidated Copper Company	Miami, Arizona	136,000	150,000
Kennecott Copper Corporation	Garfield, Utah	254,000	280,000
	Hayden, Arizona	71,000	78,000
	Hurley, New Mexico	73,000	80,000
	McGill, Nevada	45,000	50,000
Magma Copper Company	San Manuel, Arizona	181,000	200,000
Phelps Dodge Corporation	Ajo, Arizona	64,000	70,000
	Douglas, Arizona	115,000	127,000
	Hidalgo, New Mexico	163,000	179,000
	Morenci, Arizona	191,000	210,000

^aProduction of "blister" copper (99-percent Cu).

TABLE 3-2. MAJOR COPPER-BEARING MINERALS

Type	Mineral	Formula
Sulfide	Chalcopyrite	CuFeS_2
	Bornite	Cu_5FeS_4
	Chalcocite	Cu_2S
	Covellite	CuS
Oxide	Malachite	$\text{CuCO}_3 \cdot \text{Cu(OH)}_2$
	Azurite	$2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$
	Chrysocolla	$\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$
	Cuprite	Cu_2O

these ores being chalcopyrite, bornite, and chalcocite. The oxide minerals, which were formed from the weathering of the sulfides, are generally found in the upper portions of the sulfide deposits. Native copper, which consists of nearly pure metallic copper, occurs in small amounts in most major copper deposits. It is found in sufficient quantities to be of importance, however, only in Michigan's upper peninsula.

Copper ores are mined from both underground and, more commonly, open pit mines. The average tenor (copper content) of domestic ores is low, less than 1 percent.³ Materials comprising the majority of the ore include siliceous oxides, iron sulfides (pyrite FeS_2 , pyrrhotite FeS), and various other impurity metals such as zinc, lead, arsenic, antimony, and bismuth, which are typically in sulfide form. In addition, the ores contain small quantities of gold and silver.

Due to their low copper content, the sulfide ores are not smelted directly, which would use considerable energy. Rather, these ores are first beneficiated at the mine. Beneficiation involves crushing and grinding to liberate individual mineral particles, and then physical separation using the froth flotation process. The product of flotation, ore concentrates, typically contains copper, iron, and sulfur in similar proportions (approximately 20-40 percent each). In comparison, oxide ores are typically not concentrated. These ores are processed hydrometallurgically by leaching with acid, and the dissolved copper is recovered by chemical precipitation on scrap iron.

3.2 PROCESS DESCRIPTION

The pyrometallurgical processes used for extracting copper from sulfide ore concentrates are based on copper's strong affinity for sulfur and weak affinity for oxygen, as compared to iron's affinity for these elements. The conventional copper smelting process, which has been in use since the turn of the century, includes three fundamental operations:

1. Roasting (optional) of the ore concentrates in the presence of air to eliminate moisture and a portion of the sulfur.
2. Smelting of the roasted (calcines) or unroasted ore concentrates with fluxes to produce an iron-copper sulfide mixture (matte) and an iron oxide slag.

3. Converting (oxidizing) of the matte to eliminate the remaining iron and sulfur and yield blister copper (about 99 percent pure copper).

Briefly, the smelting of copper concentrates is accomplished by melting the charge and suitable fluxes in a smelting furnace. Part or all of the concentrates and fluxes may receive a partial roast before smelting to eliminate part of the sulfur and essentially all of the moisture. In the smelting furnace, a portion of the undesirable components combine with the fluxes and float to the top as a slag to be skimmed off and discarded while the copper, most of the iron and sulfur, and any contained precious metals form a product known as matte which collects and is drawn off from the lower part of the furnace. The molten matte, ideally represented as a mixture of the compounds FeS and Cu_2S , is transferred to a converter where air blown through the matte burns off the sulfur, oxidizes the iron for removal in a slag, and yields a 99 percent "blister" copper product.

Typically the blister copper is fire refined in an anode furnace, cast into "anodes," and shipped to an electrolytic refinery for further impurity elimination. A schematic flowchart of the conventional smelting process is presented in Figure 3-1. Offgases containing particulates and sulfur dioxide in various concentrations are emitted from each operation.

Four different smelting technologies are currently used by the domestic industry: the traditional reverberatory furnace, the electric furnace, the flash furnace, and the Noranda process. A more detailed discussion of the operations involved in copper smelting and each of the various technologies is presented in succeeding paragraphs.

3.2.1 Roasting and Drying

Currently, 7 of the 15 domestic smelters perform the roasting step. Of the remaining smelters, five dry the charge before smelting, and three charge the ore concentrates directly to the smelting furnace. Whether a smelter uses roasters or not is primarily determined by the copper-to-sulfur ratio of the feed, as well as by the feed impurity level. Drying is distinguished from roasting by the operating temperature, which is much lower during drying.

In the roasting process, copper sulfide ore concentrates are heated under well-controlled conditions to a high temperature (but below the

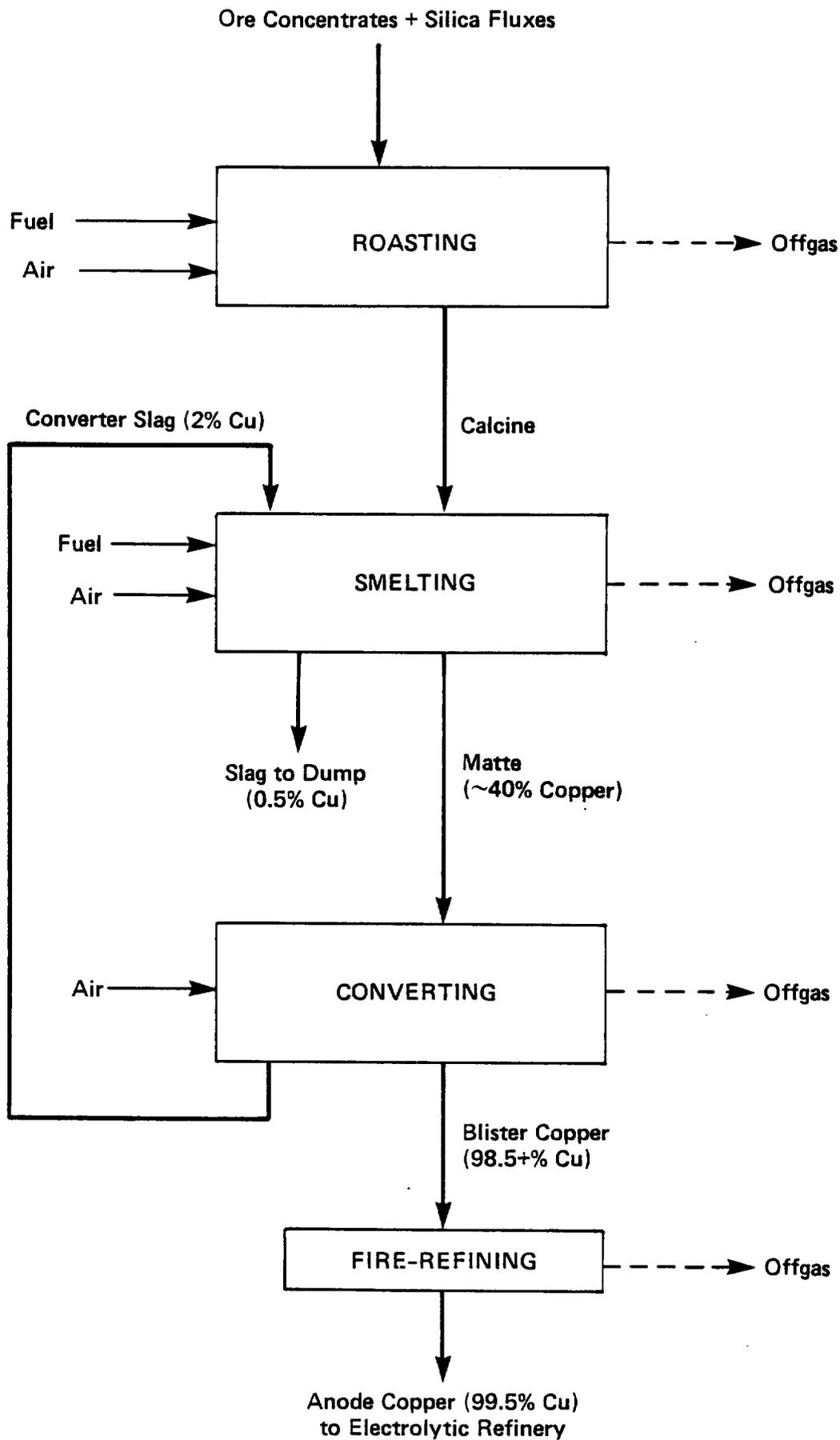
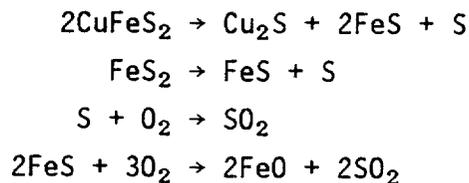


Figure 3-1. The conventional copper smelting process.

melting point of the constituents) in the presence of air to fulfill two primary objectives: (1) to dry and heat the furnace charge, which results in considerable savings of energy in the smelting step and increased smelting furnace throughput; and (2) to eliminate a portion of the concentrate sulfur as sulfur dioxide and oxidize (preferentially to the copper sulfides) a portion of the iron sulfides to iron oxides. The latter objective leads to an increased copper concentration in the $\text{Cu}_2\text{S}:\text{FeS}$ matte produced during smelting. Roasting is also used to drive off a portion of volatile impurities, such as arsenic and antimony, that are present in significant amounts in some concentrates. This particular application is most important at custom smelters, which may process feeds with high impurity levels.

Numerous chemical reactions occur during roasting. Many result in the elimination of a portion of the sulfur as SO_2 . A large percentage of the emitted SO_2 results from reactions with iron sulfides (such as pyrite, FeS_2) which are present to some extent in all concentrates. Representative reactions include the following:



The product of roasting is known as calcine. The exact composition of calcine produced from a given feed composition is dependent upon the degree of roast, i.e., the degree of sulfur removal. The degree of roast achieved depends on the roaster temperature and the air-to-concentrate ratio. Increasing the degree of roast leads to increases in the grade of matte produced in the subsequent smelting step. However, the matte grade (and hence degree of roast) are ultimately limited by the fact that adequate separation of copper from iron can only be achieved if sufficient sulfur is present to maintain all of the copper, and a significant portion of the iron in sulfide form during smelting. Other factors, discussed in succeeding sections, may further limit the degree of roast achieved at certain smelters. Domestic smelters generally eliminate between 20 and 50 percent of the sulfur in the charge during roasting.

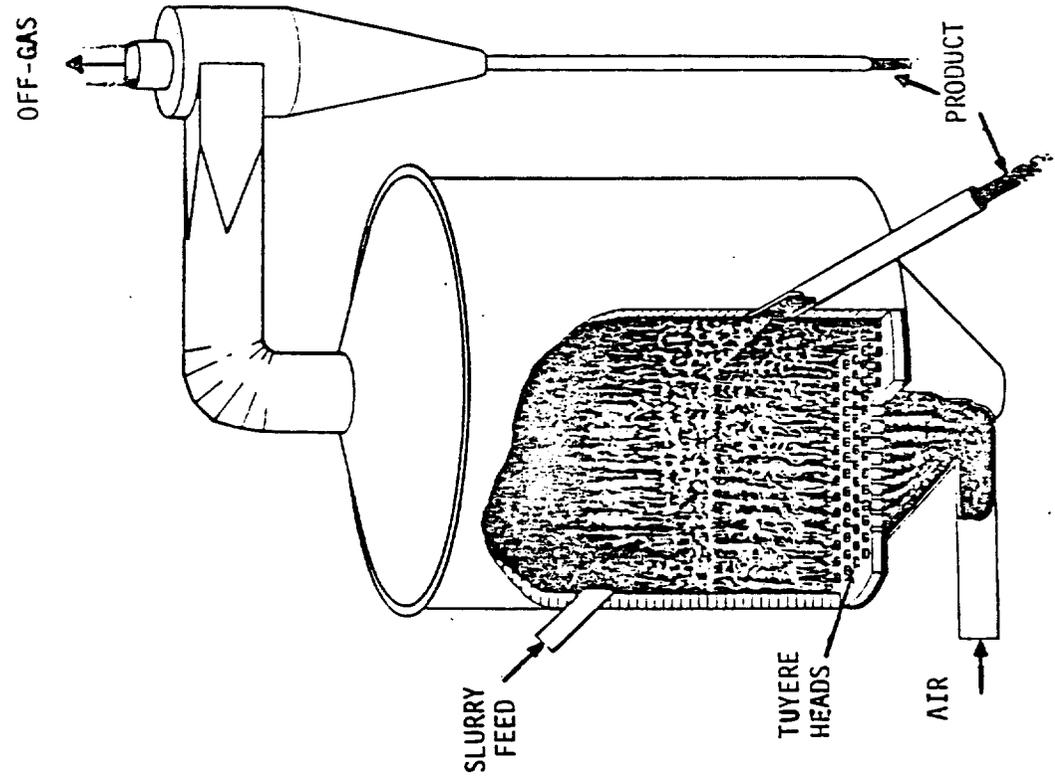
Roasters in use by the industry are either of the multihearth type or the fluid-bed type. An illustration of each is presented in Figure 3-2. Fluid-bed roasters are the more modern of the two designs. Currently three smelters use fluid-bed roasters and four smelters use multihearth roasters.

3.2.1.1 Multihearth Roasters. Multihearth roasters are cylindrical, refractory-lined vessels which are divided from top to bottom by (usually) six or seven refractory hearths. The outer shell is made of steel and has hinged doors at each level. The moist concentrates enter the roaster through an annular opening at the top, dropping to the top-most or dryer hearth. Plows or rabble blades attached to a central, rotating shaft and positioned directly above each hearth serve to expose fresh surfaces of the feed to the oxidizing air. The rabble arms are set at an angle and direct the charge alternatively to the center of the hearth or to the periphery where it drops through holes to the next lower hearth. The roasted calcine is discharged through the bottom of the roaster. The air required for the controlled oxidation of the feed enters the vessel primarily through the bottom and flows counter-currently against the descending charge. The gases exit through a flue at the top.

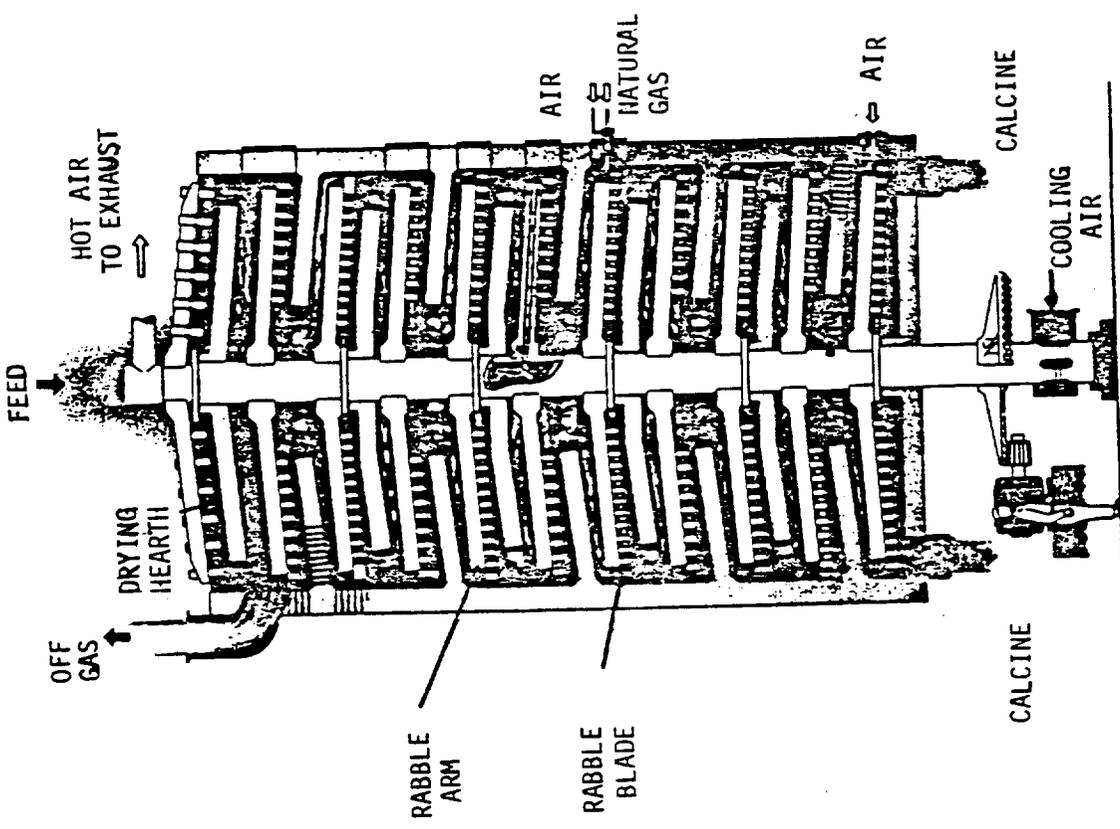
Multihearth roasters are started by preheating to a temperature at which the concentrates will be ignited by air. The temperature of the calcines as discharged is typically 540° to 590° C (1,000° to 1,100° F).⁴ As the principal roasting reactions are all exothermic, roaster operation is usually autogenous.⁵ If the concentrates are excessively moist, fossil fuel is used to provide supplementary heat.

Typically, multihearth roasters process from 180 to 360 Mg/day (200 to 400 tons/day) of feed. Offgas flow rates from multihearth roasters used in the domestic industry generally range from 400 to 480 Nm³/min (14,000 to 16,000 scfm). The SO₂ concentration in the offgases is typically in the range of 1 to 3 percent. However, new multihearth roasters are capable of producing 5 percent SO₂ in the offgases,⁶ because less dilution air enters new units.

3.2.1.2 Fluid-Bed Roasters. Fluid-bed roasters are cylindrical, refractory-lined vessels having a single grate-hearth in the bottom containing tuyere heads through which air is blown from the bottom. Finely



Fluid-bed roaster



Multi-hearth roaster

Figure 3-2. Types of roasters.

ground ore concentrates, charged continuously into the vessel through the side, form a bed which is maintained in a turbulent suspension by the air introduced--the mixture of air and solids having the flow characteristics of a fluid. The finely ground feed is introduced either as a slurry through a feed pipe, or in relatively dry form (6 to 12 percent moisture) through a screw conveyor. Roasting occurs as the sulfide particles come in contact with the fluidizing air. Because of the large surface area of the finely ground material exposed to the air stream, the residence time in the oxidizing atmosphere is short. As is the case for multihearth roasters, the roaster operates autogenously after the vessel is preheated to combustion temperatures.

Roasted solids are discharged by overflow through a side port and through entrainment in the offgas, which exits through the top of the vessel. Typically, the offgas contains 80 percent of the roasted calcine.⁷ Hence, cyclone collectors are an integral part of the roasting operation.

The roasting temperature in domestic fluid bed roasters is similar to that of multihearth roasters, typically 540° to 650° C (1,000 to 1,200° F). Due to the high chemical efficiency of the fluid bed roasters, the feed tends to overheat from the exothermic roasting reactions. Overheating leads to overoxidation of the product, which results in the formation of magnetite (Fe_3O_4). This compound is undesirable in the subsequent smelting step. Hence, the roaster temperature must be carefully controlled. Cooling is performed by adding water or inert fluxes (used in the smelting step) to the concentrates.

Offgases from fluid-bed roasters typically have SO_2 concentrations of 12 to 15 percent. The fluid-bed roaster at the Kennecott-Hayden smelter, for example, gives an offgas SO_2 concentration of 13 percent.⁸ The offgas flow rate from this unit has been reported at 880 Nm^3/min (31,000 scfm), when processing 1,000 to 1,100 Mg/day (1,100 to 1,200 tons/day) of feed.⁸

The primary advantages offered by fluid-bed roasters lie in their high offgas SO_2 concentrations and their high throughput rates as compared to multihearth roasters. Multihearth roasters offer the advantage of providing greater control over the oxidizing conditions within the vessel. Such control is of notable importance if the feed contains substantial quantities

of volatile impurities. (This point is discussed further in Section 3.5.2.1.)

3.2.1.3 Concentrate Dryers. Concentrate dryers are used to reduce the moisture content of ore concentrates and other feed materials before smelting. Typically, the ore concentrates contain from 5 to 15 percent moisture following flotation. Dryers are used to reduce the moisture content to 0.1 to 0.3 percent. Drying differs from roasting in that its only purpose is to reduce the moisture of process feed materials. Because dryers operate at a relatively low temperature of 65° to 90° C (150° to 200° F), very little of the sulfur is driven off as SO₂.

There are a number of systems that can be used to dry copper concentrates, including both multihearth and fluid-bed roasters. Perhaps the most common type, however, is the rotary dryer. The rotary dryer is a rotating cylinder inclined to the horizontal with material fed into one end and discharged at the opposite end.

In most types of dryers, air or combustion gases flow co-current or countercurrent to the movement of the concentrate. Intimate contact between the drying gases and the concentrate is usually permitted.

Dryers are always used at installations which use flash furnaces for smelting. They may be used with the other types of smelting furnaces. Also, dryers may be used upstream of fluid-bed roasters.

3.2.2 Smelting

Smelting is the pyrometallurgical process in which solid feed materials are melted together with fluxing agents to form two or more immiscible layers. The objective in copper smelting is the production of a metal sulfide mixture (matte) containing primarily FeS and Cu₂S, and a separate (oxide) slag layer containing primarily iron silicates.

During copper smelting, hot calcines from the roaster or raw, unroasted concentrates are melted in a smelting furnace with siliceous or limestone flux. Converter slag, collected dust, oxide ores, and any other material rich in copper may be added to the furnace charge. Essentially all copper present in the charge, independent of its chemical state, combines with sulfur also present in the charge to form the stable compound, cuprous sulfide (Cu₂S).⁹ Sulfidic iron compounds, such as FeS₂, decompose yielding

sulfur dioxide (SO_2) and a comparatively stable compound, ferrous sulfide (FeS). The mixture of primarily Cu_2S and FeS is known as matte, which, due to its density collects in the lower part of the furnace, from which it is periodically removed for further processing in the copper converters. Copper mattes produced by the domestic industry contain from 35 to 75 percent copper, with 40 to 45 percent being the most common. The percentage copper present in the matte is referred to as the matte grade. Matte also contains small amounts of other sulfides, such as Co_3S_2 , Ni_3S_2 , PbS , ZnS ; impurities such as As, Sb, Se, and Te; and precious metals such as Au, Ag, and Pt.¹⁰

The remainder of the molten mass, containing primarily metal oxides and gangue materials, is known as slag. Since slag is of lower density than matte, it floats on top of the matte layer, from which it is periodically drawn off and generally discarded. Slags contain generally low percentages of copper, which is present in the form of both dissolved matte and entrained matte droplets.¹¹ Since slags are generally discarded directly, the copper content is a major cause of copper loss. Because the concentration of copper in the slag increases with increasing matte grade, matte grades produced in conventional practice seldom exceed 50 percent copper.

The primary purpose of the added fluxing materials is to effect the removal of iron oxides to the slag. A portion of the iron is removed during smelting, and the balance during the subsequent converting operation. Iron oxide (FeO) is produced readily during roasting and smelting because of the higher affinity for oxygen of FeS compared to Cu_2S . Molten iron oxides are highly miscible with matte. The addition of silica, however, leads to the formation of iron silicates, which are of lower density and immiscible in the matte. Iron silicates are a major component of the slag, which is ideally represented by the compound $2\text{FeO}\cdot\text{SiO}_2$.¹² Slags also usually contain small amounts of alumina and lime, which are present naturally in the charge or are added to increase the fluidity of the slag.

(Currently, four different smelting furnace technologies are employed by the domestic industry. These include the reverberatory, electric, Noranda, and Outokumpu (flash) furnaces.) The conventional reverberatory furnace is employed by the majority of the smelters. Two companies plan to retire their reverberatories within the next few years and adopt a fifth technology, the Inco flash furnace.

3.2.2.1 Reverberatory Furnaces. The conventional reverberatory furnace as shown in Figure 3-3 is currently employed by 11 of the 15 domestic smelters. Reverberatory furnaces are long, rectangular structures consisting of a hearth, side and end walls, and an arched roof. Typical dimensions are about 11 M (36 feet) in width and 40 m (130 feet) in length.¹³ Reverberatory furnaces typically process from 800 to 1,200 Mg (900 to 1,300 tons) of charge per day. In a reverberatory furnace, fossil fuels such as oil, gas, or pulverized coal are burned above the charge being smelted. Furnace burners are placed in one end-wall, and hot gases exit the far end-wall. Flames from the burners may extend half the length of the furnace. Temperatures at the burner end of the furnace exceed 1,500° C (2,730° F). A portion of the heat radiates directly to the charge lying on the hearth below, while a substantial part radiates to the furnace roof and walls and is reflected down to the charge.

In addition to smelting the charge and allowing the settling of matte and slag into separate layers, a major function of the conventional reverberatory furnace is to simultaneously recover copper from slag produced in the converters. Molten converter slag is returned to the furnace, whereupon matte and copper that are mechanically entrained in this slag settle out by gravity. To some extent, copper oxides trapped in the slag are reduced to Cu_2S by reactions with iron sulfide and also settle out. The copper content of the slag from the reverberatory furnace is typically 0.4 to 0.5 percent.

Reverberatory smelting is a continuous process, although charging is intermittent. In green-charged furnaces, the concentrates and fluxes are typically charged along the sidewalls, where they form "banks" or piles which protect the sidewall refractory. These banks slowly melt into the bath. Charging is performed using drag chain conveyors running along the top outside of the furnace and parallel to the sidewalls. The solid material falls through drop pipes penetrating the roof arch, which are spaced evenly along the furnace length. The resulting piles of charge along the sidewalls serve to protect the sidewall refractory from burner heat. Typically, most of the charge is placed along the first half of the furnace length (from the burner end), which constitutes the smelting zone. The remainder of the furnace is termed the settling zone, in which matte entrained in the slag settles to the matte layer. Green-charged furnaces are also charged, in

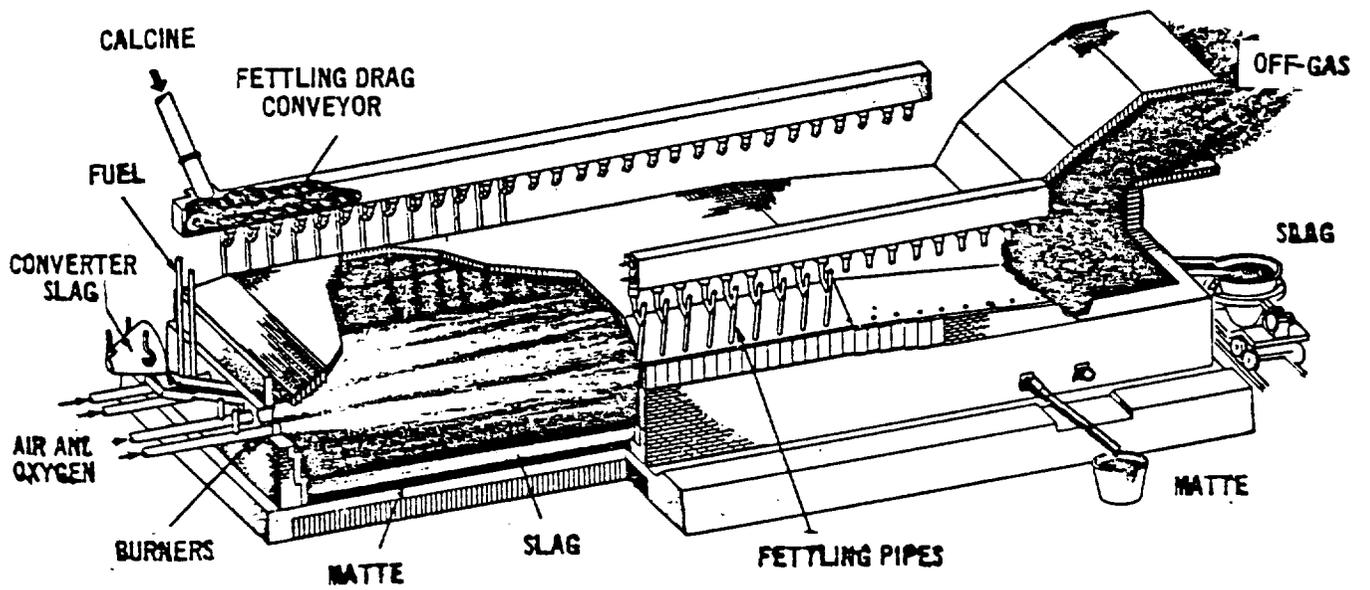


Figure 3-3. Reverberatory smelting furnace.

limited cases, by charge slingers. These devices are high-speed conveyors that "throw" the charge into the furnace through ports that are opened along the sidewalls. The result is to spread the charge evenly over the bath. The use of three slingers on each side of the furnace has been reported.

Calcine-charged reverberatory furnaces are typically charged using fixed or retractable gun-type feed pipes (Wagstaff guns) penetrating the furnace sidewalls. Typically, two such feeders are present on each side of the furnace. Calcine may also be charged through the roof arch at either the center or the sidewalls. Sidewall charging of calcines, using a drag chain conveyor/drop pipe system similar to that used on green-charged furnaces is used in some cases. However, the resulting charge banks are not as substantial as those produced with green charge because of the comparatively free-flowing nature of hot calcine. In order to provide more protection of the sidewall refractory from burner heat, most calcine-charged furnaces employ water-cooled panels on the outside of the furnace at the slag line.

Reverberatory furnaces produce a large volume of offgases containing a relatively low concentration of sulfur dioxide. Both the large offgas flow rate and the low SO_2 concentration result because essentially all of the heat is produced from the combustion of fossil fuel in air, which is 79 percent inert nitrogen. Offgas flow rates have been reported at 1,800 to 2,100 Nm^3/min (63,000 to 74,000 scfm),¹⁴ and may be substantially higher. Typically, from 10 to 30 percent of the sulfur in the original concentrate feed is eliminated in the furnace offgases. The average SO_2 concentration in the offgases generally varies between 0.5 and 1.5 percent.¹⁵ As would be expected, the smelting of roasted calcines, which have relatively little free sulfur, yields offgases containing 0.5 to 1.0 percent SO_2 . In contrast, green-charged furnaces yield offgas SO_2 concentrations of 1.0 to 1.5 percent.

The primary advantage afforded by reverberatory furnaces over most other smelting technologies is their versatility. Feed materials which are wet or dry, lumpy or fine may all be smelted readily. A major disadvantage of these furnaces is the weak SO_2 stream produced. Furthermore, since the reverberatory furnace utilizes essentially none of the inherent energy of

the sulfide charge, its energy requirement is among the greatest of the major pyrometallurgical processes.

3.2.2.2 Electric Furnaces. Electric smelting furnaces are employed by two of the domestic smelters. As shown in Figure 3-4, the heat required for smelting in these furnaces is generated by the passage of electric current through the molten bath. Carbon electrodes dip into the slag layer of the bath, forming an electrical circuit. As electric current is passed through the circuit, the resistance of the slag causes the generation of heat which results in smelting temperatures.

Typically, electric furnaces used for matte smelting are rectangular, and measure about 35 m (115 ft) in length by 10 m (33 ft) in width. A furnace of this size utilizes six Söderberg-type electrodes, 1.8 m (6 ft) in diameter, which are spaced uniformly along the long axis of the furnace.¹⁶ The current flow and voltage between pairs of electrodes are of the order of 30,000 amps and 500 volts, respectively.¹⁶ The electric furnace at Inspiration Consolidated Copper Company is designed to process about 1,640 Mg/day (1,800 tons/day) of feed.

Feed to electric furnaces is typically charged through the roof of the furnace, near the electrodes. (The feed generally consists of dried concentrates or calcines. The charging of wet concentrates is avoided) because the moisture can cause steam explosions.¹⁷ The unsmelted charge materials float on top of the molten bath. Heat is thus transferred from the hot slag (where the heat is produced) to the charge floating on its surface. Keeping the bath covered with charge maximizes the rate of heat transfer to the charge. Also, the floating charge reduces heat losses from the bath and prevents overheating of the roof refractories.¹⁸

Electric furnaces are similar to reverbs in that they offer essentially the same degree of versatility. (The physical and chemical changes occurring in the molten bath of an electric furnace are similar to those occurring in a reverberatory furnace.) Furthermore, molten converter slags are normally returned to electric smelting furnaces for the recovery of entrained copper, as with reverberatory furnaces. A major advantage of electric furnaces over reverberatory furnaces is their ease of control, resulting from a high concentration of SO₂ in the exhaust gases (on the order of 5 percent).¹⁹

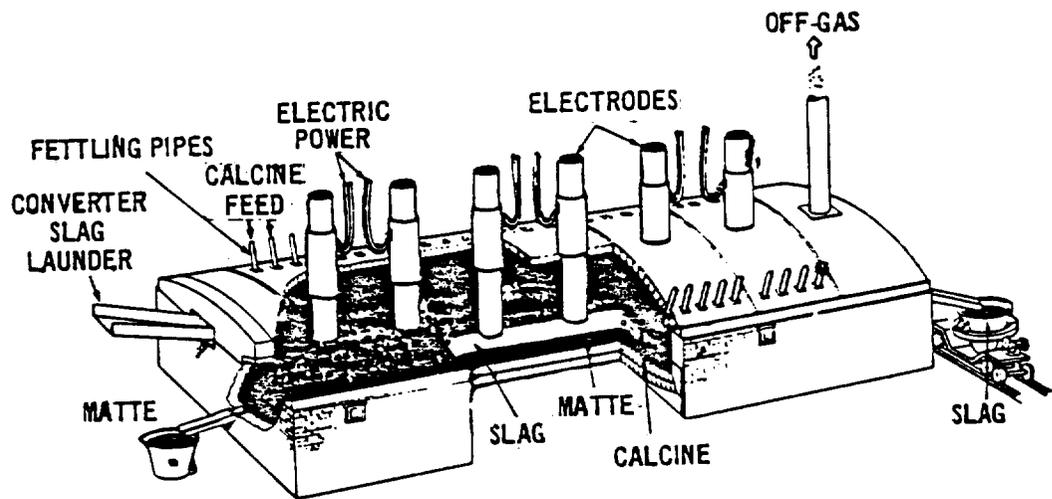


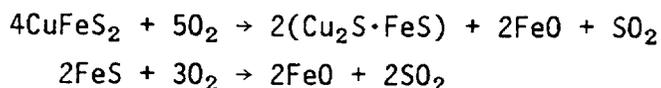
Figure 3-4. Electric smelting furnace.

Furthermore, since combustion air is not required, the offgas flow rates are less than half of those in reverberatory furnaces. The Inspiration furnace, for example, produces approximately 850 Nm³/min (30,000 scfm) of offgas containing from 4 to 6 percent SO₂.²⁰ Low offgas flow rates minimize the size and cost of downstream gas handling equipment.

The primary disadvantage of the electric furnace is that, like the reverberatory furnace, it makes limited use of the energy potentially available from oxidizing the sulfide minerals of the charge. Furthermore, its operating costs tend to be high because of the high price of electricity.²¹

3.2.2.3 Flash Furnaces. In contrast to reverberatory and electric furnaces, flash furnaces utilize the heat evolved from the partial oxidation of their sulfide charge to provide much or all of the energy required for smelting. The result is that the energy cost for flash furnace operation is considerably less than that associated with reverberatory and electric furnaces. Flash furnaces also produce offgas streams containing high concentrations of SO₂, which may be efficiently recovered as sulfuric acid or liquid SO₂. For these reasons, most of the world's new matte smelting furnaces installed since 1965 have been of the flash type.²² Currently, one of the domestic smelters employs a flash furnace, and two others intend to convert to flash smelting technology.

In flash smelting, dried ore concentrates and finely ground fluxes are injected together with oxygen, preheated air, or a mixture of air and oxygen into a hot furnace of special design. Within the furnace, the sulfide particles react rapidly with the oxidizing gas, releasing heat. Important reactions include the following:²²



The melted droplets fall to the bath below, where the matte- and slag-forming reactions are completed. The matte droplets settle through the slag layer to form the matte layer.

The combustion reactions utilize essentially all of the oxygen contained in the process atmosphere. Consequently, the regulation of the oxygen/con-

concentrate ratio in the furnace controls the extent to which the flash combustion reactions proceed and thus determines both the grade of matte produced and the heat released for smelting the furnace charge. Increasing the incoming temperature or oxygen content of the combustion air also effectively increases the heat available for smelting. As a result, in some cases it is possible for the flash combustion and smelting reactions to occur autogenously. Under these conditions, the heat released by the oxidation of iron and sulfur is sufficient to smelt the furnace charge.

The charge to a flash smelting furnace must be fine grained, and essentially "bone dry" to insure an even and homogeneous distribution of the charge as it is injected into the furnace. The copper concentrates should be of a fineness corresponding to at least 50 percent minus-200 mesh, and the fluxing material should be of a fineness corresponding to at least 80 percent minus-14 mesh.²³ Since most concentrates are obtained from ores by flotation techniques, their fineness normally meets these requirements without further grinding.²³ The fluxing materials, however, usually require additional grinding beyond that necessary for use in reverberatory or electric smelting furnaces.

In most cases it is necessary to dry the charge to bone-dry conditions (0.1 to 0.3 percent moisture) before smelting, as the concentrates typically contain from 5 to 15 percent moisture.²³ It is common practice to use the drying facilities not only for drying the charge, but also for blending the fluxing materials and the various copper concentrates available to provide a charge of uniform composition. It should be noted that the charge is not roasted, as the flash combustion process makes use of the roasting reactions to melt the charge.

The principle advantages of flash furnaces lie in their low energy requirements, their high SO₂ strength in the offgases, and their high production rates. The productivities of flash furnaces are on the order of 8-12 Mg of charge per day/m² of hearth area, which is two to four times that of reverberatory or electric furnaces.²⁴

The principle disadvantage of flash smelting is that the copper content of the furnace slag tends to be higher than that of reverberatory and electric furnaces. As a result the use of separate facilities may be

required to recover some of the copper from the flash furnace and converter slags before discard.

Flash smelting technology has been developed by two different companies: International Nickel Company (Inco) in Canada and Outokumpu Oy in Finland. The major difference between the two technologies is in the design of the smelting furnace and in the oxidizing environment within the furnace. The Inco furnace uses pure oxygen, while the Outokumpu furnace employs pre-heated air or oxygen-enriched air as the oxidizing medium. Currently, 30 Outokumpu flash furnaces are operating or are licensed to operate worldwide. Two Inco flash furnaces are currently operating worldwide, and two additional units are slated for construction in the United States. The larger number of Outokumpu furnaces is attributed to the fact that Outokumpu has been marketing its technology for a number of years, while Inco has only recently offered its technology for license.

3.2.2.3.1 Inco flash furnaces. The Inco flash furnace, shown in Figure 3-5, is the simpler of the two flash furnace designs. The furnace used by Inco in Sudbury, Ontario, is about 24 m (79 ft) long, 7 m (23 ft) wide, and 6 m (20 ft) high at the ends.²⁵ The furnace uptake extends the full width of the furnace at its center. For gas tightness, the furnace is essentially totally enclosed in a shell made of mild steel, 1 cm (0.4 in.) thick. This particular furnace has a nominal capacity of 1,360 Mg/day (1,500 tons/ day) of dry charge.²⁵

Dried ore concentrates, fluxes, and commercial oxygen are blown horizontally into the furnace through four water-cooled burners, two at each end. This design produces a high temperature flame over the entire hearth area. Water-cooled steel jackets faced with refractory brick cover approximately 20 percent of the sidewalls, mainly in the region below the gas offtake. This central zone requires cooling because it is the region of highest sulfide combustion intensity. Matte is tapped from the central zone of one sidewall, while slag is skimmed from beneath the burners at one end of the furnace.

Because pure oxygen rather than air is the oxidizing medium in the furnace, the concentration of sulfur dioxide in the Inco furnace offgases is very high, normally in the range of 70-80 percent.²⁵ At this concentra-

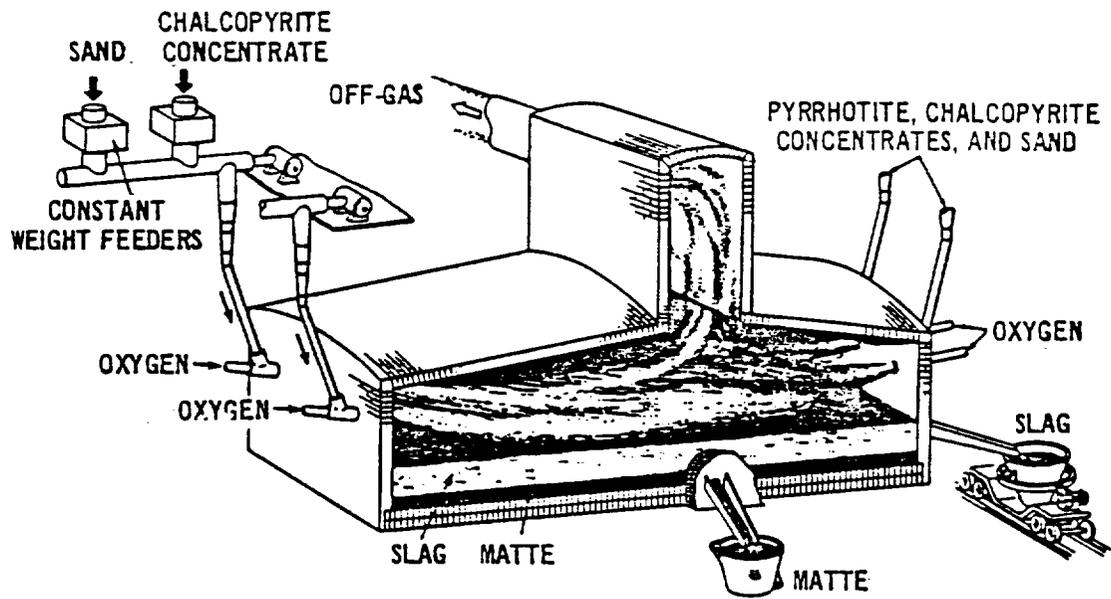


Figure 3-5. Inco flash smelting furnace.

tion, the gases are suitable for the economic production of sulfuric acid or liquid SO_2 . The use of oxygen rather than air has the added advantage of providing a low off-gas volume per unit of charge. The offgas flow rate from Inco's furnace in Sudbury when operating at 1,360 Mg/day (1,500 tons/day) of feed is $130 \text{ Nm}^3/\text{min}$ (4,600 scfm).²⁵ Several benefits accrue from the low offgas volume. The size and cost of downstream gas-cleaning equipment is reduced substantially. Also, because of the relatively low volume and heat content of the gases, Inco maintains that the use of a waste heat recovery system downstream of the furnace is not justified.²⁵ (The heat content of the gases represents about 20 percent of the heat generated in the furnace.) Finally, the low offgas flow rate results in a low gas velocity leaving the furnace. As a result, the dusting rate from the furnace is low, amounting to 2 to 3 percent of the feed rate.²⁵

The grade of matte produced at the Sudbury installation is reported as varying between 40 and 50 percent copper, depending upon the throughput rate and the amount of secondary materials charged to the furnace.²⁵ The feed at this installation is a chalcopyrite concentrate analyzing 30 percent Cu, 30 to 31 percent Fe, and 33 percent S. Inco normally returns about 50 percent of the converter slag to the flash furnace for copper recovery. The remainder is processed in other facilities because converter slag is an important bleed for the impurity nickel, which occurs at fairly high levels in the feed at this installation. The flash furnace slag, which contains about 0.7 percent copper, is discarded without additional treatment.²⁵ This copper concentration is somewhat higher than that typically encountered in slags produced by reverberatory furnaces. Inco flash furnaces appear to be useful for processing all of the converter slag generated. The Inco furnaces to be installed at the ASARCO-Hayden smelter will process all of the converter slag, and the flash furnace slag will be discarded without additional treatment.²⁶

The recycle of converter slag to the furnace requires that some additional heat be provided to maintain the bath temperature. Heat can be provided readily by increasing the oxygen-to-concentrate ratio, which results in the flash combustion of additional sulfur and iron. This scheme also leads to an increase in the matte grade. Tests made by Inco indicated

that the matte grade increased from 40.5 to 45.0 percent copper when 43 percent of the converter slag was reverted to the furnace.²⁵

Inco has reported that the furnace matte grade can be decreased by the addition of coal to the feed. Additions of less than 1 percent coal lead to decreases in matte grade of from 10 to 15 percentage points, depending on the composition of the feed.²⁵

3.2.2.3.2 Outokumpu flash furnaces. The Outokumpu flash furnace, shown in Figure 3-6, consists of three distinct sections: a reaction shaft, a settler, and an uptake shaft. The dried copper concentrates and fluxing materials are injected continuously down the reaction shaft onto the slag surface through concentrate burners located at the top of this shaft. In the burners, the charge is mixed with preheated air (450° to 1,000° C) or oxygen enriched air, preheated or ambient.²⁷ Large furnaces contain up to four burners.

Recent Outokumpu flash furnaces are 20 m (65 ft) long (inside), 7 m (23 ft) wide, and 3 m (10 ft) high (hearth to roof). The firing towers are 6 m (20 ft) diameter and 6 m high (above the roof), while the offtake towers are the width of the furnace (7 m), 3 m long, and 6 m high. This size furnace treats 1,200 Mg (1,320 tons) of dry charge per day.²⁸

The concentration of sulfur dioxide in the offgases from Outokumpu furnaces is high, typically 10-30 percent, allowing the efficient removal of SO₂ as sulfuric acid.²⁹ The SO₂ concentration varies depending upon the copper concentrate analysis, the grade of matte produced, the degree of oxygen enrichment, and the degree of combustion air preheat. The furnace matte grade is typically in the range of 50 to 65 percent.³⁰

The offgas flow rate for the Outokumpu furnace at the Phelps Dodge-Hidalgo smelter has been reported at 2,200 Nm³/min (77,700 scfm) with an SO₂ concentration of 13 percent when operated at a feed rate of 2,440 Mg/day (2,680 tons/day).³¹ This furnace uses preheated combustion air that is not oxygen-enriched.

Unlike the Inco flash furnace, Outokumpu furnaces are not autogenous unless the ingoing air contains 40 percent or more oxygen, and oil burners are placed at the top of the combustion tower and in the hearth (settling zone).²⁸ At the Hidalgo flash furnace, additional heat is provided by

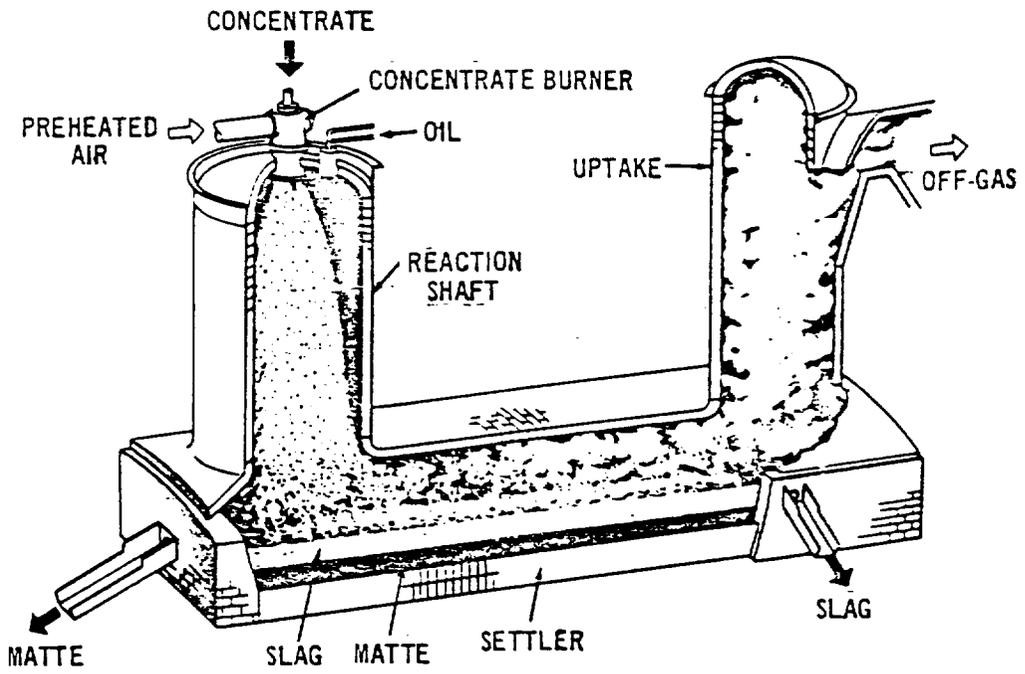


Figure 3-6. Outokumpu flash smelting furnace.

preheating the combustion air, firing oil burners, and by mixing finely ground coal with the feed.

The concentration of copper in slags produced by Outokumpu flash furnaces tends to be fairly high, typically 1 percent.³² As a result, this type furnace cannot be used efficiently to recover copper from converter slags. Also, the slags from the flash furnace must themselves be retreated in a separate process to minimize the loss of copper.

Dust losses in the Outokumpu flash smelting process are also fairly high, up to 10 percent of the feed,³³ which is substantially greater than the dust losses encountered with Inco flash furnaces. High dust losses result because significant quantities of concentrate particles do not settle from the gas/solid suspension during their passage through the furnace.

3.2.2.4 Slag Cleaning Furnaces. (Slag cleaning furnaces are designed to recover a portion of the copper entrained in molten slags from smelting furnaces and converters.) These furnaces are typically used at Outokumpu flash smelting installations because of the relatively high copper content of the slag from this technology.

Slag-cleaning furnaces are typically small electric furnaces. Normal furnace operating temperature has been reported at 1,230° to 1,320° C (2,250° to 2,400° F).³⁴ Slags charged to the furnace are allowed to settle under quiescent and reducing conditions. Reducing conditions are maintained by the addition of coke or iron sulfide to the bath. The addition of iron sulfide serves to recover copper that is in oxide form and return it to the matte phase according to the reaction:



The residence time of slags within the furnace is of the order of 5 hours.³⁵ The slag discharged typically has a copper concentration of 0.4 to 0.5 percent.³⁵

Although smelting is not the primary objective of slag-cleaning furnaces, these furnaces may be used to smelt some revert materials.

It should be noted that an alternative to slag-cleaning furnaces for recovering copper from smelting furnace and converter slags is the froth

flotation process, which yields somewhat better copper recovery but requires that the slags be slow cooled, crushed, and ground before processing.

3.2.3 Converting

(The converting operation is the final major step in the pyrometallurgical extraction of copper from sulfide ore concentrates. The purpose of converting is to eliminate the remaining iron and sulfur present in the matte, leaving molten "blister" copper (98.5 to 99.5 percent Cu).) The blister copper product is subsequently fire refined and electrorefined to produce high purity copper (99.99 + percent Cu).

Upon reaching the converters, all of the rock (gangue) and a portion of the iron and sulfur present in the original ore concentrates have been eliminated. The matte charge consists of a $\text{Cu}_2\text{S}:\text{FeS}$ melt containing small amounts of other elements and precious metals. The batch-converting process serves to eliminate, sequentially, the FeS component and the sulfur present in the remaining Cu_2S component. As mentioned previously, the separation is based on the high affinity of iron sulfide for oxygen, as compared to the oxygen affinity of Cu_2S . The quantity of sulfur eliminated during converting operations generally amounts to 40-70 percent of the sulfur in the original ore concentrates.

The extraction of copper is accomplished by adding siliceous fluxes to the molten matte and then blowing air through the mixture to oxidize the iron sulfides to iron oxides. The iron oxides combine with the silica fluxes to form a slag, which is removed from the converter. The copper sulfide or "white metal" that remains is then oxidized to blister copper through continued blowing. The oxidation reactions occurring during converting are highly exothermic, and the entire operation is autogenous. In fact, the converter gradually heats up during the process. It is common practice to take advantage of the heat liberated to melt significant quantities of revert materials and copper scrap. To some degree, the processing of these "cold dope" materials is necessary to avoid excessive temperatures which lead to high refractory wear.

Aside from their role in the elimination of iron and sulfur, converting operations are also very important in the elimination of a number of other impurity elements. The role of converters in impurity elimination is discussed in Section 3.5.2.3.

Generally within the domestic industry, two or three converters are associated with each smelting furnace.

3.2.3.1 Peirce-Smith Converters. Converting operations in both the domestic and foreign industries are dominated by the Peirce-Smith converter. Domestically, these vessels are used at 14 of the 15 smelters. As shown in Figure 3-7, the side-blown Peirce-Smith unit is a horizontal, refractory-lined steel cylinder with a large opening or "mouth" in the side. Typical (inside) dimensions are 4 m (13 ft) diameter by 9 m (30 ft) long. A vessel of this size normally processes from 350 to 450 Mg/day (380 to 500 tons/day) of matte. Compressed air or oxygen-enriched air is supplied to the converter through a header along the back of the vessel, from which a horizontal row of 40 to 50 tuyeres provide passages through the converter shell into the interior. The vessel can rotate about its major axis, swinging the converter mouth through an arc of about 120° from the vertical. When the converter is in the upright or blowing position, a large retractable hood, referred to as the primary hood, is lowered over the mouth to capture the escaping gases.

Molten matte produced in the smelting furnace is charged to the converter through the mouth by ladles, using overhead cranes, filling the vessel approximately half full. Silica fluxing materials are also charged, either through the mouth or through one end of the converter, as shown in Figure 3-7. During charging the converter is rotated to bring the mouth to an angle of about 45° from the vertical, as shown in Figure 3-8. With the converter mouth in the charging position, the tuyeres are above the level of the matte. Following charging of the matte and fluxing materials, air or oxygen-enriched air is supplied under pressure to the tuyere line, and blowing commences. Blowing rates are generally between 510 and 740 Nm³/min (18,000 to 26,000 scfm). The converter is then rotated, as shown in Figure 3-8, swinging the converter mouth to a vertical position and submerging the tuyeres to a depth of 6 to 24 inches below the surface of the matte.³⁶ The primary hood is then lowered into position over the mouth.

As air blown through the tuyeres enters the molten matte, the matte in the immediate vicinity of the tuyeres is cooled, forming accretions which obstruct the tuyere openings and reduce the blowing air flow rate. To

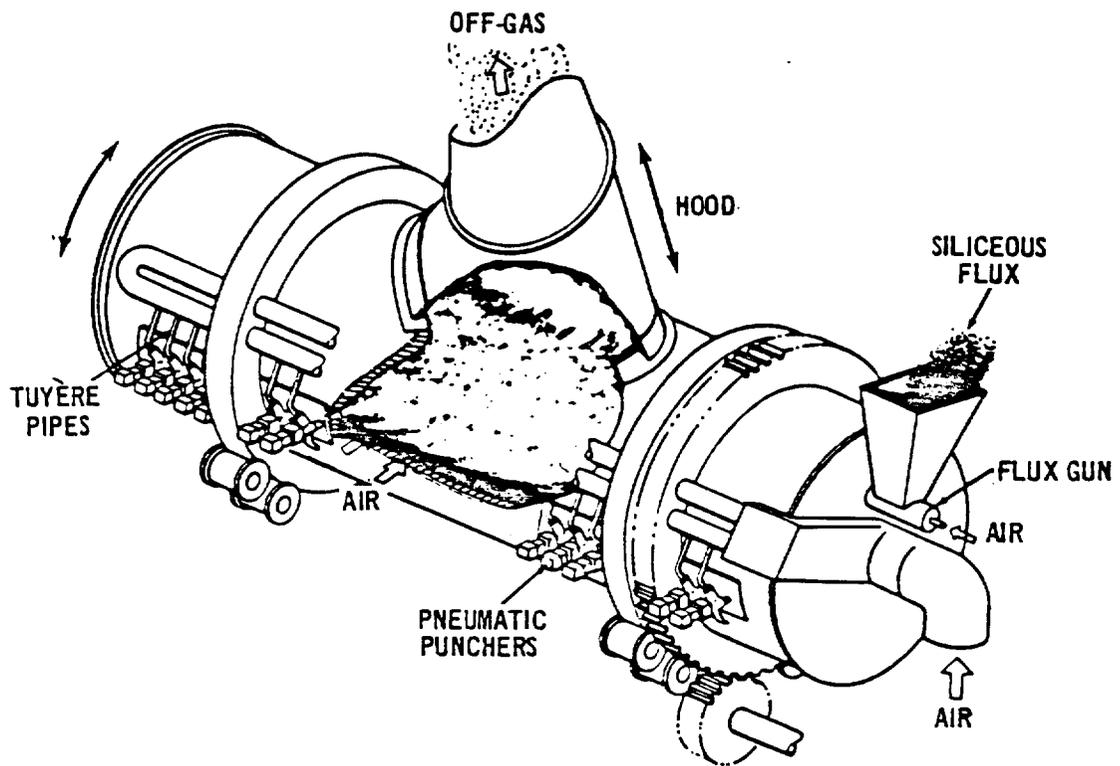


Figure 3-7. Peirce-Smith converter.

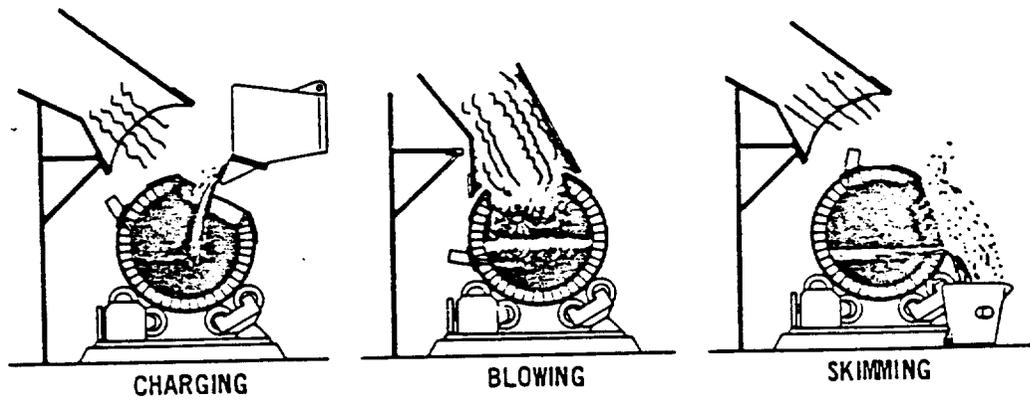
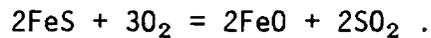


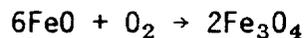
Figure 3-8. Copper converter operation.

prevent complete obstruction of these openings, the tuyeres are mechanically cleaned every several minutes by forcing an iron bar through each tuyere passage.

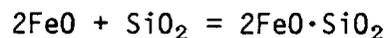
As the tuyere air passes through the molten matte, the iron sulfide is converted to iron oxide and SO_2 with the release of substantial heat according to the reaction:



The sulfur oxides are removed in the converter gases discharged through the converter mouth. The oxidizing conditions also lead to the formation of solid magnetite, according to the empirical relation:



The iron oxide produced combines with the molten silicates to produce an immiscible slag according to the usual slagging reaction:



This stage of the converter cycle operation is termed the slag blow.

Blowing is continued until a substantial layer of slag is formed in the converter. The vessel is then rotated (after raising the primary hood) as shown in Figure 3-8, swinging the converter mouth through an arc of about 120° from the vertical, and raising the tuyere line above the surface of the molten bath. The air supply to the tuyere line is shut off and the blowing discontinued. Slag is skimmed or poured from the converter into a ladle and returned to the smelting furnace or transferred to slag treatment facilities for the recovery of copper contained in the slag. The converter is then rotated to the charging position, and fresh matte, fluxing materials, and cold supplements (such as smelter reverts and copper scrap) are added to bring the converter charge back to the working level. Blowing is resumed and the converter rotated to the working position. The primary hood is lowered into position over the converter mouth.

The process of charging, blowing, and slag skimming is repeated until a charge of copper sulfide is accumulated in the converter, filling it to the working level. The vessel is then rotated to the blowing position, and the copper blow or finish blow begins. During this stage of the converter

cycle, the copper sulfide (white metal) is oxidized, forming sulfur dioxide and copper. Following the copper blow, the converter contains only metallic copper known as blister copper, which is approximately 99 percent pure. The converter is rotated to the pouring or skimming position and the blister copper poured into ladles for transfer to refining facilities. The emptied converter is then charged with fresh matte and fluxing materials, and the converting cycle repeated.

A converter generally makes from one to three cycles in a 24-hour period, with the actual blowing time comprising about 70 to 75 percent of the cycle.³⁷ The remainder of the cycle is spent in charging and skimming operations, and holding (waiting) due to normal process fluctuations within the smelter. The primary determinant of the time required for a complete cycle is the grade of matte charged to the converter, although the blowing rate is also an important factor. Low-grade mattes, which have a larger percentage of FeS, require longer cycle times than do high-grade mattes. At the ASARCO-El Paso smelter, for example, with a matte grade of 40 percent, the duration of the slag blow has been reported at 5.8 hr, while the copper blow required 3.9 h.³⁸ In contrast, at the White Pine smelter with a matte grade of 65 percent, the duration of the slag and copper blows were 0.5 hr and 3.25 h, respectively.³⁹ In addition to having a longer cycle time, low grade mattes also generate more heat during the cycle. Hence, smelters desiring to process large quantities of scrap materials in their converters tend to produce lower-grade mattes.

The offgas flow rates from converters typically range from 850 to 1,270 Nm³/min (30,000 to 45,000 scfm). The average SO₂ concentration in the offgases is normally in the range of 4 to 5 percent during the slag blow, and 7 to 8 percent during the copper blow.⁴⁰ These figures account for infiltration air that is drawn into the offgases around the primary hood during blowing operations. The volume of dilution air typically entering amounts to 100 to 200 percent of the true converter offgas flow.

The primary converter hood is designed to be relatively close-fitting to the converter mouth (or to the converter body, depending upon the design). However, some infiltration air is both inevitable and necessary. A tight seal cannot be maintained between the primary hood and the converter because

of irregularities (buildups) caused by bath splatter and pouring operations. Offgas leaving the converter mouth typically has temperatures of 1,150° to 1,200° C (2,100° to 2,200° F).⁴¹ Even though most primary hoods are water cooled, some cooling of these gases is necessary to prevent damage (i.e., warpage and buckling) to the primary hood, as well as to dampers and flues.

3.2.3.2 Hoboken Converters. An alternative to the traditional Peirce-Smith converter is the newer Hoboken or "siphon" converter, first developed by Metallurgie Hoboken, N. V. in Belgium. The Hoboken-type converter is currently used by one of the domestic smelters.

Although the Hoboken converter is essentially the same as a conventional Peirce-Smith converter, this vessel is fitted with a side flue located at one end of the converter and shaped as an inverted U, as shown in Figure 3-9. The inverted, U-shaped flue, or "siphon," rotates with the converter and is fitted with a cylindrical duct, also rotating with the converter, which leads to a fixed vertical flue. A specially designed seal exists between the rotating duct and the fixed flue. This flue arrangement permits siphoning of the converter gases from the interior of the converter directly to the offgas collection system.

The primary advantage of the Hoboken converter as designed lies in emissions control. By maintaining a slightly negative pressure at the converter mouth, it is possible to minimize or eliminate the escape of SO₂, while maintaining a high SO₂ strength in the offgases. The draft is maintained using variable-speed fans and dampers. With two converters in operation, only one of which is blowing at any time, personnel at Metallurgie Hoboken, N. V. indicate that converter off-gases averaging 8 percent SO₂ can be expected.⁴² An additional advantage is that, since the mouth is freely accessible throughout the operations, it is possible to charge large quantities of liquid or solid materials during blowing.⁴³

Personnel at Inspiration Consolidated Copper Company, which is the only domestic smelter using Hoboken converters, have indicated that their Hoboken converters have given unsatisfactory performance.⁴⁴ Problems result because there is a tendency for molten particles swept from the bath to solidify and accumulate in the siphon area. The result is severe buildups, which plug the gas flow passage and prevent proper draft at the converter

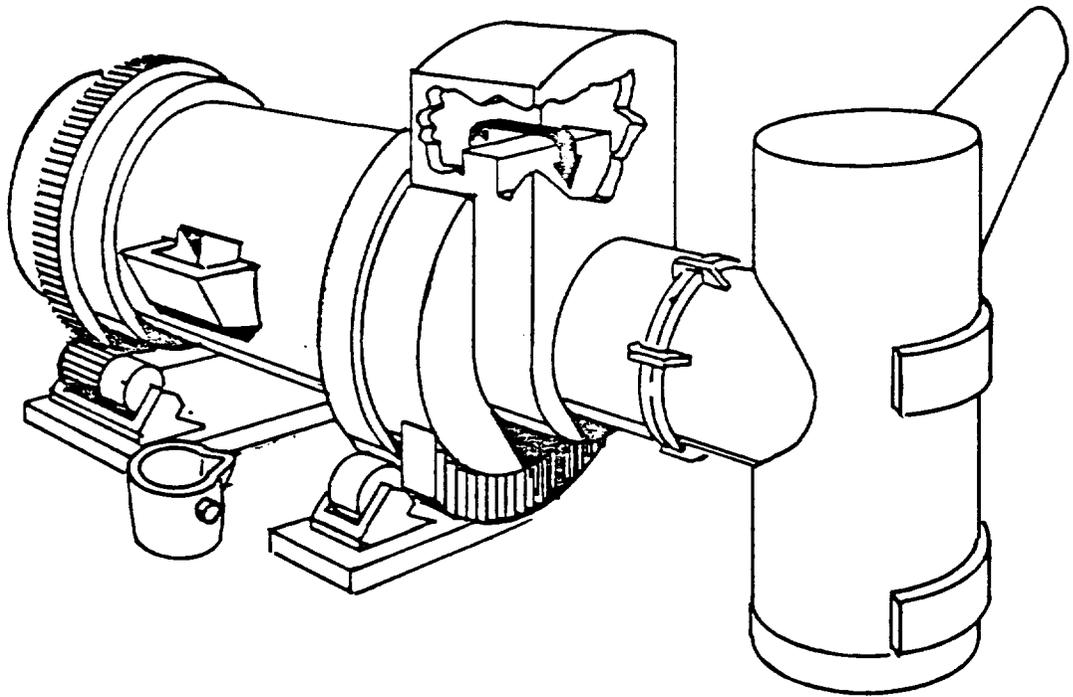


Figure 3-9. Hoboken converter.

mouth.⁴⁴ As the buildups accumulate, the converter gases vent increasingly through the converter mouth and not through the siphon. The buildups are responsible for limiting the campaign life (i.e., period of operation before major maintenance) of each converter to approximately 3 months.⁴⁵ In order to alleviate the problem, Inspiration intends to modify the converters by eliminating the siphon system.

3.2.4 Fire Refining

Fire refining operations serve to eliminate the gross impurities from blister copper. The resulting product, anode copper, is further refined electrolytically to remove remaining impurities and recover gold and silver.

(Although the majority of domestic copper produced by pyrometallurgical means is destined for electrolytic refining, it is not so processed directly because of small quantities of dissolved sulfur and oxygen.) Electrolytic refining operations require strong, thin copper anodes with smooth surfaces. Blister copper is not suitable for the production of anodes because upon cooling, the sulfur and oxygen combine to form SO_2 , which leads to gas bubbles throughout the metal and "blisters" on the surface.⁴⁶

Fire refining is performed in rotary-type refining furnaces resembling Peirce-Smith converters or in small hearth-type furnaces. Among the domestic industry, the rotary-type of furnace predominates. Blister copper is charged to the vessel directly from the converters. Dimensions of the rotary-type refining furnaces vary; however, a 4 m by 9 m (13 ft by 30 ft) furnace may be regarded as typical.⁴⁷ The hearth-type furnaces are used in limited cases where the melting of solid charge is practiced.

Fire-refining operations are accomplished by blowing gases through the molten metal. Gas flow rates are relatively low so as to accurately control the metal composition.⁴⁸ In contrast to converters, very little heat is provided by the refining reactions; hence some combustion of fuel is necessary to maintain the temperature of the furnace. The temperature of operation is about $1,130^\circ$ to $1,150^\circ$ C ($2,065^\circ$ to $2,100^\circ$ F), which provides sufficient superheat for the subsequent casting of anodes.⁴⁹

Blister copper from converting contains about 0.05 percent dissolved sulfur and 0.5 percent dissolved oxygen.⁴⁶ The removal of sulfur and oxygen is accomplished in two stages. During the first or oxidation stage,

air is blown through the blister copper in order to remove the sulfur (as SO_2). The duration of the oxidation cycle is variable, depending upon factors such as the mass and sulfur content of the charge, and the blowing rate. Times have been reported at 0.5 to 1.0 hour,⁵⁰ and at 3 to 4 hours.⁵¹ The oxidation step is completed when the sulfur content drops to a level of 0.001 to 0.003 percent.⁵⁰ This stage may be ended with the skimming of a small amount of slag from the bath surface.

The second or "poling" stage serves to remove oxygen, which has dissolved in the copper both during converting and during the oxidation stage of refining. Oxygen is removed by blowing natural gas, reformed natural gas, or propane through the molten metal. The poling stage is so-called because of the older practice of lowering green wood poles into the molten bath to supply the necessary reductants. The duration of the poling stage is variable, having been reported at 2.5 to 3 hours.⁵¹ Gas addition to the bath is ceased when the oxygen level in the anode copper is 0.05-0.2 percent, which gives a "flat set" to the anodes when they are cast.⁵⁰ At this point, the surface of the batch may be covered with a layer of low sulfur coke to prevent reoxidation of the copper.

The removal of some metallic impurities may also be achieved during fire refining. In general, oxidation and slagging techniques are employed.⁵² The concentration of lead may be reduced by the addition of silica to the bath just before the end of the oxidation stage.⁵¹ Continued blowing of air effects the removal of lead into the slag. The addition of soda ash and lime to the charge at the end of the oxidation stage is used to slag off arsenic and antimony. With successive treatments, almost complete removal of these two elements can be achieved.⁵²

It should be noted that some metallic impurities have a very high affinity for blister copper. For these elements, fire refining is virtually ineffective for reducing their concentration. A notable example is the element bismuth.⁵³ Fortunately, however, substantial elimination of bismuth can be achieved during the slag blow of converting. (Impurity elimination during converting operations is discussed in Section 3.5.2.3.)

3.2.5 Continuous Smelting Systems

In recent years, a number of foreign companies have initiated develop-

ment of continuous smelting systems. In such systems, a steady stream of blister copper is produced on an uninterrupted basis from a steady feed of ore concentrates. Continuous smelting systems are designed to make maximal use of the inherent energy of the sulfide charge, and hence are generally among the most energy-efficient of the major pyrometallurgical processes. The most notable of these smelting technologies are the Noranda process and the Mitsubishi process.

3.2.5.1 Noranda Process

The Noranda process was developed by Noranda Mines, Ltd., of Canada. As originally designed, the process allowed the production of blister copper on a continuous basis in a single vessel, by effectively combining roasting, smelting, and converting into one operation. Metallurgical problems, however, led to the operation of these reactors for the production of copper matte.) Presently, two installations operate Noranda reactors: the Noranda Mines, Ltd., Horne smelter and the Kennecott Garfield smelter in Garfield, Utah. Both of these installations produce a high grade (70 to 75 percent copper) matte,⁵⁴ which is subsequently processed in the converters.

Noranda reactors, as shown in Figure 3-10, are cylindrical, refractory-lined vessels 21 m (70 ft) in length and 5 m (16 ft) in diameter that closely resemble Peirce-Smith converters. Oxygen-enriched air is introduced into the molten bath through a row of tuyeres along one side of the vessel. The vessel may be rotated about its horizontal axis to bring the tuyeres out of the bath for servicing. At the Kennecott Garfield smelter, feed is introduced continuously to the vessel through an opening at one end using a belt-driven slinger. Matte is tapped intermittently through ports located on the cylindrical side of the vessel. Slag is tapped intermittently from the end of the vessel opposite the charging end. Offgases from the process contain 16 to 20 percent SO_2 ⁵⁵ and exit from the mouth in the top. As the mouth is used only for the removal of gas from the reactor (hence not for charging and tapping), it can be closely hooded to prevent the escape of SO_2 to the surroundings and reduce the influx of outside air into the gas stream.

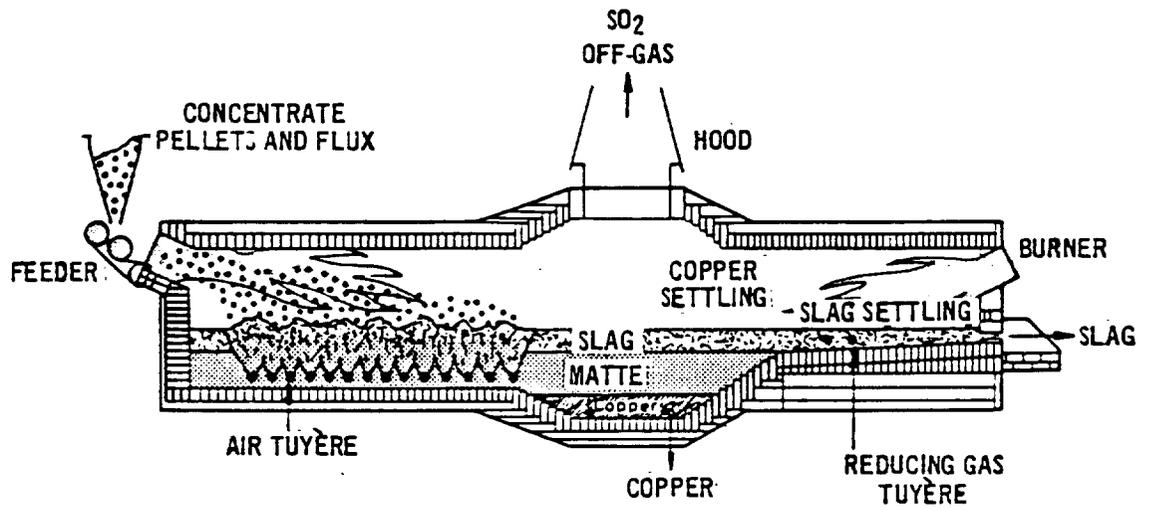


Figure 3-10. Noranda continuous smelting.

(As in flash smelting, (the Noranda process takes advantage of the heat energy available from the charge itself.) Air blown through the tuyeres creates a turbulent, well-mixed zone in which iron sulfide (FeS) is oxidized with the release of heat. (The remaining thermal energy required is supplied by coal, which is mixed with the ore concentrates;) and by two oil burners, one positioned at each end of the vessel.

Due to the turbulence within the bath, slags from the furnace contain high copper concentrations (3 to 8 percent⁵⁵) and must be further processed for copper recovery. Slags are cooled, ground, and processed by froth flotation to produce a slag concentrate, which is charged to the reactors, and a tailings product containing 0.4 percent copper,⁵⁵ which is discarded.

The Noranda process is not used as originally designed to produce blister copper directly because of problems encountered with impurity elimination.^{54 56} Impurity elimination in the Noranda process is discussed in Section 3.5.

3.2.5.2 Mitsubishi Process. The Mitsubishi smelting process was developed by Mitsubishi Metal Corporation of Japan. Early development work was carried out in a pilot plant processing 65 Mg/day (72 tons/day) of charge, which was constructed in 1968. Subsequent tests of the process were made with a prototype scale unit processing 150 Mg/day (165 tons/day) of charge, which was completed in 1971.⁵⁷ Presently, Mitsubishi operates a commercial plant rated at 650 Mg/day (720 tons/day) feed capacity, which went into operation in 1974 at their Naoshima smelter in Japan.⁵⁸ A second full-scale production plant is in operation at the Texasgulf Canada smelter in Timmins, Ontario.⁵⁹

The Mitsubishi process, as shown in Figure 3-11, employs three furnaces interconnected by a continuous flow of matte and slag. The furnaces are connected in cascade fashion so that matte and slag flow by gravity between them. In the first or smelting furnace, dried copper concentrates are smelted and oxidized to form a high grade (60-65 percent Cu) matte. A mixture of slag and matte flows from the smelting furnace to an electric settling furnace, in which the matte and slag are separated. Slag (0.5 percent copper) flows from the electric furnace, and is discarded. Matte from the electric furnace flows into the final or converting furnace,

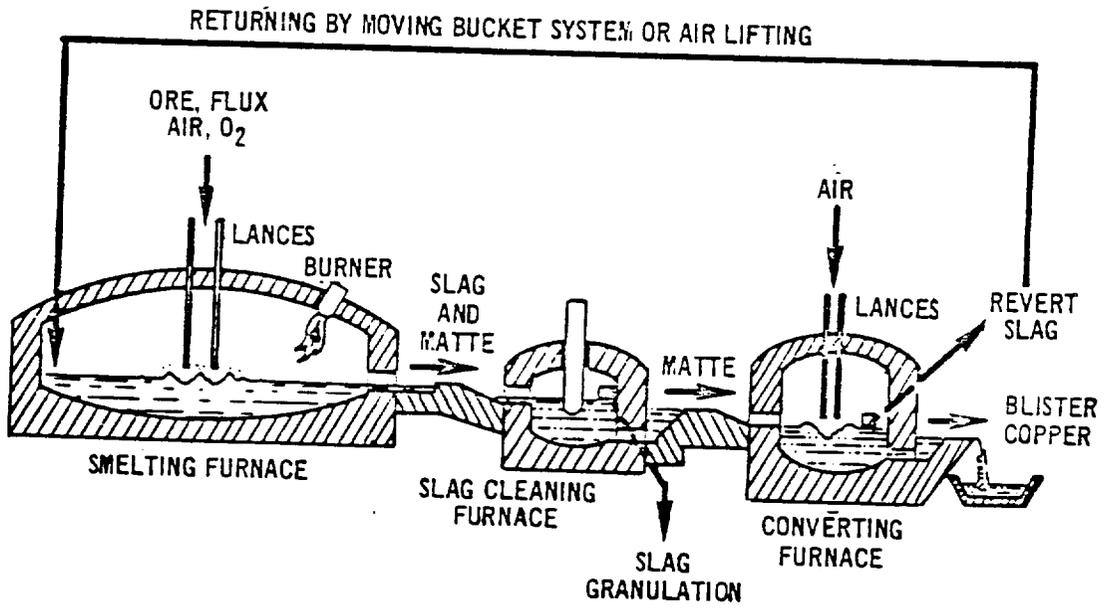


Figure 3-11. Mitsubishi continuous smelting.

where it is continuously oxidized to blister copper. Due to its high copper content (15 percent Cu) the slag from this furnace is solidified and recycled to the smelting furnace for copper recovery.

Oxygen-enriched air is introduced into the smelting and converting furnaces via vertical, stainless steel lances, which are installed in the roof of each furnace.

A major advantage of the Mitsubishi process over other processes is that materials handling operations are greatly reduced, since most matte and slag transfer is by gravity flow. (The water-granulated slag from the converting furnace is recycled to the smelting furnace by means of a bucket conveyor system.) Also, because the process makes use of the inherent energy content of the sulfide charge, its energy requirement is among the lowest of the major pyrometallurgical processes.

A possible disadvantage to this process is that, if the feed contains high levels of certain impurities, adequate impurity elimination may not be achievable. This point is discussed further in Section 3.5.

3.2.6 References

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3.3 EMISSIONS FROM PRIMARY COPPER SMELTERS

3.3.1 General

(SO₂ and particulate emissions from primary copper smelters can be categorized as either process or fugitive emissions.) (Process emissions include primary offgas emissions from roasting, smelting, and converting.) Fugitive emissions include those escaping from material transfer operations, leakage from process vessels, and leakage from primary offgas flues.) Fugitive emissions may be considered low-level emissions because they usually escape at or near ground level. The process emissions are typically discharged through a tall stack.

3.3.2 Process Emissions

If uncontrolled, process sources account for the majority of primary copper smelter emissions. (Uncontrolled emission factors for SO₂ and particulate matter from roasting, smelting, and converting operations are shown in Table 3-3.)

Under the existing NSPS regulation, control equivalent to that attained using double-contact acid plants is required for new roasters, converters, and smelting furnaces processing a charge containing a low level of volatile impurities. At this level of control, SO₂ emissions from these sources are reduced by approximately 98.5 percent, while particulate emissions are reduced by greater than 99 percent. However, reverberatory furnaces processing a charge containing a high level of volatile impurities are not subject to control of SO₂ or particulate matter. As noted in Table 3-3, these furnaces represent a significant fraction of process emissions from copper smelters.

3.3.3 Fugitive Emissions

Potential sources of fugitive emissions of particulate matter and, in most cases, SO₂ are listed in Table 3-4 and shown in Figure 3-12. The actual quantities of emissions from these sources depend to some extent on the type and condition of the equipment and the operating techniques employed by the smelter. Although emissions from many of the sources are released into a building, they are ultimately discharged to the outside. Each of the potential sources is discussed briefly here. It should be noted that a number of judgments are presented,

TABLE 3-3. EMISSION FACTORS FOR UNCONTROLLED MAJOR
PROCESS SOURCES

Operation type	Mass SO ₂ per unit of blister copper ^a		Mass particulate per unit of blister copper ^b	
	kg/Mg	lb/ton	kg/Mg	lb/ton
Roasting	780	1,560	90	180
Smelting (reverberatory furnace)	460	920	40	80
Converting	1,160	2,320	120	240

^aBased on an average of sulfur elimination data for the ASARCo-EL Paso, ASARCo-Hayden, ASARCo-Tacoma, and Phelps Dodge-Douglas smelters.

^bAdapted from Reference 1 and assumes feed contains 25 percent copper.

TABLE 3-4. POTENTIAL SOURCES OF FUGITIVE EMISSIONS

Roaster

Charging
Leakage
Hot calcine discharge and transfer

Smelting furnace

Charging
Leakage
Matte tapping
Slag tapping
Converter slag return

Converters

Charging (matte, reverts, flux, lead smelter by-products, cold dope or other)
Blowing (primary hood leaks)
Skimming
Holding
Pouring of slag and blister
Converter leaks

Anode furnace

Charging
Blowing (oxidation and poling modes)
Holding
Pouring

Miscellaneous

Dust handling and transfer
Ladles
Slag dumping

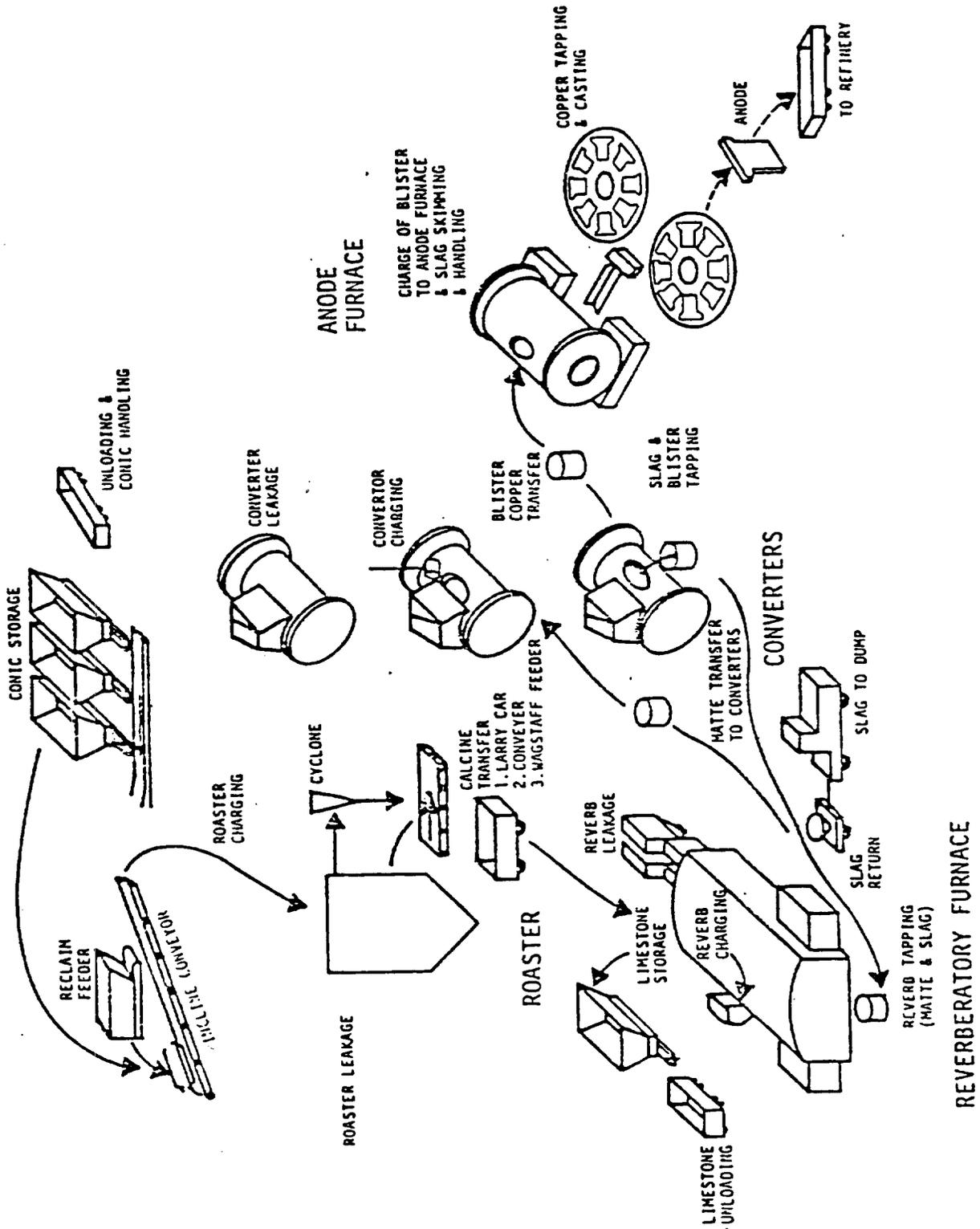


Figure 3-12. Fugitive emission sources for primary copper smelters.

based on EPA inspections and visible observations, where mass emissions data are not available.

3.3.3.1 Roasters.

3.3.3.1.1 Charging. Fugitive emissions from the charging of multihearth roasters are generally minimal. Particulate emissions are slight because of the high moisture content (8 to 10 percent) of the feed. The escape of SO₂-laden gases from the interior of the roaster through the annular charging port is effectively prevented by the flow of material cascading from the uppermost drying hearth to the first roasting hearth and by the operation of the roaster under negative pressure.

As with multihearth roasters, fugitive particulate emissions from the charging of fluid-bed roasters are slight--both because of the suppressive effect of the moisture contained in the feed materials and because charging systems are generally totally enclosed.

3.3.3.1.2. Leakage. Fugitive emissions from multihearth roasters may be emitted from leaks around the doors located at each one of the hearth levels, from holes in the actual shell of the roaster, or from leaks around the central drive shaft. Under normal operation, these emissions are minimized by operating the roasters under a slight negative pressure and by good maintenance practices.

The fluid-bed roaster is essentially a vertical cylinder of steel plate lined with insulation and fire bricks. Because it operates under a positive pressure, the system is designed for containment of the material, and leakage from the vessel proper is usually negligible with proper maintenance. Because of their high SO₂ concentration, gas leaks are readily detected if present.

Calcine is discharged from a fluid-bed roaster primarily by entrainment in the gas exiting the top of the roaster. The material is collected from the gas stream using a series of cyclones. The gas-handling system is an integral part of the roaster. As the entire system is under positive pressure, it should therefore be airtight and free of leaks. However, as hot calcine is both corrosive and abrasive, flue leakage can be a problem, resulting in some fugitive emissions if proper maintenance is not applied.

3.3.3.1.3 Hot calcine discharge and transfer. Fugitive emissions may be generated during the discharge and transfer of hot calcine from the roaster to the smelting furnace. Smelters with multihearth roasters usually use larry cars (small rail cars) to transport calcines to the furnace. When the calcine is dropped from the hopper located beneath the roaster into the larry car through the feed opening, large quantities of dust are generated as a result of material movement and pressure changes within the car.² Fugitive emissions can also occur during the transportation of the roaster calcines to the smelting furnace. In the case of larry cars, the feed opening is usually covered to minimize this effect.²

Calcine collected from the cyclones associated with a fluid-bed roaster is generally fed by a closed system to a calcine storage bin located in close proximity to the smelting furnace. Again, as this system is totally enclosed, fugitive emissions are generally negligible.

3.3.3.2 Smelting Furnaces. As mentioned previously, four basic types of smelting furnaces are used by the industry: reverberatory, electric, flash, and Noranda furnaces. The following is a discussion of the fugitive emission sources associated with these furnaces.

3.3.3.2.1 Charging. Fugitive emissions associated with the charging of smelting furnaces may be substantial, depending upon the type of furnace being used, the nature of feed materials charged, and the charging technique.

When green or calcine charge contacts the molten furnace bath, rapid reactions with the bath lead to gas formation. This in turn can cause positive pressure surges within the furnace, which can result in the release of fugitive emissions through all of the furnace openings. In the case of side-charged furnaces using green feed, there is the added possibility of a portion of the charge bank caving in or sloughing into the molten bath, which results in a similar rapid gas release. In such cases, the pressure surge can be great enough to damage the furnace arch. Generally, however, it is believed that fugitive emissions associated with charging calcine feed are greater than those from charging green feed, because of the comparatively dusty and free-flowing nature of hot calcine.

With reverberatory furnaces, the method of charging can vary depending upon whether green feed or calcine feed is used. Green-feed furnaces are most commonly charged using a drag-chain conveyor/fettling pipe arrangement. Green-feed can also be charged through openings in the furnace sidewalls using charge slingers (high-speed conveyors). With the latter system, it is possible for fugitive emissions to be released as the charge is thrown through the opening.

Reverberatory furnaces processing calcine feed can be charged by (1) fixed or retractable Wagstaff guns, which penetrate the furnace sidewalls; (2) feed pipes penetrating the arch of the furnace near the centerline; and (3) drag-chain conveyors in conjunction with fettling pipes along the sidewalls.

Electric furnaces are usually charged continuously through feed pipes in the roof. The charge usually consists of calcine or dried concentrates, because moisture can cause steam explosions. Pressure surges can occur during charging in electric furnaces as well as in reverberatory furnaces; however, generally fewer openings are present on electric furnaces.

The feed to flash furnaces is usually from a concentrate dryer. Dried concentrates from the dryer are discharged to the feed storage bin by a closed system. The feed is then conveyed to the flash furnace using variable speed drag conveyors or screw conveyors where it is injected with air into the furnace. Because the system is designed to be gas tight, fugitive emissions are not normally emitted.

Noranda reactors are charged through an opening in one end by means of a charge slinger (high speed conveyor). Some fugitive emissions are emitted as the charge is thrown through the opening,³ although the amount is generally small since the charge is moist.

3.3.3.2.2 Leakage. Fugitive emissions, especially SO_2 , can result from leakage points on most types of smelting furnaces when the pressure inside exceeds atmospheric pressure. Leakage points include thermal expansion spaces between bricks and all other furnace openings.

Reverberatory furnaces have perhaps the greatest potential for leakage if adequate draft is not maintained on these furnaces. However,

the draft cannot be excessive because outside air causes the furnace temperature to drop. In addition to thermal expansion spaces and charging ports, openings exist for admitting secondary combustion air to the burners. On those furnaces having a roof constructed of silica brick, ports are present along the furnace length to allow silica slurry to be sprayed onto the arch for maintenance.

Electric furnaces generally do not have as many openings as do reverberatory furnaces. Secondary air openings are not necessary because burners are not required. Also, arch maintenance ports like those used on reverberatory furnaces are not necessary because the roof temperature is usually not a problem. Potential leakage points on electric furnaces are the expansion spaces, spaces around the seals where the electrodes enter the furnace, and charging ports.

Inco flash furnaces are totally encased in a mild steel shell.⁴ Hence, fugitive emissions associated with furnace leakage are unlikely.

Unlike Inco furnaces, Outokumpu flash furnaces are not enclosed in a steel shell. Potential leakage points other than expansion cracks include spaces around the plug in the uptake ceiling and the damper slot between the furnace and the waste heat boiler.

With Noranda reactors, which are encased in a steel shell, leakage can occur only through openings such as the charge port or around the hood over the offtake. However, emissions are slight if adequate draft is maintained on the primary offtake hood.

3.3.3.2.3 Matte tapping. (Matte tapping is a source of fugitive SO₂ and particulate emissions from smelting furnaces) Smelting furnaces typically have from two to six matte-tapping ports with associated launders. The launder directs the flowing matte to a location where it is discharged into a ladle. Normally, only one tap port is used at a time. Typically, a single matte-tapping operation lasts from 5 to 10 minutes. Matte-tapping frequency varies with furnace capacity. Matte is tapped from reverberatory furnaces with a frequency of from five to eight times per 8-hour shift. The Outokumpu flash furnace at the Phelps Dodge-Hidalgo smelter is tapped with a frequency of from 10 to 20 times per 8-hour shift.⁵ During matte tapping, fugitive emissions

are visible at the tap port, along the launder, and at the launder-to-ladle discharge point.

3.3.3.2.4 Slag skimming. (Slag skimming is another source of fugitive emissions from smelting furnaces.) Smelting furnaces typically have from one to three slag-skimming ports. As many as two may be used concurrently. (A single slag-skimming operation usually lasts from 10 to 20 minutes.) (Slag is skimmed with a frequency of from 10 to 25 times per 8-hour shift.) As with matte tapping, emissions are evident at the skimming port, along the launder, and at the launder-to-ladle discharge point.

3.3.3.2.5 Converter slag return. Reverberatory, electric, and Inco flash furnaces generally have a single converter slag return port in the furnace wall. Converter slag is returned to the furnace using a launder or chute leading to the opening. Fugitive emissions result as the slag flows from the ladle to the furnace port. Also, some emissions may escape from within the furnace through the open port. These emissions stem from pressure surges within the furnace, which are caused by chemical reactions between the converter slag and the bath. The number of times converter slag is returned to the furnace depends upon the number of converters and the operating level of the smelter.

In Outokumpu flash and Noranda furnaces, converter slag is usually processed separately in slag cleaning furnaces or flotation plants.

3.3.3.3 Slag-Cleaning Furnaces.

Slag-cleaning furnaces are frequently used in conjunction with flash furnaces for recovering matte entrained in the smelting furnace and converter slags. Slag-cleaning furnaces are most commonly small electric furnaces. Potential fugitive emission points on these furnaces are the same as those on smelting furnaces.

The charging of molten slag to the slag-cleaning furnace from the smelting furnace is performed with the same frequency as this slag is skimmed from the smelting furnace. At the Phelps Dodge-Hidalgo smelter, slag from the flash furnace is transferred directly into the slag-cleaning furnace via a launder leading to an open port in the wall of

the slag-cleaning furnace. Fugitive emissions can be observed during the entire operation.

Fugitive emissions from furnace leakage can occur whenever insufficient draft is maintained. Leakage occurs primarily through the furnace roof, because of the presence of expansion cracks and spaces around the electrodes.

Matte is tapped from slag-cleaning furnaces in the same fashion as from smelting furnaces. However, the frequency of tapping, at about three times per 8-hour shift⁵, is lower because only a small fraction of the matte produced in the smelter is entrained in slag. The grade of matte from a slag-cleaning furnace is slightly higher than that produced in the smelting furnace, because some additional sulfur is removed in the slag-cleaning furnace. Hence, fugitive emissions per unit of matte tapped from slag-cleaning furnaces would be expected to be slightly less than those liberated (per unit of matte) from matte produced in a smelting furnace.

Slag skimming, like matte tapping, is also performed in much the same fashion on slag-cleaning furnaces as on smelting furnaces. Hence, fugitive emissions are evident at the skimming port, along the launder, and at the launder-to-ladle discharge point. The frequency of slag skimming on slag-cleaning furnaces is approximately the same as that on smelting furnaces, because only a comparatively small amount of matte settles from the slag charged.

Converter slag is returned to slag-cleaning furnaces in the same manner as it is returned to smelting furnaces. Fugitive emissions result as the slag flows down the chute and into the furnace. The frequency of this operation on slag-cleaning furnaces would be somewhat lower, as compared its frequency on reverberatory furnaces, however. This decrease results from the higher matte grade (and consequent decrease in converter slag production) in most smelters employing slag-cleaning furnaces.

3.3.3.4 Converters.

The various stages of converter operation are charging, blowing, slag skimming, and blister pouring. Each of these operations is a potential source of fugitive emissions.

3.3.3.4.1 Charging. During charging, the converter is rotated until its mouth is approximately 45 degrees from the vertical, and the primary hood is raised to its highest position. Emissions result for an instant as the converter is rotated because of the need to maintain blowing air through the tuyere lines until the tuyeres are above the level of the bath to prevent plugging. An overhead crane lifts the ladle above the mouth of the converter and pours the charge (matte or revert materials) into the converter by tilting the ladle. During the pour, visible emissions are heavy but of relatively short duration (15 to 20 seconds). When charging is completed, blowing air through the tuyeres is resumed, which results in a slight burst of emissions while the vessel is rotated to a vertical position. Once in place, the primary hood is then lowered into position.

3.3.3.4.2 Blowing. Most domestic smelters have attempted to provide relatively close-fitting primary hoods over the converter mouth to contain and capture the offgases generated during blowing operations. However, these hoods do not completely seal the opening because of irregularities around the mouth. The irregularities are caused by accretions formed by pouring operations and by bath splatter during blowing. Fugitive emissions escape from these openings. Generally, the emissions are proportional to the blowing rate and the condition of the primary hood.

3.3.3.4.3 Skimming. During skimming operations, the mouth of the converter is rotated to a position between 65 and 85 degrees from the vertical, depending upon the bath level. Some emissions occur during the brief roll-out period because the blowing air to the tuyeres is maintained until they are above the bath level. Slag is skimmed from the converter mouth into a slag ladle. Fugitive emissions are visible during the entire skimming operation, which typically lasts from 2 to 3 minutes. Although the primary hood is not necessarily retracted during this operation, it is usually isolated by dampers from the main duct system to prevent dilution air from mixing with the SO₂ gases being collected from other blowing converters. At the completion of the skim, blowing is resumed, and the converter is

rotated back to the upright position. Once in place, the primary hood is lowered.

3.3.3.4.4 Pouring. During blister copper pouring operations, the converter is rotated downward until the mouth reaches a position approximately 90 to 125 degrees from the vertical, depending upon the volume of blister copper within the converter. Again, emissions are discharged briefly during the roll-out, because blowing air is maintained until the tuyeres are above the liquid level. Steady fugitive emissions are observed as the copper is poured into the ladle. After its contents are emptied, the converter is rotated upward until the mouth reaches a position approximately 45 degrees from the vertical to await a new matte charge and the start of a new cycle.

3.3.3.4.5 Holding. (At times during normal smelting operations, slag or blister copper cannot be transferred immediately to the ladles. This condition may occur for several reasons, including insufficient matte in the smelting furnace, the unavailability of a crane, and others. Under these conditions the converter is rolled out (rotated) about 30 to 45 degrees to raise the tuyeres above the bath. An auxiliary burner may be fired through the mouth to keep the bath hot. While in the holding mode, fugitive emissions from the molten bath escape from the mouth into the converter building.)

3.3.3.4.6 Converter leaks. Since the ends of most Peirce-Smith converters are joined by bolts and springs, they occasionally leak at the end joint. When this leakage is below the molten material surface, it is usually repaired rapidly to prevent major erosion. However, in cases where it occurs above the bath surface, it may not be repaired in a timely fashion. Thus, fugitive emissions may occur at this point.

3.3.3.5 Anode Furnaces. Refining of blister copper to anode copper is performed in either rotary or hearth-type furnaces. Emissions from these furnaces occur during all phases of operation: charging, oxidizing, poling, skimming, holding, and pouring. In the hearth-type furnaces, which are used at the ASARCO-Tacoma and Kennecott-Hurley smelters, the primary offgases generated during the actual refining

operation (oxidation and reduction blows) are siphoned through a furnace offtake and vented through a stack. In the case of the more conventional rotary-type refining furnaces, which are similar to Peirce-Smith converters, emissions during blowing operations vent through the open mouth of the vessel.

3.3.3.6 Miscellaneous Sources.

3.3.3.6.1 Dust handling and transfer.⁶ Dust-handling and transfer operations can generate fugitive emissions if carelessly performed. However, most smelters take precautions to minimize fugitive emissions from dust handling and transfer. Dust transfer from control devices to storage facilities is usually performed by covered conveyors. Dust transfer from storage bins is usually made through dust-tight connections to surface transportation units such as tank trucks and dumpsters. Cleaning and unloading of dust from flues and settling chambers is performed by enclosed conveyors that feed into hoppers provided at spaced intervals underneath the flues and settling chambers. Both screw and drag-type conveyors are used. These flue dusts are usually treated in a pugmill or pelletizing disc where moisture is added. The wet dust is then transferred to a bedding area, blended with other feed constituents, and recycled. Dust from waste heat boilers and crossover flues is usually removed by manual methods, which, if properly implemented, result in minimal emissions.

3.3.3.6.2 Ladles. Visible emissions can be observed from ladles containing molten materials (matte, slag, or blister copper) as they are transported between process stages within the smelter. Emissions from a particular ladle are generally of short duration because the time required for material transport is usually short. Normal process fluctuations may require that ladles containing matte, slag, or blister copper be temporarily set aside until needed. The emissions from fuming are still short-lived, however, since the exposed surface of the material cools rapidly, forming a solidified layer or "skull" that greatly limits fugitive emissions.

3.3.3.6.3 Slag dumping.⁷ Smelting furnace slag is disposed of by water granulation or by transport in the molten state for dumping a

short distance from the smelter. Slag dumping is the more widely used method. The slag is transported to the dump site by train or slag hauler. The slag train is usually comprised of a number of slag pots or ladles on flat cars. Solidification at the surface of the slag in the pots is fairly rapid. Fugitive emissions during transportation to the dumping site are therefore limited. However, during dumping of slag at the dumping site, substantial fugitive emissions, although short in duration (less than 1 minute), can be observed.

3.3.4 Summary of Fugitive Emissions Data

Emission factors for fugitive SO₂ and particulate matter have been developed⁸ for most of the major fugitive emissions sources at primary copper smelters: roaster calcine discharge, matte tapping, slag skimming, converter slag return, converter operations and anode furnaces. Summaries of these emission factors are presented in Tables 3-5 and 3-6. There are no known emissions data for sources not included in Tables 3-5 and 3-6.

The emission factors developed for each source are based primarily on emission tests conducted by EPA at several domestic primary copper smelters. These tests were conducted in flues associated with the local ventilation systems used to capture fugitive emissions from the various sources investigated.

Using the emission test data obtained and pertinent process information, emission factors were first computed in terms of mass emissions per unit of material processed by the source.⁸ In the case of sources for which more than one data point was available, an arithmetic average was used to compute the emission factor. Because the capture systems tested were less than 100 percent effective, the emission factors were adjusted upward based on a subjective estimate of the capture effectiveness of each capture system tested to account for emissions escaping capture. The resultant uncontrolled fugitive emission factors, expressed in terms of mass emissions per unit of material processed, were then normalized to mass emissions per unit of end product (blister copper) by using representative plant material balances.⁸ On this basis, the various fugitive emission sources are readily comparable as to relative significance.

TABLE 3-5. SUMMARY OF FUGITIVE SO₂ EMISSION FACTORS FOR PRIMARY COPPER SMELTING OPERATIONS⁹

Source	Mass per unit of material processed ^a	SO ₂ emission factors		
		Mass per unit of blister copper kg/Mg (lb/ton)		
		Conventional smelters ^b	New smelters ^c	
Calcine discharge	0.5 kg/Mg of calcine (1.0 lb/ton of calcine)	2.2 (4.4)		
Matte tapping	2.6 kg/Mg of matte (5.2 lb/ton of matte)	7.0 (14.0)	4.0 (8.0)	
Slag skimming	0.24 kg/Mg of slag (0.48 lb/ton of slag)	0.6 (1.2)	0.8 (1.6)	
Converters Blowing segment only	2,198 kg/blowing hour (4,845 lb/blowing hour)	241 (482)	130 (260)	
Total converter cycle	2,060 kg/h (4,538 lb/h)	320 (640)	190 (380)	
Converter slag return	0.14 kg/Mg of slag return (0.28 lb/ton of slag return)	0.2 (0.4)		
Anode furnace		0.15 (0.30)	0.15 (0.30)	

^aExcept for converters where mass emissions per hour are given.

^bCalcine or "green" feed reverberatory smelters.

^cFlash furnace or Noranda reactor smelters.

TABLE 3-6. SUMMARY OF FUGITIVE PARTICULATE EMISSION FACTORS FOR PRIMARY COPPER SMELTING OPERATIONS¹⁰

Source	Particulate emission factors		
	Mass per unit of material processed ^a	Mass per unit of blister copper kg/Mg (lb/ton)	
		Conventional smelters ^b	New smelters ^c
Calcine discharge	1.2 kg/Mg of calcine (2.4 lb/ton of calcine)	5.2 (10.4)	
Matte tapping	0.13 kg/Mg of matte (0.26 lb/ton of matte)	0.34 (0.68)	0.2 (0.4)
Slag skimming	0.13 kg/Mg of slag (0.20 lb/ton of slag)	0.31 (0.62)	0.4 (0.8)
Converters Blowing segment only	61 kg/blowing hour (134 lb/blowing hour)	6.6 (13.2)	4.0 (8.0)
Total converter cycle	69 kg/h (153 lb/h)	10 (20)	7.3 (14.6)
Converter slag return	N/A	N/A	N/A
Anode furnace		0.95 (1.95)	0.95 (1.95)

^aExcept for converters where mass emissions per hour are given.

^bCalcine or "green" feed reverberatory smelters.

^cFlash furnace or Noranda reactor smelters.

The normalized emission factors (mass emissions per unit of blister copper) are distinguished in Tables 3-5 and 3-6 according to smelter type--"conventional" smelters, representing green- and calcine-charged reverberatory furnace operations, and "new" smelters, representing flash furnace and Noranda reactor installations.

Based on the normalized SO₂ emission factors for conventional smelters presented in Table 3-5, converters are by far the greatest source of fugitive SO₂ emissions at copper smelters. Fugitive emissions associated with the entire converter cycle are more than 45 times greater than those associated with the other fugitive sources. Converter blowing accounts for the majority of the emissions during the converter cycle. Second to converter emissions in relative significance are fugitive emissions from matte tapping, followed by calcine discharge and slag skimming. Fugitive SO₂ sources having the lowest relative significance among those for which data are available are converter slag return and anode furnaces.

With regard to new smelters, the distribution of fugitive SO₂ emissions among the various sources is similar to that noted for conventional smelters. Fugitive SO₂ emissions from converters are, again, more than 45 times greater than those from the other sources. It is noted that fugitive emissions of SO₂ from most sources at new smelters are lower in magnitude, however, than those from the same sources at conventional smelters. This decrease is due to the higher matte grade produced in Noranda reactors and flash furnaces, which corresponds to increased sulfur elimination in the process offgas stream from these furnaces, and hence a lower availability of sulfur for fugitive emissions.

Based on the normalized particulate matter emission factors for conventional smelters shown in Table 3-6, converters are the greatest source of fugitive particulates at copper smelters. The blowing phase of the converter cycle contributes the majority of the particulate emissions. Calcine discharge represents another major source of particulates, being approximately half as significant as converters. The other sources--matte tapping, slag skimming, and anode furnaces--

are relatively minor by comparison. For the "new" smelters (which do not normally employ roasters), converters are the major source of fugitive particulate matter.

Data are not available to characterize fugitive* emissions during matte tapping, slag skimming, and converter slag return operations on slag-cleaning furnaces. However, fugitive SO₂ and particulate emissions per unit of blister copper can be estimated based on the frequency at which these operations are performed on slag-cleaning and smelting furnaces. Based on previous discussions of relative frequencies, fugitive SO₂ and particulate emissions from matte tapping on slag-cleaning furnaces would be expected to be no more than about one-third the magnitude of matte-tapping emissions from flash furnaces, while fugitive SO₂ and particulate emissions from slag skimming are expected to be approximately equal to those from the same operation on flash furnaces. Fugitive SO₂ and particulate emissions per unit of blister copper from converter slag return operations on slag-cleaning furnaces are expected to be somewhat less than those from the same operation at reverberatory furnaces.

*With regard to process offgas emissions from slag cleaning furnaces, emissions data supplied by Phelps Dodge Corporation¹¹ indicate that SO₂ emissions are approximately 3 Kg/Mg blister copper (6 lb/ton blister copper), while particulate emissions are between 9.4 and 22.6 Kg/Mg blister copper (18.7 to 45.3 lb/ton blister copper).

3.3.5 References

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10. Reference 8, p. 3.
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3.4 EXPANSION OPTIONS FOR EXISTING FACILITIES

Most primary copper smelters have at least one rate-limiting operation or "bottleneck." In most smelters, the bottleneck is the capacity of the smelting furnace(s). If additional throughput is needed from the smelter, additional capacity can be added either through the installation of new process units, (i.e., new roasters, smelting furnaces, and converters), or the expansion of the existing rate-limiting equipment.

In lieu of installing new process technology when additional capacity is needed, the smelting industry, both worldwide and domestic, has traditionally chosen to add capacity by expanding existing equipment. It should be noted that the elimination of a particular bottleneck often creates another bottleneck, which must also be eliminated. For example, if the rate-limiting operation is smelting furnace capacity and the furnace is expanded, additional converters may be required, depending upon the magnitude of the increase in furnace capacity.

Various expansion options available for roasters, smelting furnaces, and converters are discussed below. In general, SO₂ and particulate emissions on an uncontrolled basis increase proportionately to increases in capacity.

3.4.1 Multihearth Roasters

Increasing the capacity of multihearth roasters by increasing their shaft rotation speed has been achieved at the Noranda Smelter in Quebec, Canada.¹ These roasters are not substantially different from those used at domestic smelters. The Wedge roasters utilized are 7.60 m (25 ft) in diameter, with an external feed or drying hearth and seven internal hearths. Two air-cooled arms are positioned directly above each hearth, one arm carrying 10 and the other 11 rabble blades. Each roaster is driven by a 15-hp motor, belt-connected to a speed reducer. The drive is provided with a shear-pin arrangement to prevent breaking of the arms in case of overload or jamming in the roaster.

Rated at 136 Mg/day (150 tons/day) of concentrate, each roaster is operated with a shaft rotation speed of 0.75 rpm. Roaster throughput was increased to about 295 Mg/day (325 tons/day) after experimental work was done to determine the maximum tonnage of feed that could be

accommodated with satisfactory sulfur elimination. At this capacity, the roaster shaft speed was 1.09 rpm.

Increasing the throughput was found to raise the temperatures throughout the roaster, with a maximum of 760° to 820° C (1,400° to 1,500° F) being achieved on the third and fourth hearths. The increased temperatures combined with an increase in gas volume resulted in an accumulation of primarily oxidized pyrite fines on the underside of the second and fourth hearths. This problem was rectified by attaching a plow to the top of the rabble arm on the next lower hearths, which mechanically eliminated any buildup.

The experience at Noranda Mines illustrates that increasing the rotation speed of the shaft can result in a significant increase in roaster capacity. Increasing the shaft rotation speed will also decrease the residence time and increase the roaster temperature. Both of these parameters are critical, as they influence the volatilization of impurities and the degree of sulfur elimination achieved. Most domestic smelters use the roaster speed as a means of obtaining a desired degree of sulfur elimination. Hence, it is concluded that changing the shaft rotation speed to increase multihearth roaster capacity would not be a viable expansion option at most domestic smelters.

Physical expansion of multihearth roasters is not considered feasible because of the geometry of these units. It is concluded that no viable expansion options are available for multihearth roasters.

3.4.2 Fluid-Bed Roasters

Major components of fluid-bed roasters include the blower, the roasting vessel, and the calcine recovery system (which may use up to 16 cyclones). The entire system is sized very closely to the rated throughput.² It is conceivable to attempt to increase roaster capacity by increasing the capacity of the blower. However, increased throughput might be precluded by (1) excessive wear in the cyclones due to abrasion and (2) the capacity of the calcine recovery system.² The potential for these problems indicates that this scheme would have to be evaluated on a case-by-case basis at domestic smelters. Such an evaluation is considered beyond the scope of this analysis.

Oxygen enrichment of the fluidizing air has been used as a means of increasing the capacity of sulfating fluid-bed roasters operated at copper smelters in Australia and Zambia.² Such roasters operate under the conditions necessary to produce copper sulfate from the sulfide charge. Based on this experience, oxygen enrichment could potentially be used to increase throughput at domestic units by 20 to 25 percent.² However, oxygen enrichment could lead to localized overheating within the bed which causes incipient melting of the feed in some cases.² Such melting can lead to bed defluidization and plugged cyclones. Also, it should be noted that this expansion option has not been demonstrated on fluid-bed roasters like those operated by the domestic primary copper industry.² For these reasons, it is concluded that oxygen enrichment is not a viable expansion option for fluid-bed roasters in general. Rather, the potential usefulness of this option would have to be determined on a case-by-case basis.

In conclusion, it appears that no viable options are available for increasing the capacity of existing fluid-bed roasters.

3.4.3 Reverberatory Furnaces

A number of options have been used in the past to increase reverberatory furnace capacity, including the conversion from green to calcine charging, physical expansion of the furnace, the elimination of converter slag return to the furnace, and the use of various oxygen-enrichment techniques. Each of these options is discussed here.

3.4.3.1 Conversion from Green to Calcine Charging. Reverberatory furnaces operating on green (unroasted) charge may increase throughput by converting to calcine-charged operation through the addition of roaster capacity. Throughput is increased because less time is required to smelt hot calcines than cold, moist concentrates. Considerable savings in energy, as well as enhanced sulfur recovery, are also afforded.

In 1969, the Kennecott Corporation modified its smelter at Hayden, Arizona, by adding a Dorr-Oliver fluid-bed roaster.³ Use of the roaster resulted in a 50-percent increase in reverberatory furnace capacity over that achieved with green-charged operation. The roaster

is fed with a mixture of copper concentrates, copper precipitates, and silica flux. The bulk of the roasted calcines are collected from the exhaust gases using eight primary cyclones and eight secondary cyclones. The collected calcine reports to calcine bins on each side of the reverberatory furnace and is fed to the furnace by Wagstaff feeders. During the conversion to calcine-charged operation, the reverberatory furnace was altered by installing water jackets (water-cooled panels) around the furnace perimeter at the slag line. These panels were needed to protect the sidewall refractory from excessive temperatures resulting from the close proximity of the burners. Before the conversion, charge banks of green feed along the sidewalls provided the necessary protection.

A similar conversion to calcine-charged operation performed at the Cities Service Company smelter in Copperhill, Tennessee, in 1961 increased the capacity of a reverberatory furnace by 40 percent.⁴ In addition, the conversion enabled the overall smelter sulfur recovery to be increased from 63 to 85 percent, because the roaster gases could be processed in a sulfuric acid plant.

The Copperhill fluid-bed roaster, designed by Dorr-Oliver, operates with slurry feed. By changing the percentage of water in the slurry, sulfur elimination in the roaster can be controlled so that the matte grade from the smelting furnace can be readily varied from 30 to over 50 percent. Calcine is removed from the roaster offgas stream using two primary cyclones and two secondary cyclones and is transferred to a bin. From the roaster discharge bin, calcine is fed intermittently to the reverberatory furnace using a single Wagstaff gun inserted through a sliding door in the side of the furnace.

In this analysis, an increase in throughput of 40 percent is assumed achievable when converting from green- to calcine-charged operation. Based on the practice of Kennecott-Hayden and Cities Service-Copperhill, it is assumed that Wagstaff gun feeders would be used for charging calcine to the furnace in lieu of side-charging of calcines. It is further assumed that smelters making the conversion would install water-cooled panels around the furnace perimeter at the slag line to protect the sidewall refractory from excessive wear.^{3 5}

3.4.3.2 Physical Expansion. Physically expanding a reverberatory furnace is considered to be a technically feasible option for increasing capacity. In the early 1970's, ASARCO increased the capacity of a furnace at its Tacoma smelter by 20 percent by increasing the furnace width.⁶ It should be noted, however, that the physical expansion of a reverberatory furnace requires an extended furnace shutdown, with possible adverse effects on smelter throughput. Also, this option may not be useful at some smelters because of physical space limitations. For these reasons, and because many industry representatives consider this scheme to be impractical, physical expansion is not considered to be a viable expansion option in this analysis.

3.4.3.3 Elimination of Converter Slag Return. Converter slag is typically returned to the reverberatory furnace in order to recover, through chemical reactions and settling, copper values that are entrained therein. Processing the slag in separate facilities such as slag cleaning furnaces or flotation plants can make more furnace capacity available for smelting concentrates or calcine.

Itakura et al.⁷ have reported increasing the capacity of a calcine-charged reverberatory furnace at the Naoshima smelter in Japan by 25 percent through the elimination of converter slag return. After cooling, crushing, and grinding, the slag was processed in a froth flotation plant. The recovered copper-rich concentrate, which was comparatively small in volume compared to the converter slag, was recycled to the reverberatory furnace. Aside from the increase in capacity, other benefits resulting included (1) decreased overall copper losses, (2) decreased magnetite buildup in the furnace, and (3) decreased flux costs.

Based on the experience at Naoshima, a 25 percent increase in furnace capacity is considered achievable when converter slag is processed in other facilities rather than returned to the reverberatory furnace.

3.4.3.4 Oxygen-Enrichment Techniques. Extensive operating experience has been accumulated using industrial oxygen as a means of increasing production capacity in reverberatory furnaces. Production increases of up to 122 percent have been reported.⁸

3.4.3.4.1 Theory of increasing production using commercial oxygen.

Adding additional oxygen to the combustion environment has the primary effect of decreasing the flow of nitrogen through the furnace per unit of combusted fuel. The displacement of nitrogen has four major effects on furnace operation:

1. The flame temperature increases, which results in an increased rate of heat transfer to the charge.
2. The residence time of the combustion gases in the furnace increases (due to their lower volume per unit of fuel), which also leads to increased heat transfer to the charge.
3. The quantity of sensible heat carried out of the furnace in the combustion gases is decreased.
4. The concentration of SO_2 in the furnace offgases is increased. This particular benefit is discussed further in Section 4.5.

The net result of these effects is an increase in furnace efficiency, manifested primarily in an increase in the production rate. Other benefits that can result with increased oxygen usage include a decrease in the fuel requirements per unit of charge and a decrease in copper losses in the slag. The latter benefit results from a decrease in slag viscosity, which comes about through the increased slag temperature.

3.4.3.4.2 Methods of oxygen introduction. Various methods of oxygen introduction into reverberatory furnaces have been used to date. These may be categorized as follows:

1. Enriching the primary combustion air with oxygen.
2. Undershooting the flame with oxygen or oxygen-enriched air.
3. Oxygen lancing through the roof.
4. Introducing oxygen directly with fuel in roof-mounted oxy-fuel burners.
5. Introducing oxygen directly with dried feed in roof-mounted oxy-sprinkle burners.

These schemes are illustrated in Figure 3-13.

The first scheme, oxygen enrichment of the primary combustion air, refers to the addition of oxygen to the air supply of the existing

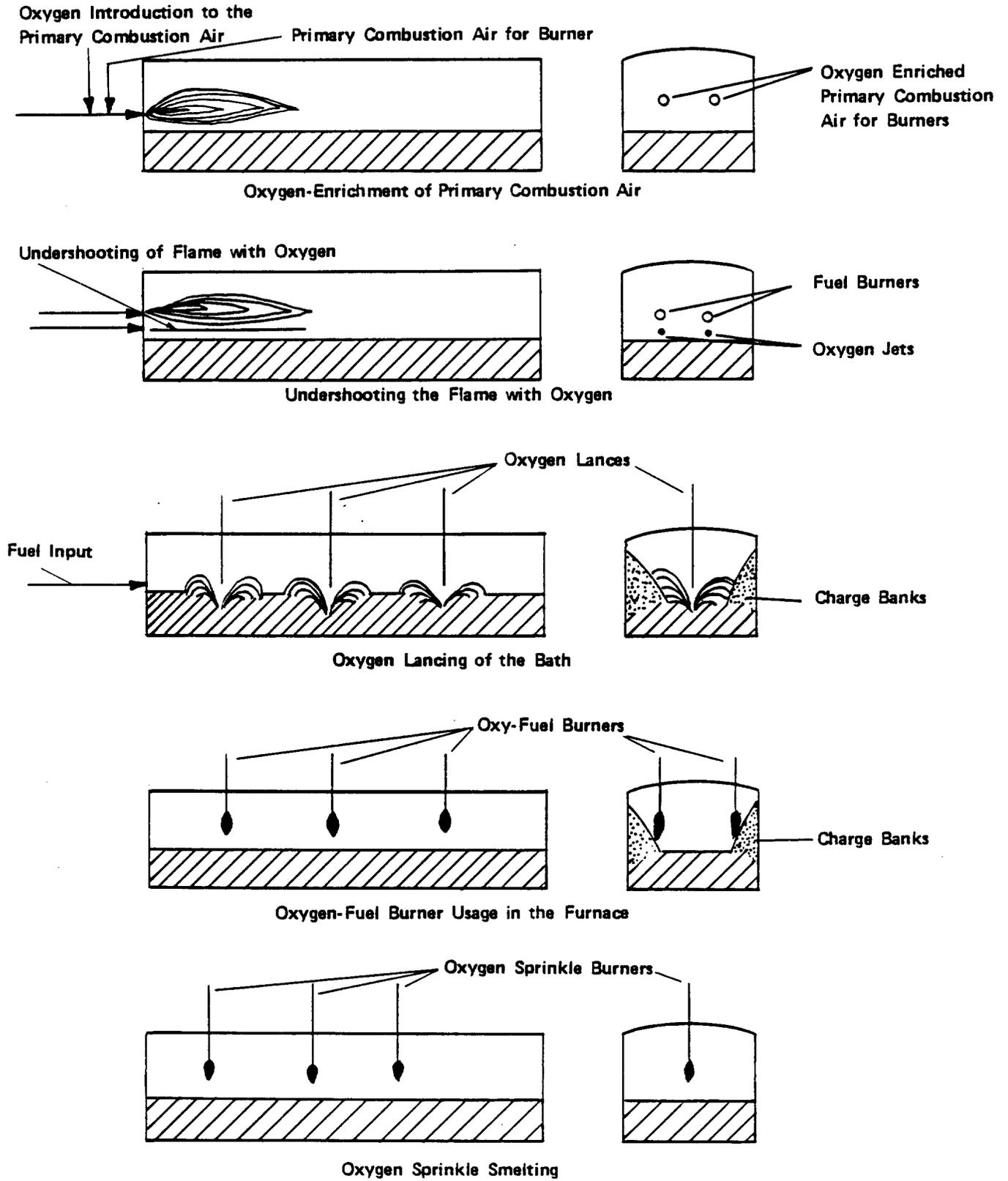


Figure 3-13. Methods of oxygen addition.

end-type burners. This method, because of its simplicity, requires very little change to the furnace proper.

With the second scheme, undershooting the flame with oxygen or oxygen-enriched air, oxygen lances (typically water-cooled) are retrofitted into the end of the furnace. These lances are typically positioned just below the existing burners.

Oxygen lancing through the roof refers to the installation of oxygen lances in vertical position on the roof of the furnace. This scheme may use up to three rows of lances, which are spaced regularly down the furnace length. The existing end-burners are used to introduce a fuel-air mixture containing insufficient oxygen for complete fuel combustion.

With the oxy-fuel scheme, fuel is mixed directly with commercial oxygen in burners that are retrofitted onto the furnace roof. These burners are positioned vertically, or nearly so, and are generally spaced regularly down the length of the furnace in two rows. If a sufficient number of oxy-fuel burners are used, the existing end-type burners are not operated.

The oxygen-sprinkle scheme, as developed by Queneau and Schumann,²⁷ differs from the other schemes in that it operates on the same principle as a flash furnace. Three specially designed burners positioned on the furnace roof are used to introduce and disperse a mixture of primarily dried concentrates and oxygen. A small percentage of ground coal may be mixed with the feed. The heat required for smelting is generated from the flash combustion of the mixture, and the molten droplets fall to the hearth below.

3.4.3.4.3 Operating experience. One of the earliest investigations of the use of oxygen in reverberatory furnaces was described by Saddington et al.⁹ of the Inco Copper Cliff smelter in Sudbury, Ontario. Tests were made on a calcine-charged nickel reverberatory furnace. Four water-cooled oxygen lances were installed in the end of the furnace, one below each of the coal burners used to fire the furnace. The lances were angled away from the furnace wall. By introducing the oxygen below the burners, the hottest zone of the flame was at the

bottom next to the bath. The first test, made primarily to examine fuel efficiency, indicated a 10-percent increase in throughput could be accompanied by a 19-percent decrease in fuel consumption. In the second test, an increase of 36 percent in throughput was achieved with approximately the same fuel consumption rate as occurred during standard operation (without oxygen enrichment). Although the oxygen was not added directly to the primary burner air, the "equivalent" levels of oxygen enrichment may nevertheless be defined. These levels were 26 percent and 27 percent during the two tests, respectively.²⁶

Achurra et al.⁸ have reported tests using oxygen enrichment in a calcine-charged reverberatory furnace at the Caletones smelter. A level of 26 percent oxygen in the primary combustion air yielded a 15-percent increase in capacity and reduced the fuel requirements per unit of charge by 19 percent. Refractory consumption, however, was noted to increase by 20 percent. In later tests, oxygen was injected through the furnace roof using lances to make the temperature distribution uniform within the furnace. An oxygen-enrichment level of 30 percent in this test yielded a 20-percent increase in smelting capacity, accompanied by a 19-percent reduction in the fuel requirement per unit of charge. No mention was made of changes in refractory wear.

Similar investigations have been made for green-charged furnaces. Eastwood et al.¹⁰ have reported tests made at the Rokana smelter in Zambia. In accordance with the practice of Inco, oxygen lances were installed near the coal burners. Furnace throughput was increased by 18 percent. The level of oxygen enrichment was not specified. In a later paper, Gibson¹¹ reported that the furnace refractory wear had not increased measurably with the use of oxygen enrichment. Furnace operating campaigns were indicated to be longer than 30 months.

Extensive tests of various oxygen enrichment schemes and various levels of enrichment have been made at the Almalyk smelter in the Soviet Union.^{12 13} In the work of Kupryakov et al.,¹² oxygen was introduced (1) through water-cooled lances positioned beneath the burners and (2) through the existing burners (primary air enrichment). In the former scheme, an oxygen-enrichment level of 25 percent yielded

a production increase of 20 percent and a decrease in the specific fuel requirement of 17 percent, while oxygen enrichment to the 30-percent level provided a production increase of 45 percent, accompanied by a 30-percent reduction in the specific fuel requirement. When oxygen was mixed directly with the primary burner air, a slightly greater efficiency was noted. With a 25-percent level of enrichment, production was noted to increase by 22 percent, with a 19-percent reduction in the specific fuel requirement. Oxygen enrichment to the 30-percent level yielded a 56-percent increase in capacity and a 36-percent decrease in specific fuel requirements. With regard to roof refractory wear, it was determined that the wear did not differ markedly from conventional operation.

When oxygen-fuel burners are used in the roof of a reverberatory furnace, the efficiency in terms of the heat utilization for smelting is considerably higher than in the schemes discussed previously. Such is the case because, primarily, the heat is directed upon the charge and the heat is transferred to a large extent by convection. Also, the flame temperature is much greater with pure oxygen than with oxygen-enriched air, resulting in a higher thermal driving force. Finally, Goto¹⁴ has pointed out that an additional heat transfer mechanism results with oxygen-fuel burners. CO_2 and H_2O are dissociated when they are formed with oxygen-fuel combustion at temperatures in the $2,000^\circ$ to $2,900^\circ$ C ($3,600^\circ$ to $5,300^\circ$ F) range, thereby absorbing heat. This dissociation heat is released when the gases are cooled sufficiently to permit reformation of the molecules. By applying the flame directly to or near the comparatively cool charge piles in the reverberatory furnace, the reformation heat is applied directly to the material to be smelted.

Extensive investigations on the use of oxy-fuel burners to increase production in a green-charged reverberatory furnace have been made at the Caletones smelter in Chile. As reported by Achurra et al.,⁸ throughput has been increased by up to 71 percent when using seven oxy-fuel burners and only one of the three original conventional burners. In this particular test, the fuel requirement per Mg of

charge showed a decrease of 40 percent from its value with conventional firing. In later tests, the furnace uptake was rebuilt to increase gas-handling capability, and production increases of up to 122 percent were achieved with 12 oxy-fuel burners. This expansion yielded a 125-percent reduction in specific fuel requirements. With regard to roof refractory wear, the tests indicated that the refractory consumption per unit of charge was the same or slightly lower than that for a conventional reverberatory furnace.^{8 15} Further information on the experience at Caletones is summarized in Section 4.5.6.

Extensive experience with oxy-fuel burners on a calcine-charged reverberatory furnace has been accumulated by Inco at its Copper Cliff smelter in Ontario, Canada. Blanco et al.¹⁶ have reported increasing throughput by 45 percent through the use of 10 oxy-fuel burners. The increase in throughput was accompanied by a 55-percent decrease in fuel consumption. In all, some 27 months of tests and operation were achieved, and the use of oxy-fuel burners continues. Calcine is charged to the furnace along the sidewalls, using drop pipes. As this furnace does not employ sidewall cooling,²⁸ the charge banks are necessary to prevent overheating of the sidewall refractory.

Tests of the oxygen-sprinkle smelting scheme have been made by Phelps Dodge Corporation at its Morenci smelter.¹⁷ The tests indicated that furnace throughput could be increased by 100 percent, while the total energy requirement per unit of charge could be reduced by two-thirds.

3.4.3.4.4 Conclusions. The operating experience discussed indicates that three methods of oxygen introduction to reverberatory furnaces have been extensively tested and are demonstrated for increasing furnace capacity: (1) the use of primary air enrichment, (2) under-shooting the flame with oxygen, and (3) the use of roof-mounted oxy-fuel burners. The oxy-sprinkle system is now being tested. The first two schemes, which are quite similar, have generally been employed to obtain production increases of less than 50 percent. In this analysis, it is assumed that a 20-percent increase in production is achievable when using either of these schemes in green- or calcine-charged rever-

beratory furnaces. It is further assumed, based on the extensive operating experience at the Rokana smelter and the fact that maximum flame temperatures shift closer to the bath when undershooting the flames with oxygen, that this scheme is preferable to oxygen enrichment of the primary burner air for increasing furnace capacity.

In light of Inco's experience with roof-mounted oxy-fuel burners, a 40-percent increase in production is considered achievable with this scheme in calcine-charged reverberatory furnaces. Furnaces using Wagstaff gun charging systems are expected to be capable of adopting oxy-fuel burners readily, as these furnaces employ sidewall cooling by design and would therefore not require sidewall charging to protect the sidewall refractory from excessive erosion.

Based on the experience at the Caletones smelter, a 50-percent increase in furnace throughput will be considered achievable for green-charged furnaces retrofitted with roof-mounted oxy-fuel burners.

3.4.4 Electric Furnaces

As with reverberatory furnaces, green-charged electric furnaces may increase capacity by converting to calcine-charged operation. The furnace capacity would increase because less time and energy are required to smelt the roasted calcine at about 540° C (1,000° F) than dried feed at a temperature of about 65° C (150° F). For this analysis, an increase of 40 percent is assumed achievable. Inspiration Consolidated Copper Company has indicated that the conversion to calcine-charged operation would be its most likely electric furnace expansion mode.¹⁸

In contrast to reverberatory furnaces, the conversion to calcine-charging in an electric furnace would not require the addition of cooling panels at the furnace slag line, because neither charge banks nor fossil fuel burners are used in electric furnaces. Also, it is not likely that extensive feed system modifications would be required in order to process calcine feed. Electric furnaces smelt dried concentrates, and the handling of dried concentrates and calcines is similar.

Both green- and calcine-charged electric furnaces can increase capacity by eliminating converter slag return. An increase in production similar to that achieved in reverberatory furnaces (25 percent) would be expected.

It is conceivable to increase electric furnace capacity by installing a larger transformer. However, up-powering the furnace would increase slag temperatures, leading to increased refractory wear.¹⁹ Hence, this option is not considered to be viable to the industry.

Physically expanding electric furnaces is also a conceivable option. However, the transformer and electrode design parameters are usually sized closely to the rated furnace capacity.¹⁹ As a result, it appears that this option would be impractical, and it is considered unfeasible in this study.

It should be noted that expansion modes employing oxygen enrichment, such as those useful for reverberatory furnaces, would not be feasible for electric furnaces. Oxygen enrichment offers no advantage because no fuel is combusted.

3.4.5 Outokumpu Flash Furnaces

Outokumpu flash furnaces can increase capacity readily by using oxygen-enrichment of the process air. Physically expanding Outokumpu furnaces is not considered technically feasible,²⁰ primarily because of the furnace geometry. No option exists for expanding furnace capacity by eliminating converter slag return, because this slag is generally processed in other facilities by design.

Outokumpu Oy has reported increasing the capacity of its flash furnaces at Harjavalta, Finland, by 60 to 70 percent when the oxygen content of the process air was raised to 30 to 40 percent.²¹ The use of oxygen yielded an SO₂ concentration in the offgases of 18 to 20 percent and reduced the oil requirement of the furnace. The increased capacity in the furnace resulted primarily from the decreased gas volume afforded by oxygen enrichment.

Phelps Dodge-Hidalgo smelter personnel have indicated that their Outokumpu furnace capacity could probably be increased by 25 percent through the use of oxygen enrichment of the combustion air.²² Expan-

sions greater than 25 percent would lead to overheating of the reaction shaft and increased logistics problems with respect to ancillary material-handling systems.

3.4.6 Noranda Reactors

The primary expansion mode for Noranda reactors is through oxygen enrichment of the blowing air. Kennecott Corporation has increased reactor capacity by some extent at its Garfield facility by increasing the oxygen-enrichment level from the design value of 30 percent to 34 percent.²³ A further increase in throughput by about 6 percent could possibly be achieved with an enrichment level of 36 percent oxygen. A level of 36 percent oxygen is considered to be the upper limit because it represents the point of autogenous reactor operation.²³ Such operation is undesirable because reactor control is difficult.

It is conceivable to increase Noranda reactor capacity by increasing the blowing rate via the installation of a larger blower. However, this scheme is not considered to be a viable expansion option because of offgas handling constraints.²³

Physical expansion of Noranda reactors coupled with increasing the number of tuyeres is also a conceivable expansion option. This option is not considered viable in this analysis because of physical space limitations, down time requirements, and offgas handling constraints.

In conclusion, no expansion options other than additional oxygen enrichment are considered viable for Noranda reactors. The use of additional oxygen would produce only a slight increase in capacity, however.

3.4.7 Converters

ASARCO has reported increasing the capacity of a Peirce-Smith converter at its Tacoma smelter through physical expansion.²⁴ The converter was lengthened by 5 feet, and 6 additional tuyeres were added, increasing the number of tuyeres from 46 to 52. As a result, the capacity of the converter increased by approximately 13 percent.

Converter capacity may be increased by increasing the air-blowing rate alone, which would decrease the time required for matte conversion.

Such an expansion could require the installation of a larger blower. However, the upper limit on blowing rate is determined by the excessive ejection of molten material from the converter. In this analysis, it is assumed that domestic converters operate at or near their maximum blowing rate. Hence, this expansion mode is not assumed to be a viable one for the industry.

Oxygen enrichment of converter blowing air appears to be an option for increasing converter capacity, because it results in an increase in the rate of conversion of matte to blister copper during blowing. Oxygen usage in converters has been widespread in the past, with 7 of the 15 domestic smelters having reported its use during the slag and/or copper blows.²⁵ The percentage of oxygen in the blowing air has not exceeded 29 percent (with 24 to 26 percent being most common), because higher levels can lead to refractory damage from increased operating temperatures.

It should be noted, however, that oxygen enrichment of converter blowing air has been used, almost exclusively, to allow increased processing of scrap materials. Indeed, scrap materials are required when oxygen enrichment is employed, to reduce converter temperatures. Charging scrap materials to the converters serves to interrupt the blowing cycles. Hence, although the actual blowing time is reduced with oxygen enrichment, it is not clear that a decrease in total cycle time ensues. Also, the use of oxygen enrichment would be contingent upon the availability of sufficient scrap materials. For these reasons, and because it has not been employed for increasing the rate of matte throughput in the industry, oxygen enrichment of converter blowing air is not considered a viable option for increasing converter capacity in this analysis.

It is concluded that physical expansion coupled with increasing the number of tuyeres is the most likely mode of increasing the matte throughput rate of a converter. Only a limited expansion can be achieved by this method, however.

3.4.8 References

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3.5 SUITABILITY OF ALTERNATIVE TECHNOLOGIES FOR PROCESSING HIGH IMPURITY FEED MATERIALS

3.5.1 Background

Domestic smelters which process high impurity (HI) feeds--i.e., those which are defined in the present NSPS as containing more than 0.2 weight percent arsenic, 0.1 weight percent antimony, 4.5 weight percent lead, or 5.5 weight percent zinc--generally employ the multihearth roaster-reverberatory furnace-converter configuration. An exception is the Phelps Dodge-Ajo smelter, which processes feeds containing 0.3 percent As with a green-charged reverberatory furnace. The industry has stated the need to maintain this configuration because of the flexibility afforded in terms of impurity elimination capability, which allows product quality to be maintained, and the capability to process secondary materials. The primary factor affording both these advantages is the low (40 to 45 percent) matte grade produced by this smelting configuration. Such a matte grade leads to long blowing times in the converters, which are highly effective for eliminating impurities. Furthermore, the heat released while blowing such a matte allows substantial quantities of secondary materials, which can include some lead-smelter byproducts, to be processed in the converters. The industry further endorses the multihearth roaster-reverberatory furnace-converter configuration because its multistep treatment allows some impurity segregation during impurity recovery.*

The rationale (under the original NSPS) for exempting reverberatory furnaces from control when processing a charge containing a high level of volatile impurities is multifaceted. At promulgation, the cost of control of the weak SO₂ stream was considered unreasonable. Operation of electric furnaces, which were considered technically capable of processing such a charge, was not affordable in the Southwest. The other alternative to the

*At the ASARCO-Tacoma smelter, for example, which processes feeds having high levels of arsenic, impurities are separated into an arsenic-rich stream (the roaster and reverb offgases) and a lead-antimony-rich stream (the converter offgases). The arsenic-rich material is roasted in a separate process to produce arsenic trioxide and recover the copper in the dust, while the latter stream is processed in a lead smelter for the recovery of lead, zinc, bismuth, and antimony.

conventional reverberatory furnace evaluated at that time was the Outokumpu flash furnace, which was in use worldwide. This technology was dismissed on technical grounds. It had not been used to smelt a charge containing more than a fixed level of certain impurities and was not considered to have been demonstrated for smelting feeds having compositions similar to those encountered at installations such as ASARCO-Tacoma. The maximum levels of impurities processed by the Outokumpu furnace were used, however, as the basis for defining a "high level of volatile impurities." No other technologies were assessed as possible replacements for the reverberatory furnace since the Outokumpu furnace was considered to be the most likely option in lieu of an electric furnace.

It is the purpose of this section to reassess, in light of the requirements of the industry, the suitability of alternative technologies for processing HI feed materials. In the assessment, distinction has been made between demonstrated and commercialized technology. A technology is considered demonstrated if pilot plant results are sufficient to define the full-scale plant, and if the pilot plant results are not the sole basis for endorsement. A technology is also considered demonstrated if it is in place in another commercial application from which it can be transferred by conventional engineering practice to the copper smelter. Commercialized technology is that technology in place in a copper smelter, including new, obsolete, and questionable technology.

3.5.2 Impurity Behavior During the Smelting Process

The ultimate objective in copper smelting and refining operations is the production of a product containing less than specified maximum levels of impurities. Impurity removal occurs at each stage of the operation: roasting, smelting, converting, fire-refining, and electrolytic refining. If the impurity burden to the plant is high, care must be taken during the first four operations to remove the bulk of the impurities. Current practice is to maintain the impurity levels of anode (fire-refined) copper below certain limits before electrolytic refining. In Table 3-7, the maximum acceptable average impurity levels in anode copper from the ASARCO-Tacoma smelter are presented.¹⁸ The typical average impurity levels in blister copper corresponding to this particular anode composition are presented for comparison.¹⁸

TABLE 3-7. MAXIMUM ACCEPTABLE IMPURITY LEVELS IN ANODE COPPER, AND CORRESPONDING LEVELS IN BLISTER COPPER PRODUCED AT THE ASARCO-TACOMA SMELTER¹⁸

Element	Maximum acceptable average concentration in anode copper, weight percent	Corresponding average level in blister copper, weight percent
Arsenic	0.20	0.35
Antimony	0.15	0.20
Lead	0.07	0.15
Zinc	N/A	N/A
Bismuth	0.02	0.03
Nickel	0.19	0.20
Selenium	0.05	0.06
Tellurium	0.06	0.06

The behavior of any specific impurity element during the copper smelting process is dependent upon thermodynamic, kinetic, and process parameters. Impurities are removed by volatilization and slagging.

Volatilization can occur for impurity elements in sulfide form, in oxide form, or in the free state, depending upon the element. Most impurities are present as sulfides in the charge to the smelter. However, oxides of most impurities can form under oxidizing conditions.* The sulfides of the impurities Sb, Pb, and Zn are more volatile than the corresponding oxides. In the case of As, both the sulfide and oxide forms are extremely volatile. Overall, arsenic compounds are perhaps the most volatile of the major impurities.

Impurity elimination through slagging occurs by the combination of the metal oxides with silica, similar to the slagging of iron oxide.

3.5.2.1 Impurity Elimination During Roasting. Conventional roasting removes impurities as volatilized materials and as chemically altered dusts. Hence, impurity elimination is affected by the temperature, residence time, and the roaster atmosphere. These same parameters govern the elimination of sulfur in the roaster. As discussed previously, the sulfur elimination during roasting is a major determinant of the matte grade produced during smelting, for a given charge composition. Overall impurity removal is maximized concurrent with the production of a relatively low-grade matte (40-45 percent copper) in the smelting furnace. Because of this constraint on matte grade, there is little latitude for direct control of impurity elimination in the roasting operation itself.¹

Impurity elimination in a multihearth roaster is generally greater than in a fluidized-bed unit for any level of sulfur elimination. In a multihearth roaster, it is possible to vary oxidizing and reducing conditions, temperature, and gas composition on each hearth. The residence times of concentrate particles in a multihearth roaster generally range from 1 to 2 hours.² A single fluidized bed roaster can provide only one set of conditions at a time, either oxidizing or reducing. The temperature

*The impurity elements As, Sb, Pb, Zn, and Bi all have a greater affinity for oxygen than does copper.

remains essentially constant throughout the bed, although hot spots may be present. The average residence time of concentrate particles in a fluidized bed roaster is much shorter compared to a multihearth roaster and can differ by as much as a factor of ten.³ This difference is sufficiently great to permit the operation of two or more fluid-bed roasters in series. This scheme would overcome the limitation of providing only one set of conditions during fluid-bed roasting. While this approach has been used in processing other materials, there is no experience with two-stage fluid-bed roaster systems in the copper industry.

The extent of elimination of impurities during roasting in multihearth roasters is indicated in Table 3-8, which provides information on impurity distributions during roasting and reverberatory furnace smelting (based on the ASARCO-Tacoma operation⁴ processing HI feed materials). It is noted that 25 percent of the feed arsenic is eliminated during roasting, while only between 4 and 8 percent of other important impurity elements are eliminated.

The sulfidizing roast process,¹⁹ developed by Outokumpu Oy in Finland, was developed specifically to eliminate volatile impurities from ore concentrate feeds before smelting. This process is demonstrated and yields substantially greater impurity removal than does multihearth roasting.

In sulfidizing roasting, ore concentrates are dried and preheated and fed to a rotary sulfidization kiln. The sulfidizing atmosphere is provided by elemental sulfur, which is vaporized and transported by a preheated nitrogen carrier gas into the kiln. The hot gas flows countercurrently to the feed and vaporizes (preferentially to copper and iron sulfides) the sulfidic compounds containing arsenic, antimony, and bismuth. These compounds are carried out of the kiln in the offgases and are condensed for recovery.

The impurity-elimination capability of the sulfidizing roast process may be summarized as follows:¹⁹

- Arsenic removal (up to 10 percent As in feed), 99 percent
- Antimony removal (up to 1.5 percent Sb in feed), 50 to 80 percent

TABLE 3-8. DISTRIBUTION OF IMPURITY ELEMENTS IN
CONVENTIONAL SMELTING WHEN PROCESSING HIGH IMPURITY FEEDS^a

Impurity element	Approximate ^b level in feed, weight percent	Percentage reporting in various streams ⁴			
		Multihearth roaster dust	Reverb dust	Reverb slag	Reverb matte
Arsenic	3-6	25	52	10	13
Antimony	0.2-0.9	6	25	50	19
Lead	0.5-1.3	5	20	19	56
Zinc	1-1.6	5	21	65	9
Bismuth	N/A	4	20	1	75
Tin	N/A	5	18	47	30
Nickel	N/A	0	2	6	92
Selenium	N/A	6	18	2	74
Tellurium	N/A	8	22	2	68

^aBased on the ASARCO-Tacoma smelter.

^bCorresponds to typical average concentrations in ASARCO-Tacoma feed.⁵
These levels are not necessarily those used by ASARCO for determining the
impurity distributions.

- Bismuth removal (up to 0.2 percent Bi in feed), 20 to 30 percent
- Sulfur removal, 12 to 22 percent

Arsenic elimination by the process is essentially 100 percent regardless of the initial level in the feed.¹⁹ Optimum arsenic elimination occurs with operating temperatures in the range of 600° to 800° C (1,110° to 1,470° F). The sulfur removed by the process is primarily that bound with the impurities arsenic, antimony, and bismuth. Hence, the energy value of concentrates undergoing sulfidizing roasting is similar to that of normal sulfidic concentrates containing low levels of volatile impurities.¹⁹ This point is of notable importance if the roasted material is to be processed subsequently in a flash furnace.

3.5.2.2 Impurity Elimination During Smelting. Impurity elimination in smelting furnaces occurs by volatilization and slagging. The amount of a given impurity that is slagged or volatilized generally varies from one furnace to another.

Rather complete data exist for the distribution of various important impurities during reverberatory furnace smelting. These data are shown in Table 3-8. As was noted for roasting, arsenic is volatilized to the greatest extent. In contrast, antimony and zinc report extensively to the slag. The majority of the lead and bismuth present in the charge report to the matte and must be eliminated during converting.

The behavior of impurities such as arsenic, antimony, lead, and zinc in an electric furnace has been investigated by the Bureau of Mines.⁶ The feed materials employed in the tests were similar in composition to those smelted in the ASARCO-Tacoma reverberatory furnace. It was concluded that, although the gas composition over the molten bath is much different in an electric furnace, the subject impurities behaved the same as in a reverberatory furnace.

Inco has reported on the extent of volatilization of arsenic, lead, and zinc in its Copper Cliff flash furnace.⁷ When producing a 40 to 50 percent copper matte, the proportions of these elements fumed were, respectively, 50 to 60 percent, 20 to 25 percent, and 5 to 10 percent. Arsenic was indicated to fume within the flash furnace as As_4O_6 , a form

consistent with the degree of exposure of the feed to the oxidizing atmosphere in this process. Through tests made in a bench-scale flash furnace (Section 3.6.4), Inco established that the proportion of the impurity fumed increased with matte grade.⁷ Furthermore, over the range of impurity concentrations examined in the bench-scale furnace (Section 3.5.4), it was determined that the proportion of the impurity fumed was independent of the level of the impurity in the feed.⁷

Although complete data are not available, impurity elimination (via slagging and volatilization) in flash furnaces is believed to be greater than in reverberatory furnaces because of the intimate mix between the feed and the hot, oxidizing atmosphere.

Mackey et al.⁸ have investigated impurity behavior in the Noranda process when operated for the production of both high grade matte and blister copper. The distribution of impurities when making a 70-percent copper matte is shown in Table 3-9. Extensive volatilization is noted to occur for arsenic, antimony, lead, and bismuth--primarily because the reactor operates much like a converter. Zinc, which oxidizes readily, reports primarily to the slag.

When blister copper is produced in the reactor directly, the distribution of impurity elements changes substantially, as shown in Table 3-10, with substantial percentages of As, Sb, and Bi reporting to the blister copper. Such behavior results since these elements are quite stable in copper and can dissolve therein before volatilization can occur. Mackey et al. concluded in their investigation that blister copper produced directly in the reactor contained higher levels of these impurities than that produced by conventional reverberatory smelting. Similar conclusions were reached by Kennecott when considering the Noranda process for their Garfield, Utah, smelter. The concentrates processed at this smelter have trace quantities of arsenic, antimony, and bismuth.⁹ Increased levels of these impurities in the blister copper were considered to result in unacceptable levels in the anode and cathode copper.⁹ For this reason, Kennecott opted to use the Noranda process for the production of high-grade matte, with subsequent oxidation to blister copper in converters.

TABLE 3-9. DISTRIBUTION OF IMPURITY ELEMENTS IN THE NORANDA PROCESS (MATTE PRODUCTION MODE)⁸

Impurity element	Percentage reporting in reactor streams		
	Offgas (dust)	Slag	70% Cu matte
As	85	7	8
Sb	57	28	15
Pb	74	13	13
Zn	27	68	6
Bi	70	21	9

TABLE 3-10. DISTRIBUTION OF IMPURITY ELEMENTS IN THE NORANDA PROCESS (BLISTER COPPER PRODUCTION MODE)⁸

Impurity element	Percentage reporting in reactor streams		
	Offgas (dust)	Slag	Reactor copper
As	19	27	54
Sb	29	36	35
Pb	24	74	2
Zn	21	78.9	0.1
Bi	52	30	18

With respect to the Mitsubishi process, no data are available with which to characterize the distribution of impurity elements. However, the possibility exists that the retention of As, Sb, and Bi might be high because of the continuous contact between the matte and blister copper in the converting furnace.¹⁰

3.5.2.3 Impurity Elimination During Converting. The converting operation provides the greatest latitude for controlling the impurity content of blister copper. The converter is considered to be a fairly ideal vessel for impurity control because of the large effective area between the gas phase and the liquid matte. Impurities are eliminated during converting by both volatilization and slagging.

The removal of impurities is most effective during slag blows. This is because, as discussed previously, impurities tend to concentrate in blister copper once it begins to form. Converting of a low-grade matte (40 to 45 percent Cu) is desirable since the duration of the slagging cycle is increased, which allows more time for impurity removal. The effect of matte grade on the removal of the impurities arsenic, antimony and bismuth during converting is illustrated graphically in Figures 3-14 through 3-16, respectively.¹¹ For antimony and bismuth, the percentage elimination decreases with increasing matte grade. In the case of arsenic, the elimination is quite constant until a matte grade of approximately 65 percent is attained, at which point a rapid decrease ensues. It should be noted that a low degree of impurity removal during converting may not be consequential if, as in the case of Noranda reactors operated for the production of high-grade matte, substantial impurity elimination occurs during the smelting step.

With regard to the mechanism of impurity elimination during converting, volatilization is more important for arsenic and bismuth, while oxidation-slagging is more important for antimony and zinc. Both mechanisms are essentially equally important for lead.¹²

3.5.3 High Impurity Feed Processing Experience with Outokumpu Flash Furnaces

The smelting of concentrates containing substantial quantities of lead and zinc impurities in a flash furnace have been reported at the Kosaka

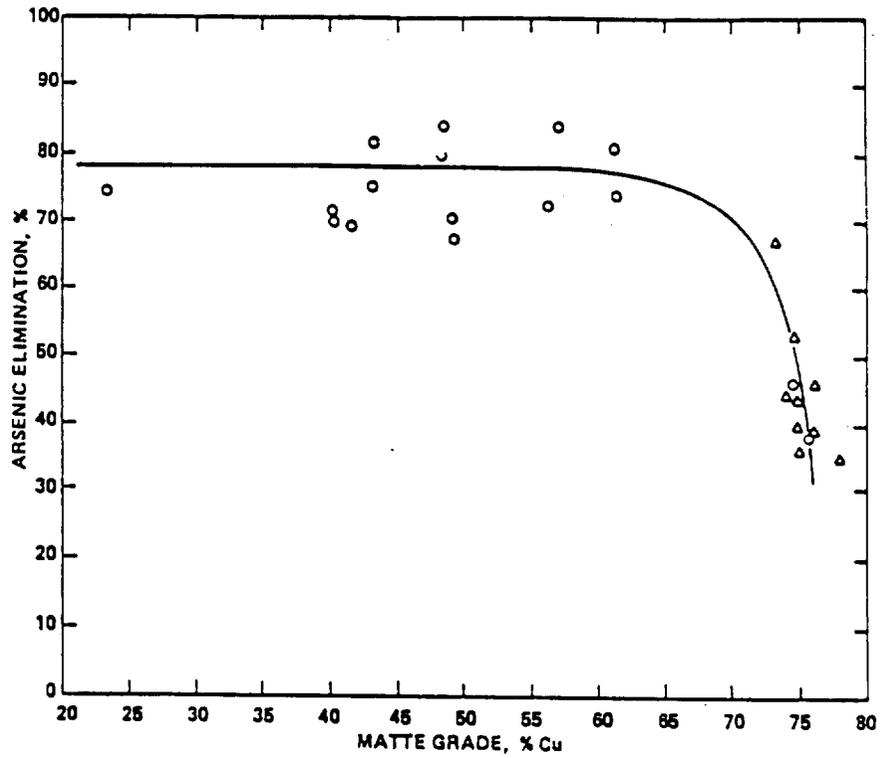


Figure 3-14. Converter elimination of arsenic as a function of matte grade.11

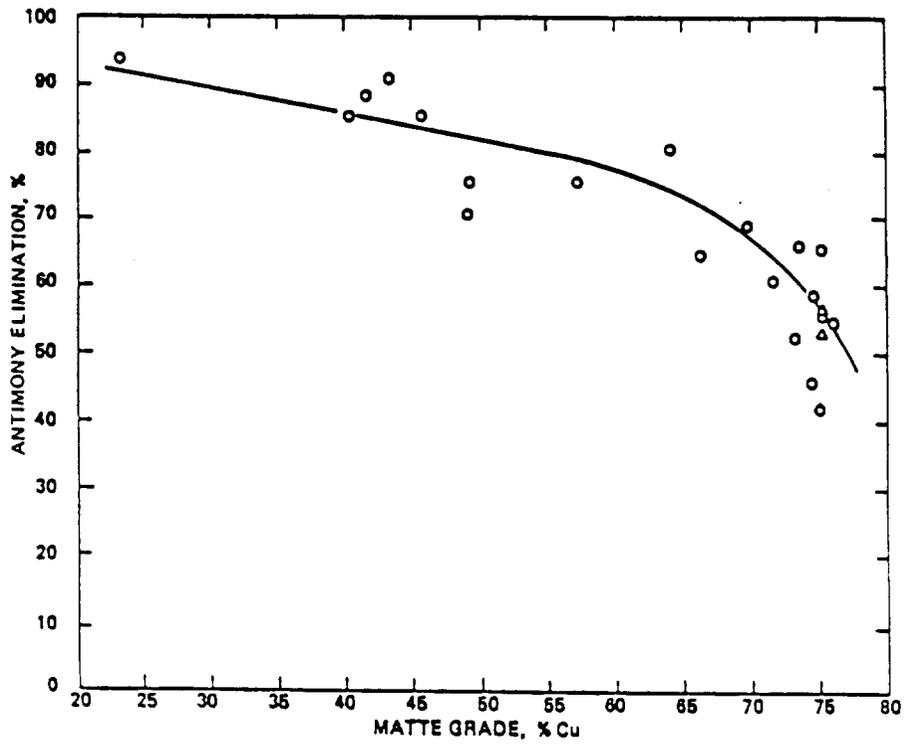


Figure 3-15. Converter elimination of antimony as a function of matte grade.11

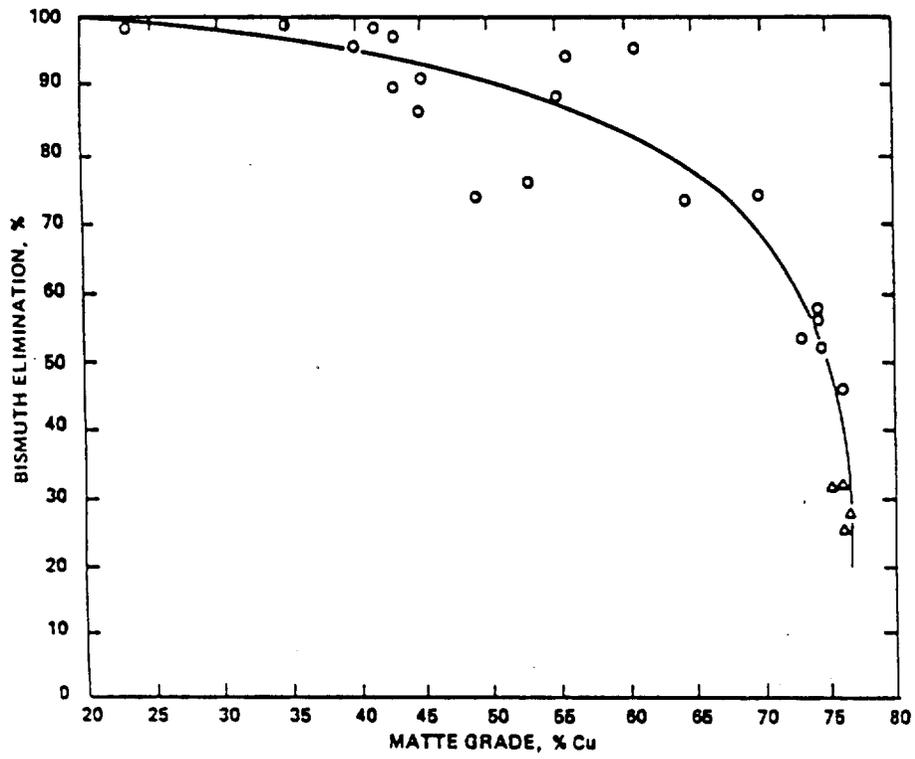


Figure 3-16. Converter elimination of bismuth as a function of matte grade.¹¹

smelter in Japan.¹³ Assays of two such concentrates are presented in Table 3-11. All of the impurities reported at Kosaka have concentrations below those levels specified in the current exemption. However, their experience processing feeds with these impurity levels is pertinent to this analysis.

Because most impurities were concentrated in the flue dusts at Kosaka, the dust production rates of both the furnace and the converters were fairly high as compared to other smelters. Initially, all of the dusts from the flash furnace were recycled. The high lead content, however, resulted in excessive accretions in the flash furnace waste heat boiler, causing low heat recovery. These problems led to the elimination of dust recycle to the furnace. As an alternative, the flash furnace dust was ultimately processed in a hydrometallurgical treatment plant which afforded the separation and recovery of copper, zinc, lead, and cadmium.

Outokumpu Oy has investigated the processing of high-impurity feeds in their technology. Concentrates containing 10 percent zinc and 5 percent lead have been smelted in a pilot plant operation.¹⁴ As a result of its investigations, Outokumpu Oy recommends the maximum feed impurity limits in Table 3-12, which vary depending upon the mode of operation of the smelter.¹⁴ Condition A pertains to operation with the recycle of all dusts produced except those recovered from the sulfuric acid plant. Condition B pertains to operation of the smelting complex in the same manner as discussed for A, but with increased purification of electrolytes in the electrolytic refining operation to compensate for slightly increased impurity levels in the anode copper. Condition C refers to operation with more outlets for impurities, such as: separate treatment of converter dusts, electric slag-cleaning-furnace flue dusts, anode furnace slag, and all or part of the flash furnace flue dust; and, possibly, increased purification of electrolytes during electrolytic refining. Where the arsenic content of the feed exceeds 5 percent, Outokumpu recommends pretreatment of the concentrate, such as by sulfidizing volatilization, before smelting.¹⁴

3.5.4 High Impurity Feed Processing Experience with Inco Flash Furnaces

Concentrates processed in the commercial flash furnace at Inco in Canada are very "clean" with respect to impurities, containing about 0.002

TABLE 3-11. IMPURITY ASSAYS OF FEED MATERIALS PROCESSED
 IN THE OUTOKUMPU FLASH FURNACE AT THE KOSAKA SMELTER¹³

Copper concentrate	Impurity concentration, percent					
	As	Sb	Pb	Zn	Bi	Cd
Concentrate A	0.10	-	2.5	3.0	0.04	0.02
Concentrate B	0.14	-	3.1	2.5	0.03	0.01

TABLE 3-12. MAXIMUM IMPURITY LEVELS RECOMMENDED FOR THE
OUTOKUMPU FLASH FURNACE¹⁴

Mode of operation	Maximum concentration of impurity in concentrate feed, percent				
	As	Sb	Pb	Zn	Bi
A	0.25	0.025	1.5	5	0.03
B	1	0.1	3	10	0.2
C	5	0.5	5	10	1.0

percent As, 0.05 percent Pb, and 0.17 percent Zn.¹⁵ Other impurities are present only in trace amounts.⁷ As indicated previously, Inco has studied the elimination of the impurities As, Sb, Pb, and Zn at higher levels in a bench-scale flash furnace.⁷ The objective of these tests was to evaluate the applicability of Inco oxygen flash smelting to concentrates having higher impurity levels than those encountered at Copper Cliff.

The miniplant flash furnace employed in the tests has a flashing space enclosed within a silicon carbide tube. The tube is covered by a refractory lid. A vertical burner is used to inject the concentrate-oxygen mixture into the furnace flashing space. Matte and slag collect in a receiving crucible sitting in the lower part of the chamber. Offgases escape the chamber via an exhaust port in the refractory lid.

The unit is capable of processing up to 15 kg (33 lb) of concentrate per hour. At this rate, the process cannot be operated autogenously as does the commercial Inco flash furnace because the heat losses greatly exceed the heat generated by combusting the feed. The additional heat required for autogenous operation is supplied by burning natural gas in an annular space between the silicon carbide tube and an outer refractory shell. Hence, the furnace temperature may be controlled independently of furnace operation.

The duration of a test is limited by the capacity of the matte-slag receiving crucible. At the normal throughputs employed, a test lasts for about 1.5 hours. Temperatures at various locations within the unit are monitored by means of thermocouples. The furnace is operated at a slightly negative pressure during tests to prevent fugitive losses of gases, fumes, and dust.

Most of the tests with increased impurity levels were made with Copper Cliff concentrate, which was doped with PbS and PbO, ZnS, and ZnO, arsenopyrite (As), and speiss (As and Sb). The range of impurity concentrations examined is shown in Table 3-13. The tests were used primarily to determine the distribution of the various impurities between the matte and slag, as a function of matte grade.

Initial tests made in the miniplant flash furnace showed that the metallurgy of the commercial flash furnace could be totally reproduced in

TABLE 3-13. RANGE OF IMPURITY CONCENTRATIONS TESTED
IN THE INCO MINIPLANT FLASH FURNACE⁷

Impurity	Range of concentration, percent
As	0.25 - 1.0
Sb	0.1 - 0.3
Pb	0.1 - 2.0
Zn	1.0 - 5.0

the miniplant furnace,* in terms of the state of oxidation of the system (slag $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio) and copper losses in the slag. Hence, conclusions (mentioned previously) reached by Inco concerning the proportion of impurities fumed from the miniplant furnace are expected to apply equally well to commercial-scale furnaces.

3.5.5 Feed Processing Experience of Other Technologies

The Mitsubishi process is currently in operation at two smelters worldwide--the Naoshima smelter in Japan and the Texasgulf Canada smelter in Timmins, Ontario. Mitsubishi Metal Company has provided information on the maximum impurity levels which they have processed.¹⁶ These levels are presented in Table 3-14. Mitsubishi indicated that there was no limitation on impurity-levels in their process and that no impurity related problems would occur at high levels, provided that considerations were made for gas handling and dust treatment.

The Noranda process, operated for the production of high-grade matte, is currently employed at the Kennecott-Garfield smelter and at the Horne smelter of Noranda Mines, Ltd., in Quebec. Feed materials at the Horne smelter have been reported containing up to 8 percent Pb and up to 10 percent Zn.¹⁷ No mention was made of impurity-related problems when processing these materials.

3.5.6 Processing High Impurity Feeds Using the Sulfidizing Roast-Flash Furnace Combination

The combination of sulfidizing roasting and flash furnace smelting was compared to conventional multihearth roasting and reverberatory furnace smelting with respect to relative abilities to process HI feed materials--subject to industry constraints. The feed composition considered was the average assay of charge processed at the ASARCO-Tacoma smelter during March 1979. This feed had a copper/sulfur ratio of 1.0, which represents the lowest available sulfur of any month during the (typical) year 1979.

A comparison of the two processes is shown in Table 3-15, which projects the composition of streams to roasting, smelting, and converting

*The only exception noted was a lower oxygen efficiency achieved in the miniplant furnace as compared to the commercial furnace. This difference, however, results from the difficulty of obtaining an absolutely uniform delivery of concentrates through the small flash burner.

TABLE 3-14. MAXIMUM IMPURITY LEVELS PROCESSED
IN THE MITSUBISHI PROCESS¹⁶

Impurity	Maximum concentration, percent
As	0.329
Sb	0.097
Pb	0.96
Zn	6.10
Bi	0.034

TABLE 3-15. COMPARISON OF REVERBERATORY FURNACE^a AND FLASH SMELTING USING FEED COMPOSITION FOR ASARCO-TACOMA (Basis 100 Parts Feed by Weight)

Component	to ^b MHR	to reverberatory furnace	to converter	to sulfi- dizing roast ^c	to flash furnace ^e	to converter
Copper	25.8	25.8	25.5	25.8	25.8	25.5
Iron ^c	17.3	17.3	17.1	17.3	17.3	17.1
Sulfur	25.8	22	16.7	25.8	20.9	16.7
Arsenic	3.18	2.38	0.41	3.18	0.03	0.005
Antimony	0.87	0.84	0.17	0.87	0.30	0.17 ^f
Lead	0.7	0.67	0.39	0.7	0.7	0.42 ^f
Zinc	1.01	0.96	0.1	1.01	1.01	0.1 ^f
Coal ^d					0.38	
Other	25.3	25.3	3	25.3	25.3	3
Total	100	95.25	63.37	100	91.7	63.0
Matte grade			43			43

^aSulfur elimination: roaster, 14.8 percent; reverberatory furnace, 20.4 percent.

^bASARCO-Tacoma average feed composition, March 1979.

^cIron assumed present as FeS₂.

^dCoal (11,500 Btu/lb) to make up energy difference for lower sulfur content.

^eSulfur elimination: sulfidizing roast 19 percent; flash furnace, 16.2 percent.

^fImpurity removal to slag and dust assumed equivalent in both furnaces.

operations in terms of the levels in the original feed. Compositions shown for the multihearth roaster-reverberatory furnace-converter configuration are based on the impurity distribution data presented in Table 3-7, and on that degree of sulfur elimination corresponding to a matte grade of 43 percent; i.e., 14 percent S eliminated in the roaster and 20.4 percent eliminated in the reverberatory furnace. For the sulfidizing roast-flash smelting scheme, sulfur elimination is shown at 19 percent for the roast, which is 5 percent higher than for the multihearth roaster. The use of this value allows projection of essentially complete arsenic removal. Sulfur elimination in the flash furnace is 16.2 percent, compared to 20.4 percent for the reverberatory furnace. To make up for the lower level of sulfur available as fuel in the flash furnace, 0.4 percent coal is added. The addition of this quantity of coal restores the energy value of the flash furnace feed to a level equivalent to having a Cu/S ratio of unity. Such feeds can be used to produce a 43 percent matte grade in flash furnaces, although additional coal may be required.

Impurity elimination in the flash furnace was assumed to equal that achieved in the reverberatory furnace, as the worst case.

It is noted that the levels of the impurities arsenic, lead, and zinc (at 0.03 percent, 0.76 percent, and 1.1 percent, respectively) in the feed to the flash furnace are all within the limits prescribed by Outokumpu for essentially total recycle of dusts within the smelter (Table 3-12, Operating Mode A). The level of a single impurity, antimony, requires operation according to Operating Mode C. Accordingly, separate treatment of flash furnace and converter dusts may be necessary to prevent antimony buildup within the smelter. (Such operation is standard practice at the ASARCO-Tacoma smelter.) However, the antimony level, at 0.32 percent, is lower than that for the reverberatory furnace (0.88 percent). In both furnaces, 50 percent of the antimony is expected to report to the slag.

With respect to the matte charged to the converters, it is noted that the levels of impurities in the flash furnace matte are approximately equal to, or lower than, the corresponding levels in the reverberatory furnace matte. Hence, blister copper quality would be preserved with the flash furnace-sulfidizing roast combination.

It should be noted that, in view of the high degree of arsenic removal achievable with sulfidizing volatilization (99 percent), feed arsenic levels of up to 10 percent can be processed. For such feeds, the arsenic levels in the feed to the flash furnace would be less than 0.2 percent, and the levels in the matte charged to the converters would be lower than the levels in reverberatory furnace matte.

3.5.7 Conclusions

Previous conclusions regarding the applicability of electric furnaces for processing HI feeds remain unchanged. Indeed, investigations made by the Bureau of Mines⁶ further substantiate the position that electric furnaces are technically demonstrated for processing high-impurity materials.

The Noranda process, operated for the production of blister copper directly, has been found to lead to increased anode and cathode copper impurity levels when processing only trace quantities of arsenic, antimony, and bismuth impurities. Hence, it is concluded that this technology would not be a feasible alternative to reverberatory or electric furnaces for processing feed materials containing elevated impurity levels.

The remaining technologies--Outokumpu flash furnaces, Inco flash furnaces, the Mitsubishi process, and Noranda reactors (matte-production mode)--all show some experience processing HI feed materials. A summary of the experience reported by each respective company is shown in Table 3-16.

Experience accumulated with the Mitsubishi process indicates that the levels of two impurities, arsenic and zinc, are higher than the limits specified in the current definition of HI feeds. However, the levels processed are not considered to differ substantially from these limits. Hence, the Mitsubishi process is not considered to offer any advantage over flash furnaces with respect to its extent of demonstration for processing feed impurities. Also, as reported by Biswas and Davenport,¹⁰ the process may not be suitable for high impurity materials in general because of the potential for increased impurity levels in the blister copper.

The Noranda process operated for the production of high-grade matte shows full-scale experience processing high levels of lead and zinc. Data are currently lacking with regard to maximum levels of arsenic and antimony processed with this technology. Overall, however, it appears quite promising

TABLE 3-16. SUMMARY OF EXPERIENCE PROCESSING HIGH IMPURITY FEEDS^a
IN ALTERNATIVE SMELTING TECHNOLOGIES^b

Company	Furnace/ process type	Nature of test or experience	Maximum level of impurity in feed, weight percent				Refer- ence
			As	Sb	Pb	Zn	
Outokumpu	Flash	Pilot- scale	N/A	N/A	5	10	14
Inco	Flash	Bench- scale	1.0	0.3	-- ^c	-- ^c	7
Mitsubishi	Mitsubishi	N/A	0.33	-- ^c	-- ^c	6.1	16
Noranda	Noranda ^d	Commercial scale	N/A	N/A	8	10	17

^aBy definition, feeds containing more than 0.2 percent As, or 0.1 percent Sb, or 4.5 percent Pb, or 5.5 percent Zn.

^bOther than reverberatory or electric furnaces.

^cMaximum levels reported were below the "High Impurity" limits.

^dOperated for the production of high-grade matte (70-75 percent Cu).

as an alternative technology that may satisfy the constraints of a domestic smelter processing HI feeds. Because the reactors operate similarly to converters on slag blow, they offer essentially the same advantages as converters with respect to impurity elimination capability. Furthermore, a variety of feed materials--including smelter reverts, precipitate copper, chopped scrap, dust, and refinery residues--have been smelted at Noranda's Horne smelter (a custom smelter).¹⁷ Hence, Noranda reactor technology is not expected to limit the capability of the industry to process scrap materials and byproducts. Additional information is needed to determine the feasibility of smelting calcines in Noranda reactors.

With regard to flash smelting technology, there appears to be no problem with the production of the low grade matte required for impurity elimination and scrap processing in the converters. The feed to Inco's flash furnace at Copper Cliff, for example, has a Cu/S ratio of 0.91 and (without converter slag return) has reported the production of a 40-percent matte grade.²⁰ Also, Inco has reported decreases in matte grade of up to 15 percentage points through the addition of coal to the feed.²⁰

Some conclusions are evident regarding the relative suitabilities of Inco flash furnaces versus Outokumpu flash furnaces for processing HI feed materials. Inco furnaces appear more suitable because they produce a lower matte grade (40 to 50 percent Cu) than do Outokumpu furnaces (50 to 65 percent Cu). Furthermore, because of the comparatively small offgas volume, Inco furnaces do not normally employ waste heat boilers, which have been indicated as a possible source of problems when processing feeds containing elevated levels of impurities in flash furnaces.

Sulfidizing roasting has been demonstrated as an effective pretreatment in reducing high levels of certain impurities in the feed. The combination of sulfidizing roasting and flash furnace smelting has been shown feasible for processing feeds characteristic of those processed at the ASARCO-Tacoma smelter. This configuration is considered demonstrated technology for feeds containing up to 10 percent arsenic, 0.9 percent antimony, 4.5 percent lead, and 5.5 percent zinc. The sulfidizing roast process reduces the arsenic and antimony levels to those smelted commercially in flash furnaces. The levels of lead and zinc are largely

unaffected by roasting, but have been processed commercially in flash smelters. The sulfidizing roast-flash furnace combination also satisfies industry constraints by (1) producing an arsenic-rich dust from which arsenic can be recovered, (2) reducing the impurity burden of the matte to levels comparable to or below those with conventional practice, and (3) producing a low-grade matte.

Inadequate information exists at present regarding the possible endorsement of the maximum impurity levels in the flash furnace feed recommended by Outokumpu under Operating Mode C (Table 3-14), i.e., 5 percent As, 0.5 percent Sb, 5 percent Pb, 10 percent Zn, and 1 percent Bi. Under Operating Mode C, separate processing of virtually all flue dusts would be required, and the possibility exists that adjustments would have to be made to electrolytic refining operations to maintain cathode copper quality. The former condition is in line with current operating practice at most smelters processing HI feeds. The option of increasing the rate of electrolyte purification at electrolytic refineries in order to accommodate anode copper with an increased impurity burden requires further investigation as to its feasibility at domestic installations.

3.5.7 References

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40 p.

3.6 BASELINE EMISSIONS

The baseline control level is that level of emission control that is required at the source under consideration in the absence of a revised new source performance standard. This level is determined from an examination of all pertinent regulations. Baseline requirements are discussed here for both process and fugitive sources.

3.6.1 Process Sources

The baseline control level for most new process sources is given by the existing NSPS regulation. For example, new roasters, converters, and smelting furnaces--with the exception of reverberatory furnaces processing high-impurity (HI) feeds--are subject to control by double-contact acid plants, or the equivalent. Under the NSPS, reverberatory furnaces processing HI feeds are exempted from control of both SO₂ and particulate matter.

The SIP regulations for each state having active copper smelters are pertinent to defining the regulatory baseline for new reverberatory furnaces processing HI feeds. Regulations governing sulfur dioxide emissions are presented in Table 3-17, and those governing particulate matter emissions are presented in Table 3-18.

In the case of both sulfur dioxide and particulate matter, many States have different regulations for new and existing smelters. Considering the regulations for new smelters alone, three States--Arizona, which has 7 smelters; Washington, which has a smelter processing HI feeds; and Tennessee--adopted the existing NSPS regulation. Nevada and New Mexico require the removal of 90 percent of the feed sulfur for all new smelters, which corresponds to the requirement that approximately 82 percent of the SO₂ in the offgases from a new reverberatory furnace be controlled.* SO₂ regulations adopted by Utah and

*Assuming the greenfield smelter operated similarly to ASARCO-Tacoma, the feed sulfur balance (uncontrolled) would be as follows:¹ multihearth roaster offgases--20 percent; reverberatory offgases--28 percent; converter offgases--47 percent; fugitives--4 percent; and reverberatory slag--1 percent. Under the existing NSPS, the roaster and converter streams would likely be controlled by double-contact acid plants, which have an efficiency of ~98.5 percent. Hence, the

TABLE 3-17. SULFUR/SULFUR DIOXIDE EMISSION LIMITATIONS BY STATE

State	Sources addressed by regulations	Emission limitations	Notes	References
Arizona	New primary copper smelters	40 CFR 60, Subpart P is adopted	Reverberatory furnaces processing high impurity feeds are exempted from SO ₂ regulations.	Reference 2, Arizona Air Regulations, Part R9-3-814.
	Existing primary copper smelters	10 percent of feed sulfur	Determined from weighted average (by feed sulfur) of feed sulfur removal required for each of the 7 smelters by the September 20, 1979, Arizona Multipoint Roll-back (MPR) SIP revision.	Reference 3.
Michigan	--	--	No regulation could be found.	Reference 2, Michigan Air Regulations.
Nevada	New copper smelters	10 percent of feed sulfur	--	Reference 2, Nevada Air Regulations, Article 8.
	Kennecott Copper Corporation, White Pine County	10,150 lb/hr SO ₂ (6-hour average). May be raised to 29,000 lb/hr on approval.	Effective date of this regulation has been indefinitely delayed. (Reference 2).	Reference 2, Nevada Air Regulations, Article 14, and 40 CFR 52.1475.
New Mexico	New smelters	10 percent of feed sulfur	Phelps Dodge-Hidalgo is considered to be a new source in New Mexico	Reference 2, New Mexico Air Regulations, Part 652.
	Existing nonferrous smelters	3,550 lb/hr (24-hour average)	Effective 12/31/82.	Reference 2, New Mexico Air Regulations, Part 652.

(continued)

Table 3-17. (continued)

State	Sources addressed by regulations	Emission limitations	Notes	References
Tennessee	New primary copper smelters	40 CFR 60, Subpart P is adopted	Reverberatory furnaces processing high impurity feeds are exempted from SO ₂ regulations.	Reference 2, Tennessee Air Regulations, Part 1200-3-16-21.
	Existing copper smelters	100 ppm from copper smelters, 500 ppm from sulfuric acid plants	Regulation evidently written for Cities Service--Copperhill, which is atypical among copper smelters.	Reference 2, Tennessee Air Regulations, Part 1200-3-19-19.
Texas	Primary copper smelters	6,000 ppm (b.v.) for reverberatory furnaces, 650 ppm (b.v.) for sulfuric acid plants and all other processes.	--	Reference 2, Texas Air Regulations, Part 131.04.01.016.
Utah	Kennecott copper smelter	6,030 lb/hr (6-hr average)	--	40 CFR 52.2335(d).
Washington	New primary copper smelters	40 CFR 60, Subpart P is adopted.	Reverberatory furnaces processing high impurity feeds are exempted from SO ₂ regulations.	Reference 2, Washington Air Regulations, Part WAC 173-400-115.
	ASARCO-Tacoma smelter	10 percent of feed sulfur	--	Reference 4.

TABLE 3-18. PARTICULATE EMISSION LIMITATIONS BY STATE

State	Sources addressed by regulations	Emission limitations	Notes	References
Arizona	New primary copper smelters	40 CFR 60, Subpart P is adopted	No particulate regulations are specified for reverberatory furnaces processing high impurity feeds.	Reference 2, Arizona Air Regulations, Part R9-3-814.
	Existing primary copper smelters	E = 3.59 P ^{0.62} for P < 30 tons/hr E = 17.31 P ^{0.16} for P > 30 tons/hr	P = process feed rate in tons/hr, E = particulate emissions in lb/hr.	Reference 2, Arizona Air Regulations, Part R9-3-515B.
Michigan	General sources	E = 4.10 P ^{0.67} for P < 30 tons/hr E = 55.0 P ^{0.11} -40 for P > 30 tons/hr	Units of P and E same as above.	Reference 2, Michigan Air Regulations, Part 3.
Nevada	Primary nonferrous smelters	1,300 lb/hr solid particulate matter 2,100 lb/hr total particulate matter	--	Reference 2, Nevada Air Regulations, Article 7.
New Mexico	New nonferrous smelters	0.03 gr/dcf	--	Reference 2, New Mexico Air Regulations, Part 506.
	Existing nonferrous smelters	0.05 gr/dcf for reverberatory furnaces.* 0.05 gr/dcf for acid plants and reverberatory feed dryers.	*Effective 12/31/82.	Reference 2, New Mexico Air Regulations, Part 506.

(continued)

TABLE 3-18. (continued)

State	Sources addressed by regulations	Emission limitations	Notes	References
Tennessee	New primary copper smelters	40 CFR 60, Subpart P is adopted.	No particulate regulations are specified for reverberatory furnaces processing high impurity feeds.	Reference 2, Tennessee Air Regulations, Part 1200-3-16-21.
	Existing sources (general)	$E = 4.10 P^{0.67}$ for $P \leq 30$ tons/hr $E = 55.0 P^{0.11-40}$ for $P > 30$ tons/hr	P = process feed rate in tons/hr, E = particulate emissions in lb/hr.	Reference 2, Tennessee Air Regulations, Part 1200-3-7.
Texas	General sources, except certain steam generators	$E = 0.048q^{0.62}$	q = stack effluent rate in acfm, E = particulate emissions in lb/hr.	Reference 2, Texas Air Regulations, Reg. I, Chapter 3.
Utah	Kennecott Copper Corporation Smelter, Salt Lake County	364 lb/hr	Annual average for smelter main stack.	Reference 2, Utah Air Regulations, Part 3.2.1.
Washington	New primary copper smelters	40 CFR 60, Subpart P is adopted	No particulate regulations are specified for reverberatory furnaces processing high impurity feeds.	Reference 2, Washington Air Regulation, Part WAC 173-400-115.
	General process sources	0.10 gr/dscf	--	Reference 2, Washington Air Regulations, Part WAC 173-400-060.

Texas appear to be tailored to the existing smelters in these States. The State of Michigan does not specify regulations for SO₂.

Since the majority of the existing smelters are located in States which have adopted the NSPS for new smelters, the baseline for SO₂ control for new reverberatory furnaces processing HI feeds is assumed to be the NSPS (which in effect is no control), for the purpose of this analysis. For particulate matter, the baseline control level will be computed based on the emission limitations presented in Table 3-18. For those states which do not specify regulations for new smelters specifically, the regulations applying to existing smelters will be used.

3.6.2 Fugitive Sources

Regulations governing fugitive emissions of SO₂ and particulates include the arsenic regulation of the Occupational Safety and Health Administration (OSHA), and the State Implementation Plans.

The OSHA arsenic standard limits occupational exposure to inorganic arsenic to 10 µg/m³, averaged over an 8-hour period. As of February 1982, exposure in various job classifications at ASARCO-Tacoma, ASARCO-El Paso, ASARCO-Hayden, Kennecott-McGill, and Kennecott-Garfield exceeded the limit. To reduce exposures, OSHA is requiring that local ventilation/hooding be installed (or upgraded, if already in place) on the following fugitive emission sources: roaster calcine discharge, matte tapping, and slag skimming.⁵ Converters are required to install secondary hooding. Approximate compliance dates are April 1984 for converter secondary hoods, and April 1983 for all other local ventilation systems.⁵

Of the five smelters affected, feeds processed by the Kennecott-Garfield smelter are believed to contain the lowest quantity of arsenic--

level of feed sulfur removal achieved would be $1 + (0.985)(20) + (0.985)(47) = 67$ percent. To meet the State requirement, however, an additional $90 - 67 = 23$ percent of the feed sulfur must be removed. Assuming that all of the additional requirement is supplied from the reverberatory stream (i.e., none of the fugitive sulfur is controlled), the level of control required on the reverberatory would be $(23/28) \times 100 = 82$ percent.

approximately 0.14 percent. It is assumed for this analysis that all new smelters processing feeds containing in excess of this amount will thus be required to install local ventilation/hooding systems on roaster calcine discharge, matte tapping and slag skimming operations, and converters.

For all copper smelters, independent of arsenic levels, the SIP regulations are believed to impose similar requirements for fugitive emissions control. The Multipoint Rollback (MPR) regulations adopted by the State of Arizona pertain to stack emissions. However, each source is required to demonstrate that fugitive emissions will not lead to violations of the National Ambient Air Quality Standards (NAAQS). As yet, existing smelters have not been able to make this demonstration. In this analysis, it is assumed that these smelters will be found to be in violation of the NAAQS as a result of fugitive emissions and will be forced to implement capture systems (on roaster calcine discharge, matte tapping, slag skimming, and converters) coupled with dispersion to achieve compliance. Furthermore, it is assumed that all other smelters will also be required to implement similar fugitive controls as a result of future revision to their SIP's. Hence, it is projected that new smelters would likewise be subjected to such controls on the fugitive sources under consideration.

3.6.3 References

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4. EMISSION CONTROL TECHNIQUES

4.1 GENERAL

This chapter describes and evaluates emission control techniques applicable to the primary copper smelting industry. The purpose of these control techniques is to reduce emissions of sulfur dioxide (SO_2) and particulate matter to the atmosphere. Control techniques for both primary process effluents and fugitive emissions are considered.

With regard to primary process effluents, the control of "weak" SO_2 streams generated by reverberatory smelting furnaces is the primary topic addressed in this chapter. The control techniques assessed for possible application to reverberatory furnace offgases are the following:

1. Contact sulfuric acid plants of the "dry gas" type.
2. Calcium-based flue gas desulfurization systems.
3. Ammonia-based flue gas desulfurization systems.
4. Magnesium-based flue gas desulfurization systems.
5. Flue gas desulfurization systems based upon a citric acid--sodium citrate buffer.

The discussion of contact sulfuric acid plants consists of a summary (Section 4.2.1), a general discussion of the contact process for producing sulfuric acid (Section 4.2.2), a discussion of sulfuric acid plant design and operating considerations (Section 4.2.3), and a summary of sulfuric acid plant performance capabilities (Section 4.2.4).

The assessments of the various flue gas desulfurization (FGD) processes are presented in Sections 4.3.2 through 4.3.5. The discussions involving each process follow the pattern outlined below:

1. A summary of the technical feasibility of applying each process to reverberatory furnace offgases.
2. A general discussion of the unit operations involved in each process.
3. A detailed discussion of the design and operating considerations involved in each process.
4. A discussion of the operational problems known to be associated with each process.
5. A survey of operating experience for each process.
6. A discussion of the applicability of each process to reverberatory furnace offgases.

General conclusions regarding the reliability and performance of the various FGD systems discussed herein are presented in Section 4.3.6.

The control of particulate matter emissions associated with reverberatory smelting furnace effluents is also assessed in this chapter. Venturi scrubbers, fabric filters (baghouses), and electrostatic precipitators (ESPs) are considered in Sections 4.4.2, 4.4.3 and 4.4.4, respectively.

Several methods by which to increase the SO₂ strength of reverberatory smelting furnace offgases are discussed in Section 4.5. These methods, all of which involve modifying furnace operation, are summarized as follows:

1. Elimination of converter slag return (Section 4.5.1).
2. Sealing points of leakage (Section 4.5.2).
3. Preheating combustion air (Section 4.5.3).
4. Operation at lower air-to-fuel ratios (Section 4.5.4).
5. Predrying wet charges (Section 4.5.5).
6. Oxygen enrichment techniques (Section 4.5.6).

A number of oxygen enrichment techniques are discussed in detail in Section 4.5.6.1, while conclusions regarding the technical feasibility of these techniques with regards to possible domestic applications are presented in Section 4.5.6.3.

Blending of reverberatory furnace offgases with strong SO₂ streams from other processes within a smelter is discussed in Section 4.6. Gas blending is assessed as a means by which to allow autothermal processing of "weak" streams in contact sulfuric acid plants. Gas blending is analyzed for two scenarios:

1. A new smelter that process high impurity ore concentrations (Section 4.6.1).
2. Existing smelters that undergo physical or operational changes to achieve a greater production capacity (Section 4.6.2).

Case 1 above necessarily assesses the technical feasibility of blending the entire weak stream, while Case 2 assesses partial blending of the weak stream, i.e., blending enough of the weak stream to ensure that post-expansion SO₂ emissions are at or below the preexpansion SO₂ emission level.

The final Section in this Chapter, Section 4.7, describes techniques which are used for the control of fugitive SO₂ and particulate matter emissions from sources within primary copper smelters. Both local and general ventilation techniques are considered. The control of fugitive emissions from roasting, smelting, and converting operations are discussed in Sections 4.7.4, 4.7.5, and 4.7.6, respectively. A summary of visible emissions data for fugitive emissions sources within primary copper smelters is presented in Section 4.7.7.

4.2 SULFURIC ACID PLANTS

4.2.1 Summary

The contact sulfuric acid process involving the catalytic oxidation of SO₂ to SO₃ is the most widely utilized process for removing SO₂ from primary copper smelter effluent gases.¹ Sulfuric acid plants can be designed to process feed streams that contain only a fraction of a percent of SO₂; however, practical limitations have usually restricted application to gas streams that contain at least 3.5 percent SO₂. As the concentration of SO₂ in the feed stream decreases, energy requirements increase, which in turn could make the process prohibitively expensive if autothermal operation cannot be maintained. Thus, autothermal operation is considered essential from an economical standpoint. Metallurgical single-stage and dual-stage

absorption sulfuric acid plants constructed in the past have commonly been designed to operate autothermally on feed streams that contain 3.5 and 4.0 percent SO_2 , respectively. It is technically feasible, however, to design acid plants that will operate autothermally on fuel streams that exhibit SO_2 concentrations below the 3.5 to 4.0 percent range. Estimates have indicated that to lower the autothermal requirement for a dual-stage absorption acid plant from 4.0 percent SO_2 to 3.5 percent SO_2 would increase the plant installed capital cost by 9 to 12 percent. Similarly, the installed capital cost of a single-stage absorption plant would increase 5 to 7 percent if the autothermal requirement were lowered from 3.5 percent SO_2 to 3.0 percent SO_2 . (See Appendix __ for supporting calculations.)

Large fluctuations in feed stream volumetric flow rate and SO_2 concentration may adversely affect sulfuric acid plant operation at copper smelting facilities. Fluctuations of either type tend to lower the conversion of SO_2 to SO_3 , thus decreasing sulfur recovery and increasing SO_2 emissions to the atmosphere.

Acid plant operation on copper smelter effluent gases is not possible without adequate gas cleaning before the gases are sent to the contact section of the plant.³ Major problems that will result if the gases are not adequately cleaned include:

1. Aggravated corrosion of heat exchangers and carbon steel ducts
2. Plugging of catalyst beds
3. Partial deactivation of the catalyst.
4. Production of poor quality acid.

Proper design and maintenance of the gas purification system are necessary to minimize these problems.

Acid plant vendors typically guarantee maximum emission concentrations of 2,000 ppm for single-stage absorption plants and 500 ppm for dual-stage absorption plants.^{4 5} A conversion of approximately 98.5 percent is required to ensure the 500-ppm concentration in the acid plant effluent. The above-

mentioned guarantees take into account the large fluctuations in volumetric flow rate and SO₂ concentration; however, no allowance is made for increased emissions due to catalyst deterioration that occurs between regularly scheduled catalyst screening operations.⁵ During steady state operation, which is practically impossible due to the transient nature of copper smelter effluent gas streams, conversions of 99.8 percent and above are expected in dual-stage absorption plants.

Prior to exiting the acid plant stack, sulfuric acid mist formed downstream from the absorption tower(s) must be removed from the effluent gases. Sulfuric acid mist generally contains particles that are less than 5 µm in diameter and thus is very difficult to remove from the gas stream.⁶ Typical guarantees from domestic vendors of acid mist eliminators specify removal efficiencies (by weight only) of 99 percent or greater for high-efficiency mist eliminators.⁷ However, when submicron particles are involved, collection efficiencies based on weight and particle size must be considered. Monsanto Enviro-Chem's H-E Type Mist Eliminator guarantees collection efficiencies of at least 92 percent (by size and weight) over a particle size range of 0.1 µm to 10 µm.⁷ Guarantees of this magnitude limit mist loadings to 35 mg/m³ (0.015 gr/scf) or less, which virtually eliminates plumes of greater than 10-percent opacity.⁵

4.2.2 General Discussion

The basic steps involved in the contact process for producing sulfuric acid from SO₂-laden gases are:

1. Gas cleaning and conditioning
2. Gas drying
3. Catalytic oxidation of SO₂ to SO₃
4. Absorption of SO₃ into a sulfuric acid solution to form additional sulfuric acid.

These procedures are shown schematically in Figure 4-1. Adequate gas cleaning before the gas stream enters the contact section of the acid plant is essential. Particulate matter and volatilized metals must be efficiently removed to avoid costly shutdowns and maintenance.^{5 8} Generally, the feed gases first enter a weak acid scrubber where they are cooled to approximately

54° C (130° F) by water evaporation.^{3 4 8} The gases are then cooled to about 29° C (85° F) to reduce their water content to the required level. The subsequent cooling is generally accomplished in an additional packed- or tray-type scrubber with liquor coolers in the recirculated weak acid stream. Finally, the gases are passed through electrostatic mist precipitators to remove traces of dust and acid that may remain after cooling. The types of equipment used in the gas purification section of an acid plant may vary somewhat; however, typical installations use scrubbing towers, coolers, and electrostatic mist precipitators as the primary conditioning equipment.⁸

After the gases are cleaned, they must be dried before entering the contact section of the plant. This is accomplished by contacting the cleaned gases with 93-percent acid. Common procedure involves drying the gases to moisture contents below that required and then adding water prior to conversion.⁸ This procedure results in better control of the moisture content of the gases. The cooled, dried gases are then passed through a series of gas-to-gas heat exchangers where their temperature can be raised to the optimum temperature for the conversion of SO_2 to SO_3 . Single-stage absorption acid plants utilize three or four stages of catalyst, which constitute the converter. The clean, dry gases pass through the catalyst beds where the conversion of SO_2 to SO_3 takes place. Since the conversion of SO_2 to SO_3 is exothermic, the heat of reaction generated in each catalyst bed must be removed for the optimum conversion temperature to be maintained. This is accomplished by routing the exit gas stream from each catalyst bed through the tube side of the gas-to-gas heat exchangers that are used to raise the temperature of the incoming gases just prior to their entry into the contact section of the plant. The resultant SO_3 -laden stream that exits the converter is then passed to an absorber where the SO_3 is absorbed by strong sulfuric acid.

In a dual-stage absorption plant, the unabsorbed SO_3 and remaining SO_2 in the gas stream are reheated and reintroduced into the converter, where a portion of the remaining SO_2 is converted to SO_3 . The gases leaving this second stage of conversion are then passed to an interstage absorption tower where the SO_3 is absorbed from the gases. The exiting gases are then treated to remove acid mist prior to being vented to the atmosphere.

4.2.3 Design and Operating Considerations

Proper design of the gas purification section of an acid plant is essential in avoiding excessive shutdowns and maintenance. The presence of high levels of solid or gaseous contaminants in copper smelter offgases can present many difficulties in the design of the gas purification system. Generally, these contaminants must be removed before the gas stream enters the contact section of the plant. The offgases contain varying amounts of entrained dust as well as fumes formed by the vaporization of volatile components.⁵ Contaminants in the offgas stream include compounds of arsenic, cadmium, antimony, and mercury. Copper, lead, and zinc dusts are also commonly entrained in copper smelter offgas streams. Dust and fumes are generally reclaimed for their economic value through the use of cyclones, electrostatic precipitators, and baghouses. However, in many cases, additional cleaning is required to remove residual quantities of contaminants that would otherwise hinder the operation of the acid plant.

Special design considerations are necessary if the offgases contain appreciable amounts of halogens. If fluorine is present in the gas stream, two scrubbing towers in series may be required to achieve its complete removal.^{3 4} This must be done primarily to prevent poisoning of the catalyst in the contact section of the plant. A carbon brick lining must be used for the first scrubber since fluorine will attack the more commonly used acid-proof refractory linings. This scrubber is usually a venturi style or open spray type tower in which the gas stream is quenched to its saturation temperature. The second scrubber is usually a packed or tray-type tower. In this tower, the gases must be cooled to achieve the proper water content for acid production. If the dust and/or fluorine content of the gases is not excessive, both gas cooling and scrubbing can be accomplished in a single-packed or tray-type tower.

Because of the possible presence of halogens, the materials of construction are important considerations in the proper design of a gas purification system.⁴ If halogens are not present in significant quantities, 20-alloy stainless steel is suitable for pumps, valves, and the liquor coolers that are used to cool the gases to achieve the proper water content.³ However, if appreciable amounts of halogens are present in the gases, this

equipment must be constructed of higher alloy steels, graphite, or glass. Another alternative would be to line the equipment with an appropriate plastic. The scrubbing towers usually consist of a carbon steel shell with an impervious membrane and an acid brick lining, although plastic can be used for lining in some areas.

Although halogens and dust are almost completely removed in the scrubbers, some acid mist will remain entrained in the gas stream. Acid mist is formed when small amounts of SO_3 present in the gas stream react with water vapor in the gases to form sulfuric acid mist. Most of the acid mist is condensed in the scrubbers; however, a small portion does remain in the gas stream. Sulfuric acid mist generally consists of particles that are less than $5 \mu\text{m}$ in diameter and is very difficult to remove from a gas stream except by electrostatic precipitation.⁶ If acid mist was allowed to enter the contact section of the plant, it would cause aggravated corrosion of carbon steel ducts, heat exchangers, and the main blower. Thus, the mist must be removed as completely as possible by electrostatic precipitation. Gases exiting the scrubber(s) commonly contain $3,530 \text{ mg/Nm}^3$ (1.4 gr/scf) or more of H_2SO_4 as acid mist.⁴ This mist is generally removed by two electrostatic mist precipitators that are placed in series in order to improve efficiency and reliability. The mist precipitators are usually constructed of lead. Removal efficiency is commonly greater than 99 percent. The gases that enter the contact section of the plant should contain only SO_2 , O_2 , N_2 , and H_2O vapor. Major problems that will result if the gases are not sufficiently cleaned include:

1. Aggravated corrosion of heat exchangers and carbon steel ducts
2. Plugging of catalyst beds
3. Partial deactivation of the catalyst
4. Production of poor quality acid.

After the gases are dried in the contact section of the plant, they become essentially noncorrosive. Hence, carbon steel ducts can be used for the remainder of the plant. The total pressure drop through a clean, well-maintained dual-stage absorption plant is usually about 0.5 atm

(7.25 psig).³ Normally, an additional 0.060 to 0.075 atm (0.9 to 1.1 psig) are added in the design of the main blower to compensate for pressure buildup that may occur in the system.

When multihearth roasters are used, it is not uncommon for trace amounts of organic contaminants to pass through both the gas cleaning section of the plant and the catalyst beds. These contaminants will result in the production of dark, discolored acid ("black" acid). These trace organic contaminants are produced in multihearth roasters when various organic agents used in the floatation process are vaporized or only partially decomposed. Normally, within fluid-bed roasters, these organic floatation agents are completely decomposed, and thus the product acid is free of organic contaminants.⁵ Techniques do exist to purify or bleach discolored acid, but they are usually costly and may produce undesirable side effects. For example, organic contaminants can be oxidized by hydrogen peroxide; however, the oxidation is accompanied by the release of water which dilutes the product acid. However, there are outlets for sulfuric acid that are not sensitive to acid color, such as the production of fertilizers or refinery alkylation processes.⁵

A major consideration in the design of a metallurgical acid plant is the concentration of SO_2 in the acid plant feed gases. Although sulfuric acid plants can be designed to process feed streams that contain only a fraction of a percent of SO_2 , economical considerations have limited applications to higher concentrations. Metallurgical sulfuric acid plants that have been constructed in the past have commonly been designed to operate autothermally on feed streams that contain 3.5 to 4.0 percent SO_2 . Single-stage absorption plants are commonly designed to operate autothermally at 3.5 percent SO_2 , while dual-stage absorption plants are designed to operate autothermally at 4.0 percent SO_2 .^{3 4 5} It is possible, however, to lower these autothermal operating requirements by simply designing the plants to operate autothermally at lower feed stream SO_2 concentrations. This has not been the practice in the past since the incremental cost of reducing the autothermal requirements rises quite rapidly when SO_2 concentrations below the 3.5 to 4.0 percent range are considered. Thus, a somewhat larger capital investment is required to

build sulfuric acid plants that will operate autothermally below the 3.5 or 4.0 percent SO_2 levels.

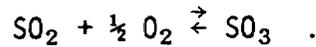
Estimates have indicated, however, that the incremental costs associated with lowering the autothermal requirements by 0.5 percent may not be excessive. To lower the autothermal operating requirement for a dual-stage absorption sulfuric acid plant from 4.0 to 3.5 percent SO_2 , the installed capital cost would increase 9 to 12 percent, depending upon the size of the plant. Similarly, the capital cost of a single-stage absorption plant would increase 5 to 7 percent if the autothermal requirement were lowered to 3.0 percent SO_2 . (See Appendix ___ for supporting calculations.)

If acid plants do not operate autothermally, supplemental heat must be supplied to maintain the appropriate conversion temperature in the catalyst beds, which in turn increases operating costs substantially.¹⁰ Offgas streams from reverberatory furnaces typically exhibit SO_2 concentrations in the 0.5 to 2.5 percent range.⁵ Consequently, an acid plant designed to operate autothermally on such a gas stream would cost substantially more than a plant designed to operate autothermally at 3.0 or 3.5 percent SO_2 . Also, as the concentration of SO_2 in the field stream decreases, the physical size of the required equipment increases, thus presenting practical limitations.²

The amount of gas cooling required in the gas purification section of the plant depends upon the SO_2 concentration in the inlet gas stream.^{3 4 5} Feed streams that contain less than 4 percent SO_2 frequently require extra cooling in order to remove excess water vapor. Gas streams containing less than 3 percent SO_2 may require refrigeration in order to condense enough water to obtain an acceptable water-to-sulfur ratio. Careful control of the gas stream water content is essential in preventing dilution of the product acid below commercial-grade strength.⁸

The oxygen content of the feed gases is also an important consideration in metallurgical acid plant design. Oxygen is generally fed in excess of the amount required by the reaction stoichiometry. Most plants operate at an oxygen-to-sulfur-dioxide ratio (O_2/SO_2) of not less than 1.1.¹¹ In some cases when the gas stream has an SO_2 concentration of 9 percent or more, it does not contain sufficient oxygen for the conversion of SO_2 to SO_3 . When this occurs, it is often necessary to dilute the gas stream with air or other offgases to enhance the oxygen content of the stream.⁵

Many of the considerations upon which acid plant converter design is based are themselves based upon the reaction kinetics and equilibrium thermodynamics of the conversion reaction. The conversion of SO₂ to SO₃ is represented by the following chemical equation:



The equilibrium constant K_p , which governs this reaction, is given by the following expression:

$$K_p = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} P_{\text{O}_2}^{\frac{1}{2}}} ,$$

where

P_{SO_3} = the equilibrium partial pressure of SO₃

P_{SO_2} = the equilibrium partial pressure of SO₂

P_{O_2} = the equilibrium partial pressure of O₂.

The optimum conversion temperature of approximately 438° C (820° F) is chosen to maximize K_p while maintaining an acceptable rate of reaction.⁹ In dual-stage absorption plants, the removal of SO₃ in the first absorption tower shifts the SO₂/SO₃ equilibrium in favor of SO₃ formation, resulting in a significantly higher conversion of SO₂ to SO₃.⁵

For maximum operating efficiency, metallurgical sulfuric acid plants should operate on a gas stream of uniform flow rate and composition. Large fluctuations of either type tend to lower the conversion of SO₂ to SO₃, thus decreasing acid production while increasing SO₂ emissions to the atmosphere. Therefore, metallurgical acid plants must be designed with the worst possible operating conditions in mind. This requires that adequate process control technology be incorporated into the design, which will allow operators to compensate for variations in SO₂ concentration. Variations in feed stream volume are generally less of a problem than variations in SO₂ concentration and can be tolerated within reasonable limits.⁵

Since capital and operating costs are directly related to the gas volume that is to be handled, a design that will significantly reduce the volume of gas in the plant will have a major effect on both cost factors.^{10 11} The most cost-effective design will maximize the SO₂ concentration in the feed stream while simultaneously reducing the total gas volume. One of the most effective means of reducing the total gas volume is oxygen enrichment of the combustion air that is utilized by smelting equipment.^{5 6} Elimination of dilution is another means by which the total gas volume may be reduced. Air infiltration can be minimized by an effective maintenance program and the use of tight-fitting gas collection hoods. The Onahama smelter was able to reduce the percentage of infiltrated air in reverberatory furnace offgas streams from 50 percent to 15 percent by reducing air infiltration.¹² Section 4.5 contains discussions of several methods that can be used to increase the SO₂ concentration in smelter offgases.

4.2.4 Acid Plant Performance Characteristics

Metallurgical acid plant vendors currently guarantee maximum SO₂ emissions concentrations of 2,000 ppm for single-stage absorption plants and 500 ppm for dual-stage absorption plants.^{4 5 13 14} However, it is essential to note that these guarantees refer to emissions that occur during new plant performance tests.⁵ Such tests are conducted for 3 to 5 consecutive days while the plant is operating on gases that contain the percentages of SO₂ specified in the design basis, and while the plant is not experiencing any malfunctions. It is essential to note that these guarantees are for maximum SO₂ emissions and thus include inherent allowances for increased emissions due to inlet SO₂ fluctuations.⁵ However, these guarantees do not include allowances for increased SO₂ emissions due to catalyst or plant deterioration with age. Furthermore, these guarantees are for acid plant performance only and obviously do not include emissions that are bypassed to the atmosphere during periods of acid plant shutdown for catalyst screening or replacement or other acid plant maintenance. One domestic manufacturer of metallurgical sulfuric acid plants guarantees maximum SO₂ emissions of 650 ppm from its dual-stage absorption plants for a period of 1 year after startup.¹³ This particular guarantee obviously includes allowances for increased SO₂ emissions that occur during

the 1-year period between startup and the first scheduled catalyst screening.

The degree of catalyst deterioration over a given period of time will depend largely on the levels of impurities present in the feed stream. Table 4-1 presents estimates of the maximum levels of impurities that can be tolerated in smelter offgases that are to be processed in a sulfuric acid plant. The degree of catalyst deterioration experienced at these various impurity levels can be accommodated by an acid plant that shuts down once per year to screen the catalyst and repair equipment.⁵ Table 4-1 also contains the estimated upper levels of impurities that can be removed by typical gas purification systems with prior coarse dust removal. As discussed previously, more elaborate cleaning systems must be designed if the feed stream contains contaminants that pose special problems, such as halogens. The details of the more elaborate designs vary depending upon the contaminants involved, but, generally speaking, the designs involve the use of more efficient dust or mist collectors and the scrubbing of gases with liquids that absorb the contaminants. Although complete removal of impurities from the feed stream is not practical, 99.5 to 99.9 percent overall removal is considered to be attainable.⁵

Since vendor guarantees on SO₂ emissions are commonly based on those emissions that occur during new plant performance tests, the effect of catalyst deterioration on SO₂ emissions must be determined in order to accurately assess acid plant performance capability over time. Sulfur dioxide emission data gathered by simultaneous EPA source testing of the No. 6 and No. 7 single-stage absorption acid plants at the Kennecott Garfield smelter during the period of June 13-16, 1972, indicate that normal catalyst deterioration and differences in acid plant design and technology can result in a 30-percent increase in SO₂ emissions.¹⁶ A summary of this analysis can be found in Appendix ____.

At the time of the EPA source testing, the No. 6 (Parsons) plant was in the second month of its 12-month catalyst cleaning cycle, and the No. 7 (Monsanto) plant was in the twelfth and last month of its catalyst cleaning cycle. A statistical analysis of the emission data leads to the conclusion that the 30-percent greater average emissions of the No. 7 plant, compared to the average emissions of the No. 6 plant, are statistically significant

TABLE 4-1 ESTIMATED MAXIMUM IMPURITY LIMITS FOR METALLURGICAL OFFGASES USED TO MANUFACTURE SULFURIC ACID¹⁵

Substance	Approximate limits (Mg/Nm ³) ^a	
	Acid plant inlet	Gas purification system inlet ^b
Chlorides, as Cl	1.2	125 ^d
Fluorides, as F	0.25	25 ^e
Arsenic, as As ₂ O ₃	1.2 ^c	200
Lead, as Pb	1.2	200
Mercury, as Hg	0.25	2.5 ^f
Selenium, as Se	50.0	100
Total solids	1.2	1,000 ^g
H ₂ SO ₄ mist, as 100% acid	50.0	-
Water, as H ₂ O	-	400,000

^aBasis: dry offgas stream containing 7 percent SO₂.

^bFor a typical gas purification system with prior coarse dust removal.

^cCan be objectionable in product acid.

^dMust be reduced to 6.0 if stainless steel is used.

^eCan be increased to 500 if silica products in scrubbing towers are replaced by carbon; must be reduced if stainless steel is used.

^fCan be increased to between 5 and 12 if lead ducts and precipitator bottoms are not used.

^gCan usually be increased to between 5,000 and 10,000 if weak acid settling tanks are used.

at the 90-percent probability level. It is important to note that this difference in emissions reflects not only catalyst deterioration, but also factors such as differences in emissions due to design or construction variations between Parsons 1967 acid plant technology and Monsanto 1970 acid plant technology. However, it is safe to assume that the major portion of this difference is due to catalyst deterioration.⁵

Although there are no analogous data available for dual-stage plants, metallurgical acid plant vendors have agreed that the EPA estimate of a 30-percent increase in SO₂ emission concentrations as the upper limit for deterioration of catalyst performance between catalyst screenings for single-stage acid plants is also a reasonable estimate for dual-stage acid plants.⁵ In most cases, the frequency of catalyst screenings is primarily a function of pressure drop rather than conversion efficiency. Normally, the first catalyst bed is constructed with a depth that is approximately 50 percent greater than the theoretical design depth in order to compensate for the anticipated decrease in conversion efficiency as the catalyst becomes partially plugged and the pressure drop increases between catalyst beds.⁵ Catalysts are guaranteed for various periods, although longer guarantees necessitate the use of more catalyst for a larger conversion efficiency over time. Screening periods generally vary from 1 to 2 years, depending upon blower capacity and the particulate collection efficiency of the gas purification system.⁵

Analysis of the previously mentioned EPA source tests (full text in Appendix ____) at Kennecott Garfield showed SO₂ emissions during normal operations of less than 2,000 ppm when averaged for long periods, such as a week.¹⁶ "Normal" operations were defined by analyzing acid plant operating logs to ascertain when upset conditions, i.e., malfunctions, startups, shutdowns, etc., were in evidence. It is significant to note that the long-term average SO₂ concentration is considerably less than the emission concentration (2,700 ppm) corresponding to the vendor guarantee of 95-percent conversion at an inlet concentration of 5 percent SO₂.

As mentioned previously, metallurgical sulfuric acid plants operate at maximum efficiency when the feed stream is uniform in flow rate and composition. However, offgas streams from some copper smelter operations, most notably

copper converting, exhibit large fluctuations in both volumetric flow rate and SO₂ concentration. While it is widely accepted that fluctuations in feed stream flow rate and SO₂ concentration adversely affect acid plant performance, little data exist to quantify the effect on SO₂ emissions.⁵ By further analysis of the Kennecott Garfield data, it is shown that instantaneous SO₂ emission concentrations varied greatly (<1,000 ppm to >7,000 ppm) depending upon fluctuations in the feed stream SO₂ content (<1 percent to >7 percent). Analysis showed that when the data were averaged over 4-hour periods, there were 13 data periods during which the average SO₂ emissions exceeded the vendor's guarantee (2,700 ppm).¹⁶ Increasing the averaging time to 6 hours decreased to seven the number of periods that exceeded the reference emission level (2,700 ppm). Increasing the reference SO₂ emission level from 2,700 ppm (the vendor's guarantee) to 3,000 ppm (approximately 10 percent greater) reduced the number of periods exceeding the reference emission level by approximately 50 percent. Further increases in either the averaging time or the reference SO₂ emission level selected for comparison did not significantly decrease the number of periods that exceeded the reference concentration. Further analysis of the same data, based on the actual time during which SO₂ emissions exceeded the reference concentration level, led to the same conclusions. Thus, from this analysis, which does not consider catalyst deterioration, it appears that an averaging time of 6 hours and a reference emission level that is 10 to 20 percent above commonly accepted vendor/contractor SO₂ emission guarantees effectively masks normal, short-term fluctuations in SO₂ emission.¹⁶

Sulfur dioxide emissions from a dual-absorption sulfuric acid plant operating on copper converter offgases were monitored by EPA through the use of a continuous monitoring system. This testing was performed at the ASARCO, El Paso, Texas, copper/lead smelter from mid-May through November 1973. The data were validated to ensure their accuracy and then analyzed by EPA. The analysis showed that 6-hour averages effectively mask the extreme fluctuations that are encountered with copper converter offgases. Sulfur dioxide emissions were limited to 250 ppm or less 95 percent of the time; however, the inlet SO₂ concentration was rather low and no catalyst deterioration was detected during the test period. Based upon readings

that were taken at 3-minute intervals, the inlet gas stream SO_2 concentration averaged 3.8 percent SO_2 for the entire test period. Further analysis that took into account a possible 10-percent increase in emissions due to catalyst deterioration and extrapolated the data to allow for the highest inlet SO_2 concentrations expected from copper, lead, or zinc primary smelting operations (~9-percent SO_2) showed that SO_2 emissions can be limited to 500 ppm or less 95 percent of the time and 650 ppm or less 98.8 percent of the time. A complete analysis of these data is included in Appendix ____.

Acid mist emissions from dual-stage absorption sulfuric acid plants are normally less than acid mist emissions from single-stage absorption plants since the mist loading of the second absorption tower is usually less.⁵ However, an acid mist eliminator must be installed following the first absorption tower in dual-stage acid plants in order to protect downstream equipment from corrosion. Absorption towers have inherent lags and are sensitive to many variables, including inlet SO_3 concentration, absorbing acid strength, temperature, and gas stream flow rate. However, currently available control technology is adequate to restrict acid mist emissions to low opacity wisps, except for infrequent upsets.⁵ Such upsets are caused when the absorbing acid concentration becomes greater than the azeotropic, thus allowing SO_3 to remain unabsorbed in the gas phase and to eventually create a visible acid mist plume as it combines with water after leaving the stack. It is important to note that mist eliminators are particulate collection devices and obviously cannot prevent acid mist emissions that occur during this type of upset condition, since the mist is produced by SO_3 combination with water after the gas stream exits the mist eliminator.

Manufacturers of mist eliminators commonly guarantee collection efficiencies of 99 percent or greater.⁷ However, it is important to note that these guarantees are generally based only on the total weight of entrained particulate removed from the gas stream. When guaranteed collection efficiencies are restated as percentages of particles collected by size rather than weight alone, they generally decrease substantially. Therefore, when a mist elimination device is chosen for a particular application, collection efficiency by particle size and weight should be considered. High-efficiency mist eliminators are available that provide high collection

efficiencies (by size and weight) over a large particle size range. Monsanto's H-E Type Mist Eliminator guarantees collection efficiencies (by size and weight) of at least 92 percent over a particle size range of 0.1 μm to 10 μm .⁷ Guarantees of this magnitude limit maximum stack emissions to 35 mg/m^3 (2.2×10^{-6} lb/ft³) or less.⁵ Lower efficiency models generally ensure emissions of 70 mg/m^3 (4.4×10^{-6} lb/ft³) or less. Under the worst conditions, the 70 mg/m^3 emission value can represent a 20-percent opaque plume, but normally the emissions from a high-efficiency mist eliminator are less than 10 percent opaque.⁵

The use of sulfuric acid plants to control SO_2 emissions from primary copper smelters is a well-demonstrated technology. Currently, 12 of the 15 active domestic primary copper smelters produce sulfuric acid from process offgases. Six of these twelve facilities use dual-stage absorption plants.

4.3 SCRUBBING SYSTEMS

4.3.1 Background

Historically, there has been little economic incentive to desulfurize process offgases containing sulfur dioxide in concentrations ranging from 0.05 to 3.5 percent. This category includes offgases which are generated by reverberatory smelting furnaces as well as offgases generated by fossil-fuel-fired steam generators, refinery sulfur recovery plants, sulfuric acid plants, and lead sinter machines. Prior to the last decade, the control of SO_2 emissions from these sources was practically nonexistent. However, techniques for removing SO_2 from "weak" SO_2 streams have received a great deal of attention over the last 10 to 15 years. Consequently, numerous methods have been devised to remove SO_2 from weak streams.

The approach most commonly used in cases where weak stream SO_2 control has been practiced has involved the use of scrubbing systems that chemically react the SO_2 with liquid phase absorbents to yield sulfur compounds that can be either discarded, reprocessed, or sold directly as obtained for use in other industries. The term "scrubbing system" is commonly used to describe such systems, since a scrubber (absorber) is used to effect the required pollutant mass transfer.

The three major types of scrubbing systems are summarized as follows:

1. Noncyclic systems--These open-loop systems generate a throw-away product. The scrubbing liquor makes only one pass through the scrubber.
2. Cyclic nonregenerative systems--These closed-loop systems produce a sulfur-containing compound that is either discarded or sold. As much of the scrubbing liquor as possible is recovered and recycled through the scrubber.
3. Cyclic regenerative systems--These closed-loop systems recover SO_2 and have a relatively small waste product for disposal. The absorbent is regenerated and the scrubbing liquor is recycled through the scrubber.

In as far as applications to weak streams of reverberatory furnace origin are concerned, consideration must be given to the fact that reverberatory furnace effluents contain a wide variety of contaminants in addition to SO_2 . The presence of high concentrations of oxygen (relative to O_2 concentrations commonly encountered in gases generated by fossil-fuel-fired generating plants), particulates, acid gases, metallic fumes, and high gas temperatures must be carefully considered, especially where cyclic absorption systems are being considered. In most scrubbing systems, some type of offgas conditioning would be required prior to the absorption of SO_2 in the scrubbing media.

Over the past decade, several scrubbing schemes utilizing various absorbents have been applied to metallurgical weak streams on either a pilot- or full-scale basis. Two types of scrubbing systems have been applied to reverberatory furnace effluents on a full-scale basis. One is a calcium-based system which uses a lime/limestone slurry as the scrubbing medium, and the other is a magnesium-based system which uses a magnesium oxide slurry as the scrubbing medium. The calcium-based system is a cyclic nonregenerative type; the magnesium-based system is a cyclic regenerative type. Both systems are located at the Onahama smelter in Japan. Other scrubbing systems that have been applied to metallurgical weak streams on either a pilot- or full-scale basis are citrate-type systems and ammonia-based systems. Discussions of the four above-mentioned types of scrubbing systems are presented in the following sections.

4.3.2 Calcium-Based Scrubbing Systems

4.3.2.1 Summary. Calcium-based scrubbing systems have been demonstrated for the control of SO₂ emissions from fossil-fuel-fired power plants since the 1930s. During the last 10 years, applications to metallurgical offgas streams have also been demonstrated. In the United States, a calcium-based scrubbing system has been controlling a weak SO₂ stream (<0.6 percent) from a molybdenum ore roaster since 1972.⁵ Operation of this particular system at the Duval Corporation near Tucson, Arizona, has also demonstrated the feasibility of operating a calcium-based system in an area where water is scarce.

Perhaps the most significant application of calcium-based scrubbing technology to occur on metallurgical processes over the past few years has been the system installed at the Onahama smelter in Japan in late 1972. This system controls a portion of a weak SO₂ stream that originates from three green-charged reverberatory furnaces. Both system reliability and SO₂ removal efficiency are reported to be high.¹⁹

It has been demonstrated for some time that calcium-based scrubbing systems are viable control methods for gas streams with low SO₂ concentrations (500 to 5,000 ppm). However, the lime/limestone system at Onahama was the first system to fully demonstrate control of a weak SO₂ stream from reverberatory furnaces. Experience at Onahama has also demonstrated that by proper furnace scheduling, a relatively steady SO₂ concentration can be maintained in the weak stream.¹⁹ ⁶ Also, since the SO₂ removal efficiency of these systems will increase at SO₂ feed stream concentrations below those found in the effluent from green-charged reverberatory furnaces, there is no reason to suspect that application of this technology to calcine-charged reverberatory furnaces would not be successful.

4.3.2.2 General Discussion. Calcium-based scrubbing systems may be of two types: noncyclic or cyclic-nonregenerative. In the noncyclic system, the absorbent passes through the scrubber on a once-through basis. Early work on this type of system was conducted by the London Power Company in the 1930s;⁵ ²³ alkaline Thames River water provided the absorbent. The system removed a high percentage of the sulfur dioxide (about 90 percent), but the acidic effluent from the process lowered the pH of the Thames to an

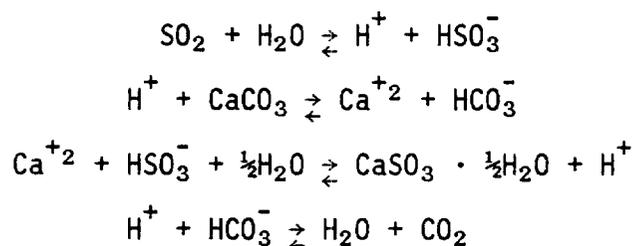
undesirably low level. The noncyclic system has inherent water pollution problems in some situations that would preclude its use on a large scale. This system also has the drawbacks of requiring a very large amount of water and of cooling the gas to an unduly low temperature.

Also in the 1930s, technology was developed on cyclic-nonregenerative scrubbing systems that employed calcium-based absorbents. The two most widely accepted cyclic-nonregenerative calcium-based scrubbing systems employ either calcium carbonate (limestone) or calcium hydroxide (slaked lime) as the absorbent. Simplified flow diagrams for the lime/ limestone slurry scrubbing processes are presented in Figure 4-2. The principal process steps are as follows:

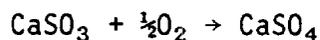
1. SO₂ absorption
2. Demisting
3. Liquor loop operation
4. Lime/limestone handling operations.

SO₂ absorption occurs when the SO₂-laden process offgases are vented to a scrubber where they are scrubbed countercurrently with the absorbent slurry.

The chemistry of the absorption step is quite complicated. As many as 28 chemical equations have been postulated by some authorities to characterize the reactions involved. The following rather simple mechanism is thought to be representative of the reactions that occur:⁸

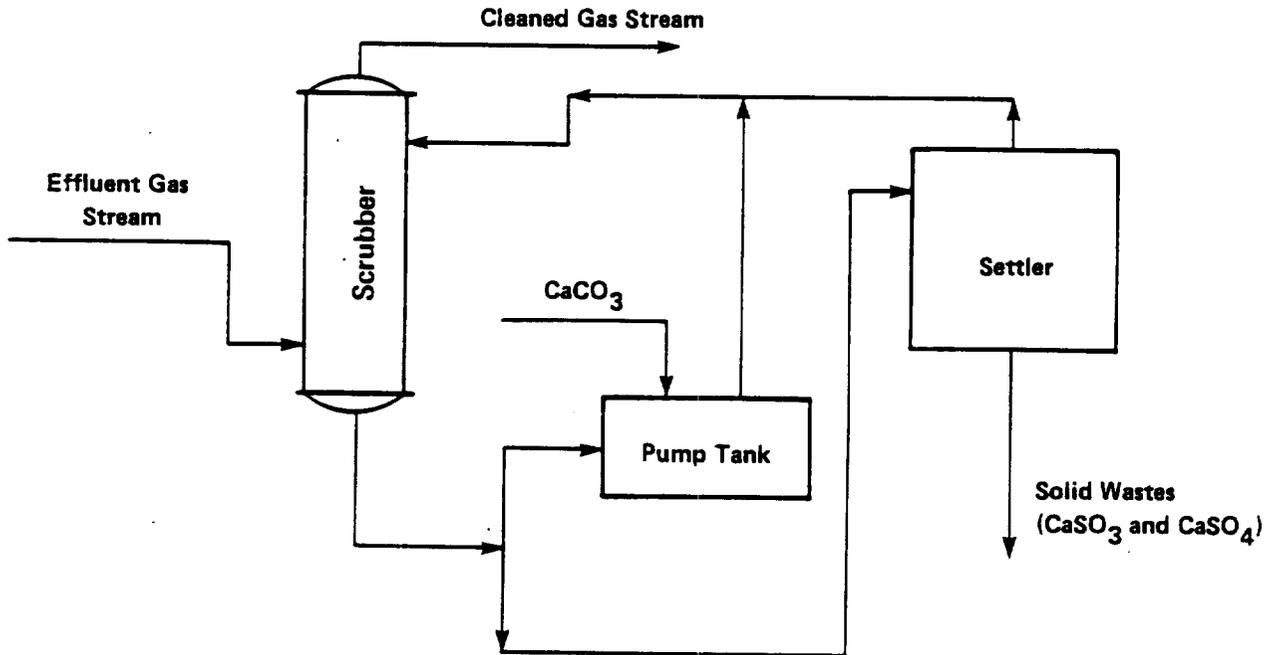


Some of the calcium sulfite formed will oxidize to form calcium sulfate as follows:



The reactions that take place within the absorbers are heterogeneous in nature because they involve the gas, liquid, and solid phases that are

I. Scrubber Addition of Limestone



II. Scrubber Addition of Lime

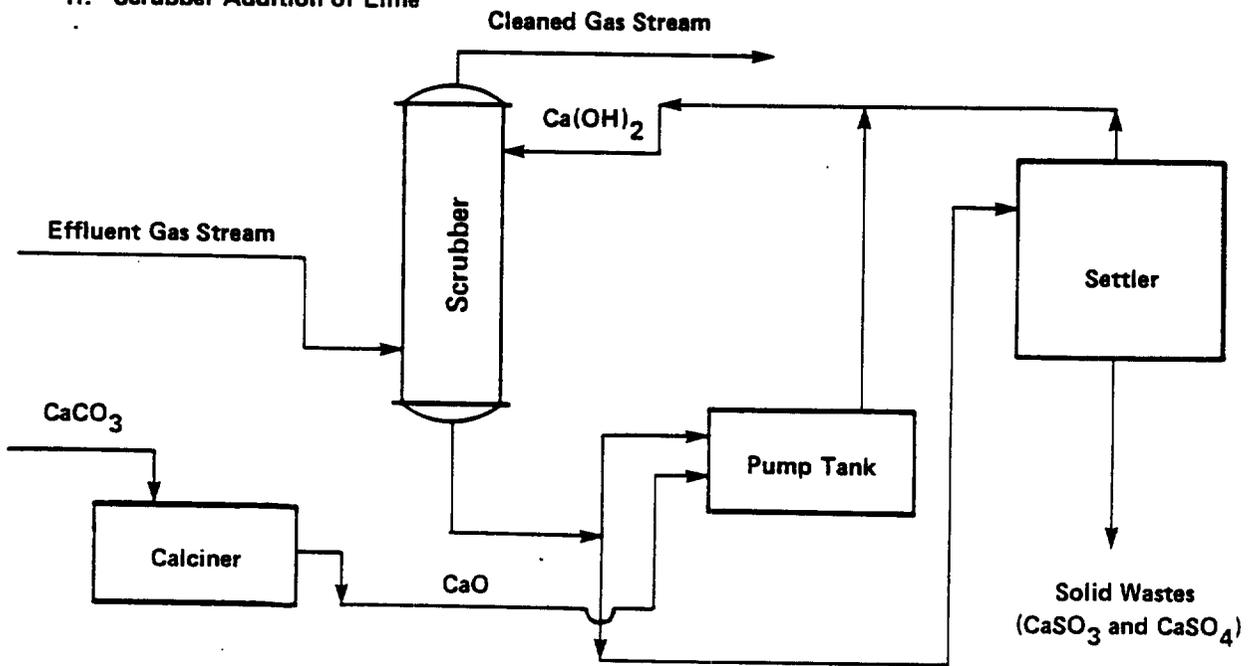


Figure 4-2. Calcium-based scrubbing processes.

present. The scrubbed gases are then trapped in a chevron mist eliminator which is washed with clear water to prevent the escape of acidic droplets to the atmosphere. The resultant gas stream is then vented to the atmosphere. Liquor loop operation involves splitting the SO_2 -laden slurry, with a portion going to the pump tank and a portion going to the settler. If the limestone scrubbing process is used, calcium carbonate is added to the pump tank as makeup; if the lime scrubbing process is used, calcium oxide is added as makeup. Effluent from the pump tank and settler is recycled to the scrubber in both types of processes. In most cases, solids in the pregnant slurry [calcium sulfite (CaSO_3) and gypsum (CaSO_4)] are removed in the settler and pass to disposal. It is possible, however, to oxidize the slurry to create a solid product that consists almost entirely of gypsum. This is normally done when the gypsum can be sold, as is the case at the Onahama smelter in Japan. Limestone-handling operations consist of field storage and transfer of mined limestone to a milling and sizing plant for preparation. If the lime scrubbing process is to be used, the limestone must be calcined onsite to calcium oxide, or lime must be purchased directly instead of limestone.

For a given set of scrubber operating parameters, lime scrubbing, though increasing scrubbing efficiency, may necessitate calcining of the limestone with resulting increased costs.⁵ Limestone is the absorbent chosen in most cases. Although it is not as reactive as lime, it is less costly. In some areas the cost of lime as CaO is twice or more than that of limestone.¹⁸ For applications in the utilities industry where high-sulfur coals are involved, the cost differential between the two absorbents becomes such a major item that it usually outweighs the advantages commonly associated with lime, namely slightly lower capital costs, higher SO_2 -removal efficiency, a lower liquid-to-gas flow (L/G) requirement, and probable higher reliability.¹⁸ It should be noted, however, that in the western part of the country where most of the primary copper smelters are located, relatively long shipping distances reduce the cost differential, since limestone (CaCO_3) weighs nearly twice as much as lime (CaO).

4.3.2.3 Design and Operating Considerations. Several factors may significantly affect the SO_2 -removal efficiency of limestone scrubbing systems. These may be summarized as follows:

1. Design of the scrubber proper
2. Type and size of the limestone used
3. Inlet gas temperature
4. pH of the absorbent slurry
5. Solids content of the absorbent slurry.

The design of the scrubber is critical to the limestone scrubbing process. Sulfur dioxide removal efficiency must be maximized by improving the SO_2 gas phase mass transfer rate at the liquid interface, which is dependent upon the scrubber type selected and its operating parameters. The ratio of liquid-to-gas flow, L/G, is important because of its effect of reducing the gas phase resistance to the mass transfer of SO_2 . Sulfur dioxide removal efficiency is favored by high L/G and low inlet SO_2 concentration.^{5 8 18} As the SO_2 concentration in the feed gases increases, removal efficiency will decrease. A fairly high ratio, about 6,700 $\ell/1,000 \text{ Nm}^3$ (50 gal/1,000 scf), has been necessary in most power plant applications to achieve a high degree of SO_2 removal (>80 percent). Generally speaking, the higher the SO_2 concentration in the feed gases, the higher the L/G will have to be in order to maintain an acceptable SO_2 removal efficiency.

The type and particle size of the limestone used as the absorbent will affect SO_2 -removal efficiency as well as determine how efficiently the absorbent is used. The ability of carbonate stones to chemisorb SO_2 varies greatly. For example, calcite (CaCO_3) stones have been shown to be superior to dolomite (MgCO_3) stones as far as SO_2 -removal efficiency is concerned.⁵ Calcite stones maintain a consistently high SO_2 -removal efficiency until nearly exhausted. The degree to which the limestone is ground will affect the SO_2 -absorption capacity of the absorbent slurry. The limestone must be finely ground; however, studies have shown that the absorption capacity does not change appreciably when the particle size is less than 100 mesh. Personnel at the Onahama smelter report that limestone shows nearly as good an SO_2 -absorption capacity as slaked lime [Ca(OH)_2] if it is ground to minus 325 mesh.¹⁹ Particle size does not appear to be critical when lime is used, apparently because the particle size of most slaked limes is inherently small.⁵

Test data have indicated that SO₂-removal efficiency decreases linearly as the temperature of the feed gas stream increases.⁵ The equilibrium considerations that govern the degree of SO₂ absorption depend upon the partial pressure of SO₂ in the inlet gas stream, which in turn depends upon the inlet gas stream temperature. The partial pressure of SO₂ increases by about 18 percent for a temperature increase of 5.6° C (10° F). If the partial pressure of SO₂ is allowed to increase too much, SO₂-removal efficiency will eventually become zero, and the inlet gas stream will actually begin to strip SO₂ from the absorbent slurry. Thus, in some cases, pre-cooling of the inlet gases may be necessary.

As mentioned above, the degree and rate of SO₂ absorption depend upon the difference between the partial pressure of SO₂ in the gas stream and the vapor pressure of SO₂ above the absorbent slurry. The pH of the absorbent slurry has a distinct effect on the vapor pressure of SO₂ above the slurry, and thus pH can affect the degree of SO₂ removal. The vapor pressure of SO₂ above the absorbent slurry must be kept quite low in order to provide a driving force for absorption, especially if the SO₂ concentration in the feed gases is low as in reverberatory furnace offgases. The effect of slurry pH on the SO₂ equilibrium vapor pressure, P^{*}SO₂, is shown in Figure 4-3. As indicated, the SO₂ vapor pressure is highest at low pH. Control of pH is normally accomplished by adding makeup lime/limestone slurry at the pump tank.^{6 23}

High slurry solids loadings provide improved rates of solubility for calcium, thus providing more effective replenishment of the calcium ion.⁵ The most efficient SO₂ removal has consistently been obtained with slurry solids loadings of 12 to 15 percent.

4.3.2.4 Operational Problems. A considerable amount of progress has been made in reducing the frequency of operational problems that have tended to reduce the reliability of calcium-based scrubbing systems in the past. Currently, the primary cause of forced outages is mechanical failure of pumps and other operating equipment, while corrosion and erosion are probably the next most significant causes.¹⁸ Chemical difficulties, e.g., scaling, that are related to the complex system chemistry have also been a source of trouble. Many of the parameters that affect the SO₂ absorption

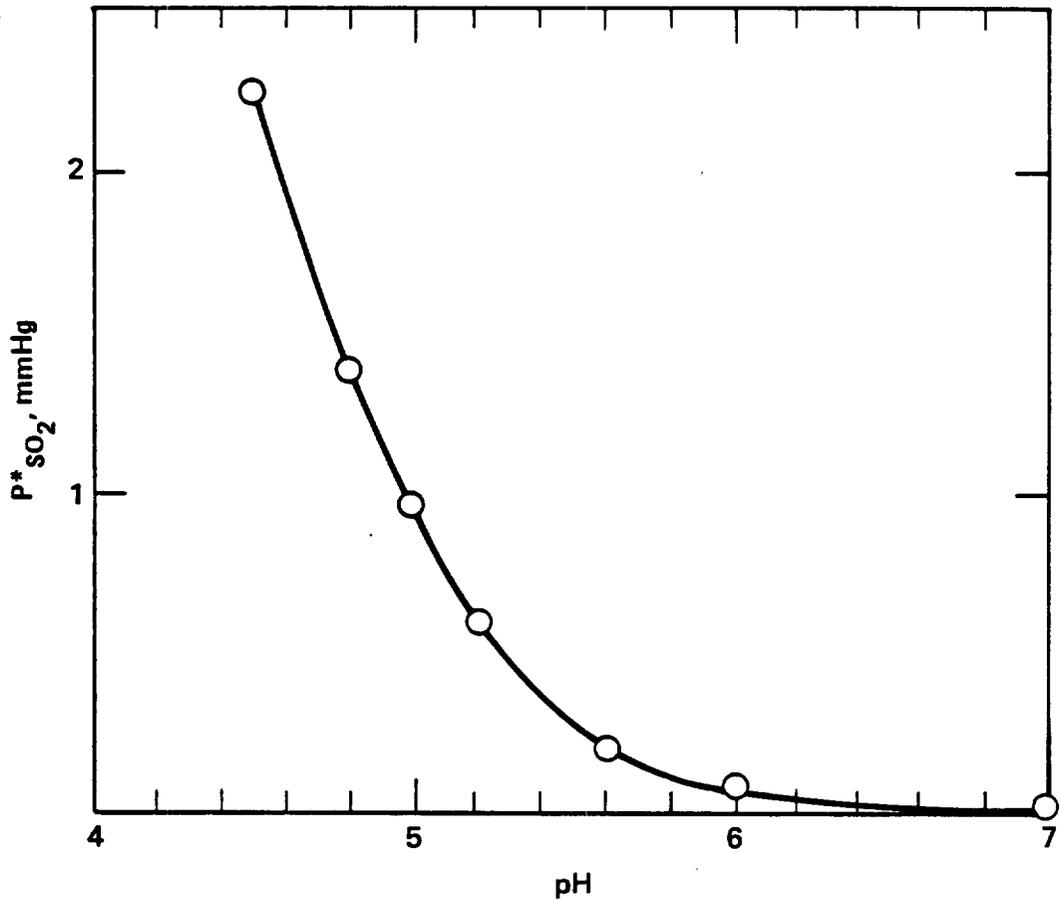


Figure 4-3. Effect of pH of calcium sulfite-bisulfite solution on SO₂ equilibrium vapor pressure.²³

efficiency also affect the frequency and extent to which operational difficulties occur.

Because of the high L/G requirement, very large pumps are commonly used in calcium-based scrubbing systems. Failures may occur due to the large stresses that must be placed on the pumps. The most common types of failure involve rotary parts and rubber linings.¹⁸ An important aid in maintaining the best possible reliability is a well-planned program of preventive maintenance. Also, spares should be provided wherever feasible, especially for pumps. Simplicity of design is important in areas where frequent maintenance is likely. For this reason, simple spray-type scrubbers are preferred even though they are less efficient in effecting mass transfer.¹⁸

Lime/limestone scrubber slurry is both corrosive and erosive in nature. As a result, some system components may require frequent maintenance and/or replacement. Stainless steel is required to prevent corrosion where metal contacts acidic solutions.⁸ While a high slurry solids loading tends to enhance SO₂ absorption, it may also increase the rate of erosion within process equipment. Erosion is reduced by applying elastomer linings in pumps, piping, and other surfaces that are subjected to heavy slurry impingement. High-temperature surfaces are protected with acid-proof gunite or glassflake reinforced polyester resin linings.

Solids deposition and the resultant plugging of equipment have been major problems in the operation of calcium-based scrubbing systems. These problems may be especially troublesome in limestone scrubbing systems. The deposition can occur at several locations within the system, namely at wet/dry interfaces, on scrubber surfaces, in scrubber packing, and in the mist eliminator.¹⁸ Solids deposition may occur when suspended material in the slurry is deposited either by sedimentation or by evaporation of the liquid phase, or it may occur as "scale" that is formed by crystallization of calcium sulfite and/or calcium sulfate.¹⁸ Scaling occurs when the pregnant scrubbing solution becomes supersaturated to a point at which heterogeneous crystallization takes place as a result of nucleation and crystal growth. Generally, utilities do not analyze the deposited solids; however, solids formed in the absorbers at the Onahama smelter have been analyzed.¹⁹ The results of these analyses are presented in Table 4-2.

TABLE 4-2. COMPOSITION OF SCALE FROM THE ONAHAMA
LIME-GYPSUM^a PROCESS¹⁹
(Percent)

Sample origin	CaO	CaSO ₄	CaSO ₃
Lower zone of no. 1 absorber	33.0	43.8	2.6
Upper zone of no. 2 absorber ^b	34.0	40.6	5.7
Upper zone of no. 2 absorber ^b	34.9	35.7	8.3
Lower zone of no. 2 absorber	36.6	29.3	17.0

^aLime was the absorbent used in this process at the time that these analyses were performed.

^bRepetitive samples from the same origin.

Note: CaO, CaSO₄, and CaSO₃ were not the only compounds present in the scale; thus the individual analyses do not add to 100 percent.

For scaling to occur, supersaturation in the pregnant scrubbing solution must reach certain levels for calcium sulfite and calcium sulfate. Conditions that promote scaling can be prevented by increasing L/G, which lowers the concentration of sulfite and sulfate formed per scrubbing cycle.⁸ The pregnant slurry can then be pumped to a holding tank where seeding with calcium sulfate crystals can be used to dissipate the supersaturation. If the formation of calcium sulfite crystals can be controlled such that their rate of formation is less than the rate of crystal growth on the seed crystals, desupersaturation will occur predominantly as a result of crystal nucleation on the seed crystals.⁶ However, if the calcium sulfite rate of formation exceeds the rate of crystallization on the seed crystals, the predominant mechanisms of desupersaturation will be either scaling on equipment surfaces or formation of small, new, freestanding crystals. Therefore, careful control of L/G, the slurry solids loading, and the seed crystal injection rate is necessary to ensure that desupersaturation occurs by crystal nucleation on seed crystals.

Careful control of the slurry pH has been identified as the most critical factor in the prevention of scaling.^{6 19} Operating experience at the Onahama smelter has shown that the best operating pH is slightly above 4.¹⁹ If the pH is less than 4, oxidation of calcium sulfite occurs in the scrubbers, resulting in calcium sulfate scale formation. Also, at low pH values SO₂-removal efficiency may be adversely affected. If the slurry pH is appreciably above 4, calcium sulfite will become insoluble, resulting in calcium sulfite scale formation. A rapid decrease in pH caused by SO₂ absorption followed by a rapid increase in pH due to limestone addition can cause sulfite precipitation on the limestone slurry particles as well as on the equipment surfaces. This will result in blinding of the reactive surfaces and thus lead to inefficient absorbent use. Consequently, it is desirable to maintain the slurry pH just above 4 without large fluctuations.

The inlet gas stream temperature also has an effect on scaling. The evaporation of water from the slurry due to high inlet gas stream temperatures will create wet-dry interfaces at which scaling tends to occur.⁵

Prevention of scaling is essential in maintaining stable operation and high SO₂ removal efficiency. Careful pH control coupled with induced

desupersaturation of the slurry at a point outside of the scrubbing circuit have been shown to be extremely effective means of minimizing scaling.¹⁹

4.3.2.5 Survey of Operating Experience

4.3.2.5.1 Domestic utility-related applications. The U.S. utility industry has tried many approaches to flue gas desulfurization over the past decade. The relative simplicity and lower costs of limestone-based scrubbing systems have made these systems the most popular.²⁴ Table 4-3 lists the major domestic utility-related FGD installations that employ the limestone scrubbing process. The technology currently preferred by the U.S. utility industry has the following features:¹⁸

- Simplicity of scrubber design. Single-stage spray scrubbers with a minimum of interior parts are the most frequently used type.
- Low-pressure drop to conserve energy. This is another reason for selecting spray scrubbers.
- High liquid-to-gas flow rate (L/G) to get adequate mass transfer and to avoid scaling.
- Direct entry of hot gas into the scrubber, with provision to prevent splashback into the inlet duct so as to avoid wet/dry interface deposition.
- Adequate retention time in the slurry recirculation tank to allow time for the limestone to neutralize sulfurous acid picked up in the scrubber and for dissipation of the sulfate and sulfite supersaturation developed during passage through the scrubber.
- High slurry solids content (12 to 15 percent) in the scrubber loop to provide seed crystals on which dissolved sulfite and sulfate can precipitate.
- High use of limestone to prevent scaling in the mist eliminator. This requires a fairly low pH (5.0 to 5.5) in the circulation tank, which has an adverse effect on SO₂-removal efficiency. To offset this, means to increase mass transfer are used such as very high L/G, staged scrubbing, or chemical additives.
- Use of simple chevron-type mist eliminators mounted in a horizontal position in the top of the scrubber and washed intermittently with jets of fresh water at relatively high pressure.

TABLE 4-3. MAJOR DOMESTIC UTILITY-RELATED FGD INSTALLATIONS
THAT USE THE LIMESTONE-SCRUBBING PROCESS.²⁴

Station/unit Power company	Size (MW)	Startup date	New or retrofit	Percent sulfur in coal	Design SO ₂ removal efficiency (percent)
Cholla No. 1 Arizona Public Service	115	10/73	Retrofit	0.4-1	58.5 overall 92 in the absorber
Duck Creek No. 1A Central Illinois Light	400	8/78 ^a	New	2.5-3	75
La Cygne No. 1 Kansas City Power & Light	820	2/73	New	5.0	76
Lawrence No. 4 Kansas Power & Light	125	12/68	Retrofit	0.5	76
Lawrence No. 5 Kansas Power & Light	400	11/71	New	0.5	65
Martin Lake No. 1 Texas Utilities	793	10/77	New	1.0	60
Sherburne No. 1 Northern States Power Company	710	3/76	New	0.8	50
Sherburne No. 2 Northern States Power Company	680	9/77	New	0.8	50
Southwest No. 1 Springfield City Utilities	200	4/77	New	3.5	80
Widows Creek No. 8 Tennessee Valley Authority	550	5/77	Retrofit	3.7	80
Will County No. 1 Commonwealth Edison	167	2/72	Retrofit	4.0	82
Winyah No. 2 South Carolina Public Service	280	7/77	New	1.0	70

^aOne module operated from September 1976 to April 1977.

Note: This table presents domestic installations as they existed in 1978.

Commonwealth Edison's Will County No. 1 station, which started up in February 1972, consists of two identical parallel wet scrubbing systems.⁵ Each system consists of a venturi for particulate removal, followed in series by a turbulent contact absorber (TCA) for SO₂ absorption. The SO₂ control system is guaranteed to achieve 80 to 85 percent SO₂ removal.^{5 24} This removal efficiency has been achieved; however, operational problems have prevented continuous operation in the past.⁵ These problems included demister plugging, nozzle plugging by construction debris, power loss to the pond reclaim pumps, vibration, loosened screens in the pump and in the recirculation tank, reheater plugging, failure of expansion joints, and breakage of the paddle on the slurry tank mixer. However, only the demister plugging problem proved to be chronic, and the solution to the problem involved redesigning the demister washers. Scaling has not been a serious problem with the system.

Kansas City Power and Light's La Cygne Unit No. 1, which began operation in February 1973, has proved to be one of the most reliable large domestic utility FGD systems.²⁴ The system was designed to achieve a 76-percent SO₂ removal efficiency. The La Cygne unit was plagued with numerous startup problems, most of which were not due to FGD system operation. However, despite the problems at startup, the availability of the system improved steadily. Availability increased from approximately 76 percent in 1974 to about 93 percent in 1977. The actual SO₂ removal efficiency has varied from 70 to 83 percent.²⁴

The Northern States Power Company Sherburne County Station No. 1 and No. 2 units have demonstrated excellent reliability. Availability for Unit No. 1, which began operation in March 1976, averaged 85 percent during the first 4 months after startup.²⁴ Reliability over the subsequent 12-month period was in excess of 90 percent. Unit No. 2 demonstrated availabilities in excess of 95 percent during its first 4 months of operation. Both units were designed to achieve 50-percent SO₂ removal. Actual SO₂ removal efficiencies have been in the 50- to 55-percent range.

Based on the operating experience of domestic utility-related limestone scrubbing systems, there seems to be sufficient evidence to suggest that these systems can operate at their design SO₂ removal efficiencies

while simultaneously maintaining a high degree of reliability, generally in excess of 90 percent.²⁴ As suggested by Table 4-3, the majority of the full-scale utility-related limestone FGD systems in place are not designed to achieve overall SO₂ removal efficiencies in excess of 90 percent. There is, however, no evidence to suggest that SO₂ removal efficiencies of 90 percent or greater could not be achieved with lime/limestone systems. In fact, two limestone FGDs have achieved SO₂ removal efficiencies of 90 percent or greater during demonstration runs, while seven lime FGDs have achieved SO₂ removal efficiencies of 90 percent or greater. These units are summarized in Table 4-4.

In summary, the domestic utility-related experience indicates that both high SO₂ removal efficiencies and high system reliabilities are achievable. The critical factors behind the successful operation of these systems are proper system design and maintenance.

4.3.2.5.2 Applications to metallurgical offgases. Lime/limestone scrubbing technology has been applied to metallurgical offgas streams of foreign and domestic origin. The Duval Corporation, located near Tucson, Arizona, is operating two four-stage model 500 turbulent contact absorbers (TCAs) to remove SO₂ from offgas generated in molybdenum sulfide roasters.⁵ The units, designed by UOP, use lime slurry as the absorbent and are rated at 1,420 Nm³/min (50,000 scfm) each. The system began operation in July 1971 and experienced extensive problems with scaling and plugging. However, these problems have been overcome and the system is reported to be working well.¹⁸ This system processes offgases containing 0.35 to 0.75 percent SO₂, and generates an offgas stream with an SO₂ concentration of less than 200 ppm.⁶ Sulfur dioxide removal efficiencies are commonly in the range of 92 to 96 percent. The successful operation of this system demonstrates that scrubbing systems using water recycle can be successfully operated in areas where water is scarce.

In late 1972, the Onahama Smelting and Refining Company, Ltd., installed a lime-gypsum plant at its Onahama smelter for fixation of SO₂ in the reverberatory furnace offgas. This facility was the first commercial-scale plant of this type in Japan designed to treat smelter offgas containing up to 3-percent SO₂.¹⁹ A flow chart of this system is presented in

TABLE 4-4. LIME/LIMESTONE FGD SYSTEMS THAT HAVE ACHIEVED SO₂ REMOVAL EFFICIENCIES OF 90 PERCENT OR GREATER ON OFFGASES GENERATED BY COAL-FIRED STEAM GENERATORS²⁴

Utility company	Station	Unit number	Size (Mw)	Nature of application	Type of process	SO ₂ removal achieved (%)
Arizona Public Service	Cholla Four Corners	1	115	Full-scale	Limestone	92
		5	160	Demonstration	Lime	95
Duquesne Light	Phillips	1-6	410	Full-scale	Lime	90+
Louisville Gas and Electric	Cane Run Paddy's Run	4	175	Full-scale	Lime	90
		6	65	Demonstration	Lime	99.5
Southern California Edison	Mohave Mohave	1	170	Demonstration	Limestone	95
		2	170	Demonstration	Lime	95
U.S. Air Force	Rickenbacker ^a	1-9	20	Full-scale	Lime	99
Kentucky Utilities	Green River	1-3	64	Full-scale	Lime	90+
Tennessee Valley Authority	Shawnee	10	10	Prototype	Lime/Limestone	95-99

^aDenotes a military base.

Note: Data in this table reflect the domestic FGD situation in 1977.

Figure 4-4. At the Onahama smelter, converter gases along with a portion of the reverberatory furnace offgases are routed to two acid plants where approximately 30 Gg (33,000 tons) of 98-percent sulfuric acid are produced per month. The remainder of the reverberatory offgases serve as the feed-stock for the gypsum plant. The feed stream flow rate varies from 1,800 to 2,400 dry m³/min at standard conditions.² Initially, only quick lime was used as absorbent. Soon after startup, however, a serious problem involving scaling in the absorbers evolved. Scaling problems were eventually solved by improving certain process characteristics and operating conditions.^{6 19} One important improvement involved the substitution of limestone for a portion of the more expensive quick lime. The Onahama system uses two stages of absorption in conjunction with the use of seed crystals to minimize scaling.

Currently, system reliability is high (~99.3 percent) while an SO₂ absorption efficiency of 99.5 percent is maintained. The average SO₂ emission concentration from the plant is in the 40-60 ppm range.⁶ Good-quality gypsum suitable for board or cement is produced by the subsequent oxidation of the calcium sulfite that is produced.¹⁹

In addition to the full-scale applications discussed above, some pilot-scale tests were conducted by the Smelter Control Research Association, Inc., (SCRA) at the Kennecott smelter located in McGill, Nevada. These tests were performed on reverberatory furnace offgases in order to investigate the effects of parameters such as L/G and feed stream SO₂ concentration on SO₂-removal efficiency. Results indicated that SO₂-removal efficiency was highest at low SO₂ inlet concentrations and high L/G ratios.⁸

4.3.2.6 Applicability to Reverberatory Smelting Furnaces.

4.3.2.6.1 Transfer of utility-related scrubbing technology. To assess the feasibility of applying utility-related scrubbing technology to weak SO₂ streams generated by reverberatory smelting furnaces, feed stream characteristics must be compared. There are several differences between the waste gases from power plants and from smelters in regards to composition, flow rate, and other characteristics.¹⁸

The average SO₂ content of reverberatory furnace offgas streams would be higher than the average SO₂ concentration in power plant effluents. The

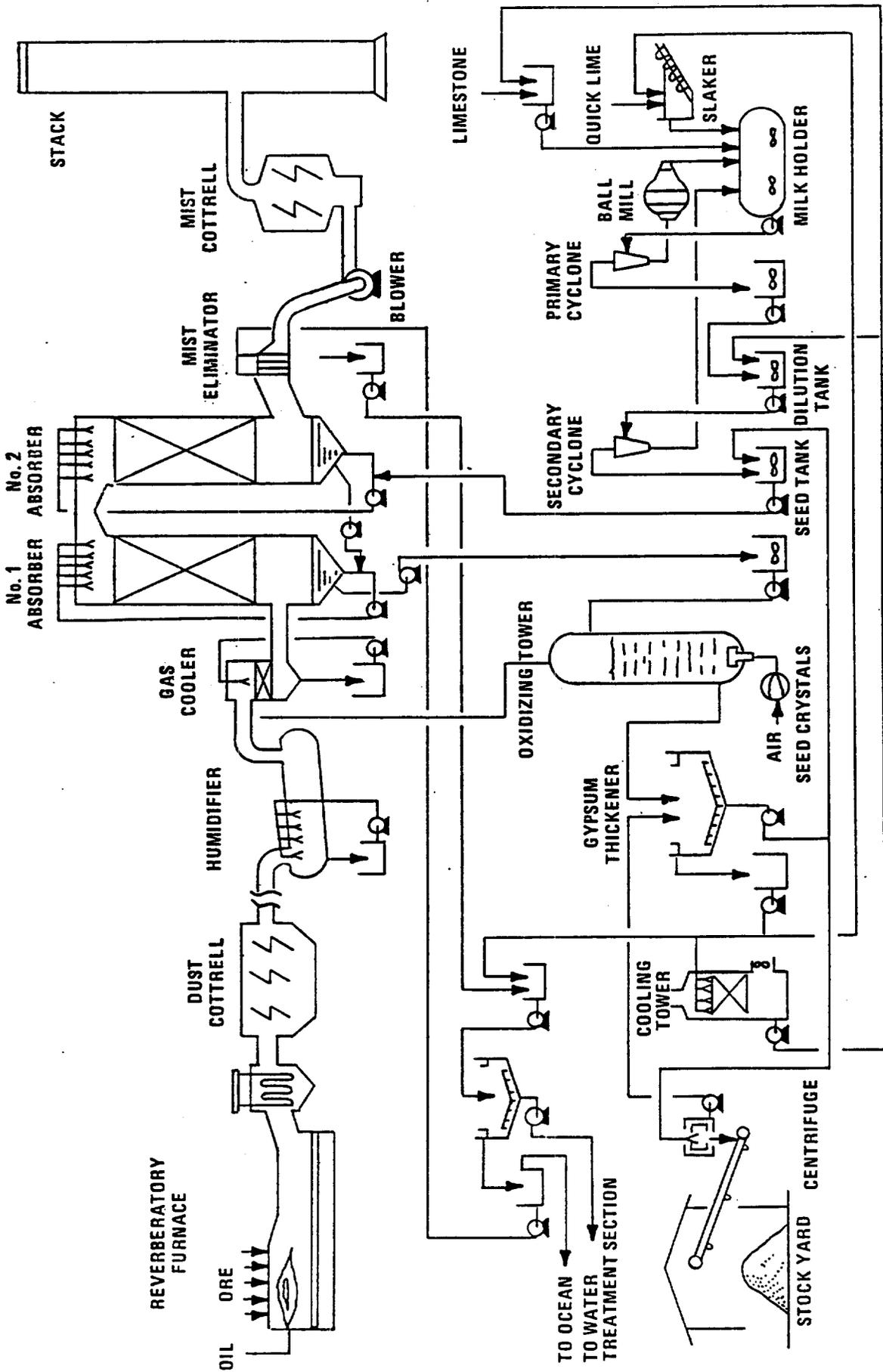


Figure 4-4. Flow diagram of the lime/gypsum plant at the Onahama smelter.¹⁹

concentration of SO_2 in reverberatory furnace offgas is typically in the range of 0.5 to 2.5 percent.⁵ Generally 1.5 percent is taken to be the average value, which is about four times the highest level found in the flue gas from coal-fired boilers.¹⁸

Utility-related scrubbing experience,¹⁸ along with pilot studies performed on reverberatory furnace effluent,⁸ indicate that operation at high SO_2 -removal efficiencies becomes progressively more difficult as the feed stream SO_2 concentration increases. Problems arise at higher SO_2 concentrations because the amount of sulfite and sulfate formed per scrubbing cycle, the "make-per-pass," becomes higher since L/G is almost never increased in proportion to the inlet SO_2 concentration.¹⁸ Thus, a single-stage scrubbing system would soon be loaded with sulfite and attendant scaling.⁸ At a feed stream composition of 1.5 percent SO_2 , it would be difficult to accomplish the required SO_2 removal without exceeding the allowable "make-per-pass," which would result in higher than desired levels of supersaturation that would in turn cause scaling problems. An extremely high L/G would be required to keep the "make-per-pass" within acceptable limits; however, at such a high L/G, flooding or excessive entrainment would occur.¹⁸ Therefore, multistaged scrubbing for reverberatory furnace effluent desulfurization is indicated, with each stage having its own reaction tank.^{8 18} This was confirmed by the SCRA studies cited previously. At Onahama, two absorbers are employed, each removing about 50 percent of the SO_2 contained in the feed stream.⁶ Several general conclusions were developed from the pilot studies which were conducted at the Kennecott-McGill smelter by the SCRA. Analysis of the data obtained led to the following conclusions, assuming 90-percent SO_2 removal from a reverberatory gas stream containing 1-percent SO_2 was desired⁸:

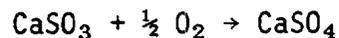
1. A venturi followed by several stages of absorption would be required.
2. A high L/G would have to be maintained.
3. A high-quality limestone ground to a moderate fineness would be required.
4. The feed stream SO_2 concentration would be stabilized as much as possible.

In contrast to utility boiler operations that produce offgas streams of a relatively steady SO₂ concentration, a reverberatory furnace can produce offgas streams of varying SO₂ concentrations. Immediately after charging, concentrations of SO₂ may be greater than the daily average.⁸ Such surges in SO₂ concentrations in reverberatory furnace offgases can potentially cause serious problems. Application of calcium-based scrubbing to such a stream is potentially difficult because control of the absorbent feed rate, which is usually accomplished by monitoring pH levels, may be too sluggish to keep up with the rapid changes in concentration.¹⁸ This problem can be alleviated by having excess capacity built into the absorbers,⁸ or by supplying a feed stream that does not exhibit such wide swings in concentration. The latter approach was taken at Onahama. Through proper scheduling, the Onahama smelter manages to keep the feed stream SO₂ concentration steady at about 2.5 percent.^{6 18} Wide variations in feed stream flow rate could also cause problems in system control; however, the gas flow from a reverberatory furnace is fairly uniform.^{5 6 18}

Some degree of feed gas pretreatment is necessary in order to process reverberatory furnace offgases in calcium-based scrubbing systems. It is expected that gases that are to be treated by slurry scrubbing for SO₂ removal would be precleaned in an electrostatic precipitator.⁸ However, gas pretreatment as part of a calcium-based scrubbing process would be primarily for cooling and humidification at approximately 54° C (130° F) in order to achieve high SO₂-removal efficiency and to prevent evaporation and scaling in the scrubber(s). If the solid product is to be of the throwaway type, exhaustive particulate removal is not warranted. Cooling to this extent is considered to be uneconomical in the utility industry since the gas stream must be reheated in order to improve its buoyancy as it exits the stack. Ordinarily, flue gas at about 149° C (300° F) is fed directly into the scrubber.¹⁸ After undergoing waste heat recovery and dust removal, reverberatory furnace offgases generally have a temperature of about 370° C (700° F). At Onahama, gases are cooled to approximately 45° C (113° F) prior to entering lime/limestone absorbers.¹⁹ Onahama representatives have indicated that this degree of cooling is necessary to maintain a high SO₂-removal efficiency.¹⁸

Disposal of solid wastes may also present a problem in the application of calcium-based scrubbing technology to weak SO₂ gas streams from reverberatory furnaces. Standard practice for sludge disposal in the utility industry involves mixing ash with the sludge and then landfilling the mix.¹⁸ Dry lime may also be added to the sludge prior to disposal.²² Mixing the sludge with ash prevents the sludge from maintaining a "swampy" consistency for long periods of time after disposal. The addition of lime gives the sludge a harder and stronger consistency. Since the dust content of reverberatory furnace offgases may be up to ten times greater than that of power plant effluents, one might contemplate mixing these dusts with the sludge and then dumping the dust/sludge mixture into abandoned mines or quarry pits.^{8 18} However, the metals content of smelter dusts is always high, prompting operators to recycle the dusts in order to recover metal values.

Several sources have reported that sludges composed mainly of gypsum tend to have better disposal properties than sludges composed primarily of calcium sulfite.^{6 8 22} Thus, forced oxidation of the calcium-sulfite slurry may be a means of improving the disposal properties of the slurry. When forced oxidation is used, gypsum is formed via the following reaction:



At the Onahama smelter, oxidation of the slurry is a principal feature of the process since gypsum is desired as a salable product. The oxidation is carried out in oxidation towers where the slurry reacts with oxygen to yield gypsum crystals.^{6 19}

In conclusion, the higher SO₂ concentration and other differences in reverberatory gas stream characteristics do not appear to be serious obstacles in as far as the transfer of current utility-related lime/ limestone scrubbing technology is concerned. The most significant problem appears to be that the rapid and sometimes large fluctuations in SO₂ concentration could create major process control problems for calcium-based scrubbing systems. However, through the proper scheduling of smelting operations, it is feasible to operate so as to produce a reverberatory furnace offgas stream that exhibits a relatively steady SO₂ concentration. Thus, the potential process-

control-related problems could be minimized or perhaps eliminated by the careful scheduling of operations.

4.3.2.6.2 Assessment of applicability based upon existing scrubbing systems that process metallurgical effluents. As indicated previously, the lime/ limestone scrubbing system that is currently in operation at the Onahama smelter is reported to be operating with high reliability as well as high SO₂-removal efficiency.^{18 19} Therefore, application of this technology for the control of weak SO₂ streams generated by reverberatory smelting furnaces should be considered technically demonstrated. The SO₂ concentration in the effluent from the green-charged reverberatory furnaces at Onahama varies from 2.5 to 2.8 percent, demonstrating the ability to stabilize the SO₂ concentration.⁶ Lowering the SO₂ concentration by diluting the feed stream would actually improve the SO₂-removal efficiency, but gas-handling equipment would have to be enlarged.⁶ Since the SO₂-removal efficiency of these systems is increased by lowering the SO₂ concentration in the feed stream, lime/limestone systems could be expected to operate satisfactorily on domestic calcine-charged reverberatory furnaces, which produce offgas streams with SO₂ concentrations that vary from 0.5 to 1.5 percent.⁶ The expected SO₂ removal efficiency on domestic green-charged reverberatory furnaces would naturally be the demonstrated efficiency obtained at Onahama, approximately 99.5 percent.¹⁹

The work at Duval indicates that the efficiency of a calcium-based scrubbing system operating with turbulent contact absorbers can be 92 to 96 percent with very little downtime.⁶ The system now in place at Duval has also demonstrated another important point. The operation of this system in an area where water is scarce has shown that the proper use of water recycle techniques does allow operation with high reliability in such areas. This is an important consideration because the bulk of the domestic smelters are located in the desert southwest part of the United States.

4.3.3 Ammonia-Based Scrubbing Systems

4.3.3.1 Summary. Ammonia-based scrubbing systems of the Cominco type (designed by the Consolidated Mining and Smelting Company of Canada, Ltd.) have been demonstrated for the control of SO₂ emissions from Dwight-Lloyd sintering machines, zinc roasters, and sulfuric acid plant tail gases since

the 1930s.⁵ The successful operation of these units has demonstrated their ability to maintain high SO₂-removal efficiencies while operating on metallurgical feed streams that exhibit wide variations in both volumetric flow rate and SO₂ concentration. Sulfur dioxide removal efficiencies in excess of 90 percent have been achieved and sustained in these applications at Cominco's facility in Trail, B.C. Cominco-type units can easily maintain high SO₂-removal efficiencies over the range of SO₂ concentrations encountered in reverberatory smelting furnace effluents.⁶

It is concluded that the Cominco-type process is a technically viable option for the control of SO₂ emissions from properly cleaned reverberatory furnace offgases.

Ammonia-based scrubbing systems of Cominco design, which use sulfuric acid in the acidulation step, produce a strong SO₂ stream and ammonium sulfate. If the ammonium sulfate produced is not marketable, operation of these systems may not be economically justified. In anticipation of this problem, investigations into an ammonia-based scrubbing system that uses ammonium bisulfite for acidulation rather than sulfuric acid have begun.²⁷ This type of system produces ammonia and ammonium bisulfite via thermal decomposition of the ammonium sulfite that is produced. The ammonia and ammonium bisulfite are then recycled back to the absorbent makeup and acidulation steps, respectively.

The ammonium-bisulfite acidulation scheme has not achieved large-scale application; however, a TVA/EPA-sponsored pilot study conducted at TVA's Colbert Power Plant has provided some data on the operation of this type of system. Extensive tests have been run on a 3,000 cfm unit to establish important operating parameters and develop solutions to process difficulties. The pilot plant generally operated with SO₂-removal efficiencies of 90 percent or higher, with a feed stream concentration of 0.2 to 0.3 percent SO₂, and an exit gas concentration of 200 to 300 ppm SO₂.⁸ Despite the extensive work accomplished to date, the ammonium bisulfite acidulation scheme cannot be considered fully developed for commercial application; however, this process is forecasted to be the SO₂-removal system of the future,²⁷ as it provides ammonium bisulfite and ammonia for recycle while simultaneously eliminating the need to market ammonium sulfate.

4.3.3.2 General Discussion. Ammonia-based scrubbing systems have received considerable attention in the history of SO₂ removal from process offgases. The reasons for this include the relatively high affinity of ammonia solutions for SO₂ and the ability to keep all the compounds involved in solution, thereby avoiding scaling and silting problems in scrubbers.⁵

Sulfur dioxide removal from gas streams by ammonia-based scrubbing has been studied intermittently by various groups since the 1880s.⁸ The earliest reference found was a British patent issued to Ramsey in 1883.^{6 8 25 27} The earliest studies were aimed at obtaining a regenerable system where the ammonium bisulfite solution from the absorber could be regenerated by heat in a stripping column.²⁷ However, during the course of the regeneration cycle, the ammonium salts produced would release ammonia that would subsequently contaminate the recovered SO₂. Consequently, the SO₂ produced was unfit for sulfur, liquid SO₂, or sulfuric acid production without further treatment. In addition, these earlier systems consumed a great deal of process steam while controlling SO₂-emission concentrations only to the 1,000- to 1,500-ppm range.²⁷ Oxidation of ammonium sulfite/bisulfite salts by oxygen in the gas stream was another problem that hampered the early systems. Oxidation reactions of this type were catalyzed by numerous contaminants, mostly metallic oxides,⁸ transferred to the solution by the gas stream. Additional investigation of the equilibria and chemistry involved in ammonia-based processes was necessary in order to alleviate many of the shortcomings associated with the earlier systems.

Commercial and experimental modifications have evolved over the years with the greatest developmental emphasis being placed on methods of regenerating the scrubbing liquor in order to reduce operating costs while producing a variety of useful products. Among the most widely studied methods of scrubber liquor regeneration are:⁸

1. Thermal stripping to yield primarily sulfur dioxide
2. Oxidation to yield primarily ammonium sulfate
3. Disproportionation to yield ammonium sulfate and elemental sulfur
4. Acidulation to yield sulfur dioxide and an ammonium salt.

Acidulation of the scrubber effluent has proven to be the most popular route, having treated metallurgical gases as well as sulfuric acid plant tail gases for over 50 years.²⁷ Two basic variants of this scheme exist; however, the basic unit processes involved are identical. The principal process steps of the acidulation scheme are:

1. Gas cleaning
2. Sulfur dioxide absorption
3. Acidulation of the absorber effluent
4. Stripping.

The most popular scenario involves absorber effluent acidulation with sulfuric acid.^{5 8 27} A simplified flow diagram of this process, more commonly known as the Cominco process, is presented in Figure 4-5. The gas stream is first conditioned in the gas cleaning section of the facility. Generally, the gases are cooled, fine solids are washed out, and any SO_3 that may be present is absorbed in water, forming weak sulfuric acid.⁵ The cool, clean gases then pass to the bottom of an absorption tower where they are contacted countercurrently with an ammoniacal solution. To improve SO_2 removal efficiency, absorption is commonly performed as a staged operation. The effluent from the absorption step consists of ammonium sulfite, ammonium bisulfite, and ammonium sulfate, with ammonium bisulfite being the primary constituent. All of these components are kept in solution, thus eliminating scaling problems such as those associated with calcium-based systems. Off-gases from the absorption step are vented to the atmosphere.

The acidulation step consists of pumping the absorber product liquor to a continuous stirred tank reactor where it is reacted with sulfuric acid. The ammonium sulfite/bisulfite/sulfate liquor from the absorbers reacts with the sulfuric acid to yield ammonium sulfate, sulfur dioxide, and water. The reactions involved in this step are rapid at ambient temperature and pressure.²⁷

An SO_2 stripper completes the basic system. Liquor from the acidulation step is fed to a packed column where the SO_2 is stripped from solution by contact with air or steam. The recovered SO_2 can be utilized for the production of sulfuric acid, liquid SO_2 , or elemental sulfur. The

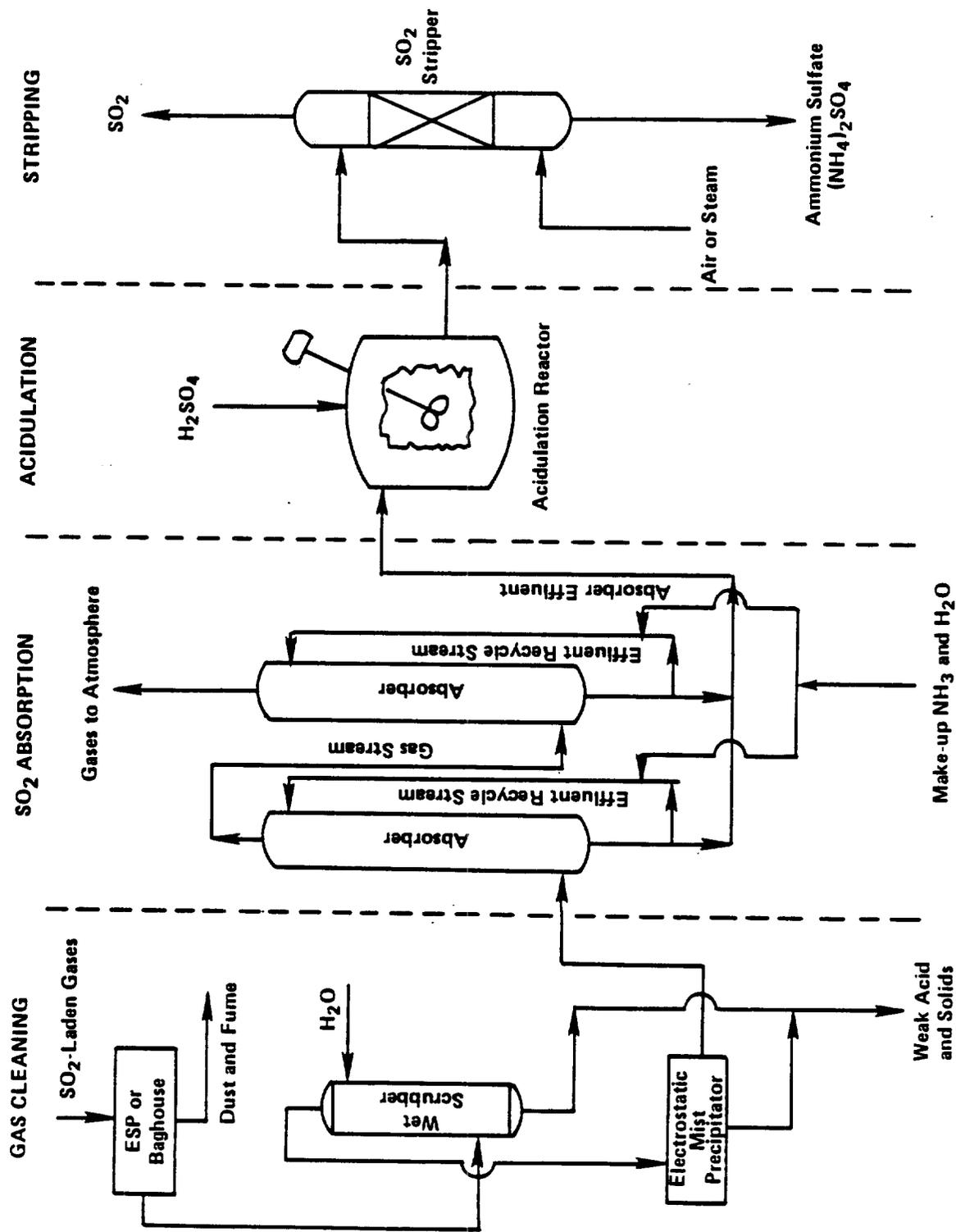


Figure 4-5. Ammonia scrubbing process with sulfuric acid acidulation.

liquid ammonium sulfate can be sold as is, fed to an ammonium phosphate fertilizer plant, or crystallized to a dry crystalline material and marketed.²⁷ If crystallization of the ammonium sulfate is desired, the system may include a single-effect or multieffect evaporator-crystallizer, a crystal centrifuge, a dryer, screens, conveyors, and a solid storage facility.

Another variation of ammonia scrubbing that uses acidulation with ammonium bisulfite rather than sulfuric acid might be used in areas where ammonium sulfate is not marketable.^{8 27} This type of system would use ammonium bisulfite to acidulate the absorber product liquor, thus producing SO₂ and ammonium sulfate. A simplified flow diagram of this process is presented in Figure 4-6. As indicated, the ammonium sulfate produced in the acidulation step would be decomposed at approximately 385° C (725° F) in an electrically heated or fuel-fired furnace via the following reaction:



The resulting ammonium bisulfite and ammonia are then recycled back to the acidulation and absorbent makeup steps, respectively. Laboratory tests have shown that ammonium bisulfite behaves very similarly to sulfuric acid in the acidulation step and should give comparable results.⁸

4.3.3.3 Design and Operating Considerations. Proper design and operation of the gas cleaning system is necessary to insure the reliable operation of ammonia-based scrubbing systems. The primary purposes of the gas cleaning step in ammonia-based processes are:

1. To cool and humidify the feed stream in order to prevent excessive evaporation of the absorbent
2. To remove residual particulate matter that may catalyze the oxidation of ammonium sulfite to ammonium sulfate in the absorbers.

Waste gases from any process must be cooled to a reasonable temperature prior to being fed to an absorption tower in order to avoid excessive evaporation of the scrubbing solution. With regards to ammonia-based scrubbing, the optimum feed stream temperature is established as a tradeoff between mass transfer considerations and the costs of precooling.⁸ Since

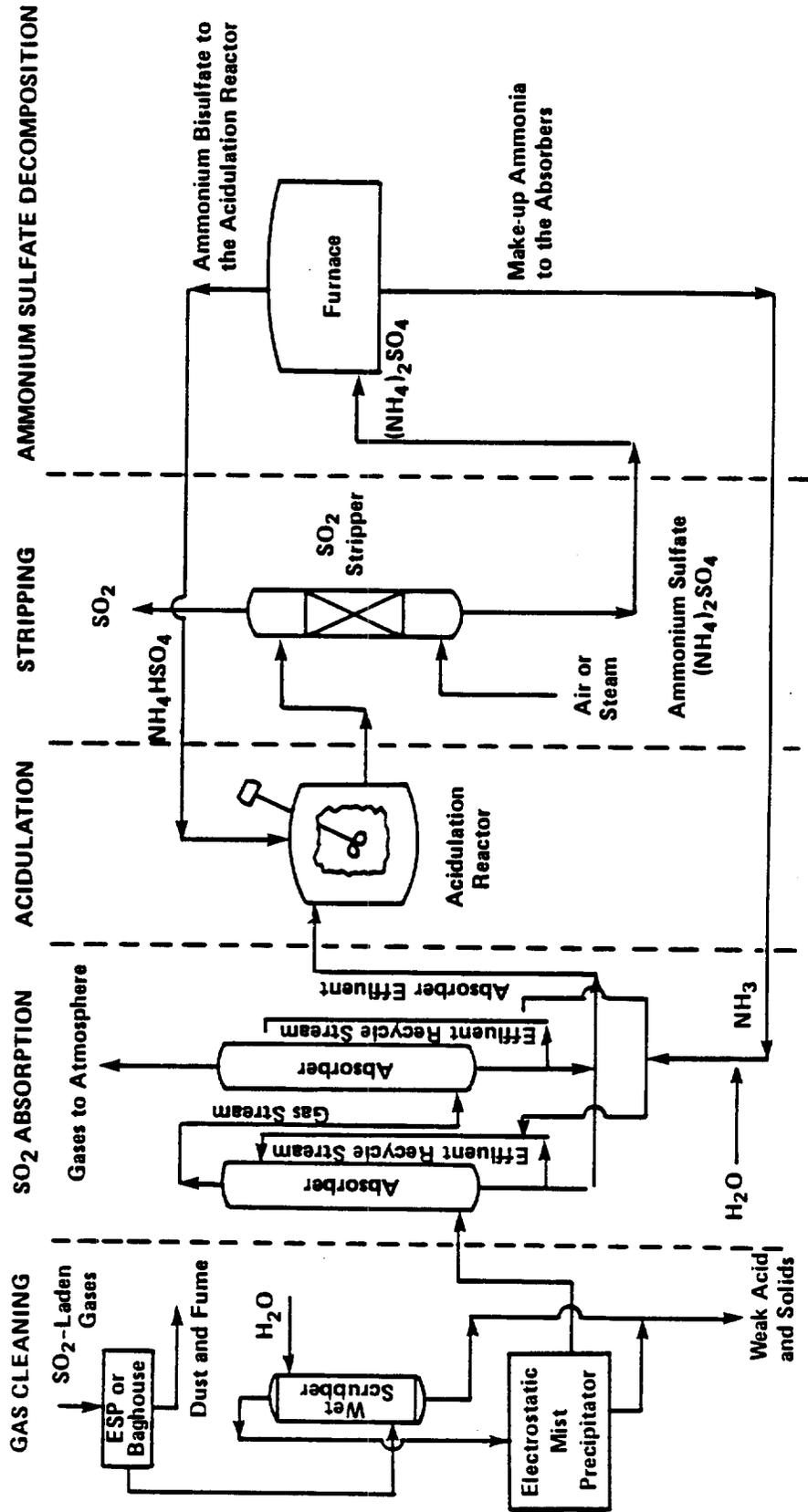


Figure 4-6. Ammonia scrubbing process with ammonium bisulfite acidulation.

the absorption of SO_2 is exothermic, interstage cooling could also be required to maintain an acceptable temperature in the absorbers ($\leq 54^\circ \text{C}$).⁸ However, if the feed stream is sufficiently weak (< 1 percent SO_2), precooling in a wet scrubber along with the humidification cooling that occurs naturally in the absorbers should eliminate the need for interstage cooling.⁸ Operating experience at Cominco's acid plant tail gas cleanup system has shown that humidification cooling of the 40°C (104°F), dry inlet gas stream resulted in 25°C (77°F) absorption tower operation without prestage or interstage cooling.⁸ At a TVA/EPA-sponsored pilot study on coal-fired boiler gases at TVA's Colbert Power Plant, liquor temperatures of up to 54°C (130°F) have been used in the absorber (after precooling) while an acceptable SO_2 -absorption efficiency was maintained.⁸ In both of these cases, feedstocks were well below 1 percent SO_2 . The TVA/EPA pilot plant utilizes the ammonium bisulfite acidulation scheme to process a feed stream that varies from 0.2 to 0.3 percent SO_2 .

In applications to primary copper smelter effluents, gas precleaning would also be necessary in order to minimize SO_3 and particulate concentrations in the absorber(s). Sulfur trioxide as well as certain metallic oxides that are present in smelter effluents would tend to promote the oxidation of ammonium sulfite to ammonium sulfate in the absorber proper.⁸ Particulates tend to serve as nuclei upon which ammonium sulfate will form.⁶

The most significant operating parameters in the absorption step have been shown to be:^{6 8}

1. Scrubbing solution temperature
2. Total concentration of SO_2 and NH_3 in solution
3. Concentration of individual ammonium salts (sulfite, bisulfite, and sulfate), which also determines pH
4. Ratio of liquid to gas flow, L/G
5. Type of internal absorber construction.

The important absorber operating parameters are necessarily related to the vapor-liquid equilibria of the system and the associated approach to equilibrium conditions. Studies have shown that the reactions involved in the

absorption of sulfur dioxide by ammoniacal solutions are quite rapid and do not affect the overall absorption rate.²⁵ Thus, mass transfer is the rate-determining process in the absorption step.

The SO₂ gas-to-liquid mass transfer rate has been shown to be a strong function of the system temperature.^{8 25} The transfer rate will decrease as the system temperature increases. The SO₂ transfer rate at 23° C (73° F) is approximately 4.4 times greater than the rate which exists at 52.5° C (126.5° F).²⁵ Thus, decreasing the solution temperature enhances the equilibrium absorption of SO₂.

Minimizing the total SO₂ concentration in solution will enhance SO₂ absorption efficiency as will minimizing S/C, the molar ratio of SO₂ in solution as ammonium bisulfite to SO₂ in solution as ammonium sulfite. This is because of the effects that these parameters have on the SO₂ vapor pressure, $P^*_{SO_2}$, and the solution pH; both of which effect the equilibrium absorption of SO₂. The system pH can be well correlated over the range of operation (4.8 to 6.6) as a function of bisulfite-sulfite ratio only.⁸

While decreasing the solution temperature enhances the equilibrium absorption of SO₂, it also serves to minimize ammonia losses from the system.^{6 8} Minimizing the total NH₃ concentration in solution also serves to minimize ammonia losses. However, while minimizing S/C tends to favor SO₂ absorption, it also tends to increase ammonia losses from the system. Thus, the choice of an optimum S/C is a tradeoff between the equilibrium SO₂ absorption and the rate of ammonia loss.

The solution pH must also be determined as a tradeoff between SO₂ absorption and the rate of ammonia loss. Experience at the TVA/EPA pilot plant has indicated that a solution pH below 5.6 allows essentially no SO₂ absorption while a pH above 6.8 results in unacceptable rates of NH₃ loss.⁸

Two primary factors that affect the approach to equilibrium in the absorption column(s) are the internal absorber construction and the liquid-to-gas flow rate, L/G. Absorption of SO₂ in ammoniacal solutions has been accomplished in both packed and tray-type columns.⁸ In the older units treating Cominco's zinc roaster and acid plant waste gases at Trail, B.C., wood-slat packing was used in one or more stages with L/G's ranging from 2.1 to 4.3 l/m³/min (16 to 32 gal/1,000 cfm).^{5 8} The acid plant tail gas

cleanup system at Olin-Mathieson's facility in Pasadena, Texas, also employed this type of absorber.⁸ The more recent TVA/EPA pilot plant work involved the use of multistage marble bed and valve tray arrangements.⁸ Sulfur dioxide removal efficiencies in excess of 90 percent have been achieved on a steady basis at each of these installations.⁸

Although the liquid-to-gas flow rate required to achieve a specified SO₂-absorption efficiency will vary depending upon the type of absorption column used, high L/G's are generally required to achieve acceptable SO₂-removal efficiencies. The benefits from the higher mass transfer rates associated with high L/G's more than offset the cost of the higher pressure drop.²⁵

4.3.3.4 Operational Problems. There is no detailed information available on ammonia-based scrubbing system operation without prior removal of particulate matter; however, the potential for problems is evident.

It would appear that excessive precipitation of solids in the absorber(s) could be a problem if no gas stream pretreatment was provided.⁸ Studies performed in the USSR have been the basis for claims that these solids can be easily removed by filtration; however, domestic study does not verify these claims. A yellow solid, identified as a homogeneous iron-ammonia-sulfur compound, was formed in the absorber liquor at the TVA/EPA pilot plant even though 90 percent or higher particulate removal was accomplished prior to gas stream entry into the absorber. In contrast to the Soviet claims, attempts to remove the solids by filtration were unsuccessful because the precipitated solids and flyash formed a gelatinous, thixotropic material that blinded the filter media.⁸ However, it should be noted that in an application to smelter offgases, precipitated solids may not behave in this manner.

As mentioned previously, the presence of particulate matter in the feed stream may also cause undesirable reactions to occur in the absorber(s), most notably sulfite oxidation. Particulates tend to catalyze the oxidation of ammonium sulfite, resulting in ammonium sulfate formation in the absorber(s). If smelter process offgases were not cleaned prior to entry into the absorber(s), Cominco considers that problems could arise from fouling of cooler lines and other process equipment.⁵ Cominco precleans

and conditions the offgases from their Dwight-Lloyd sintering machines prior to SO₂ absorption.

It is generally accepted that the presence of particulate matter in the absorbers has no effect on absorption rates;⁵ however, particulate matter would have to be removed from the solution prior to acidulation as it would interfere with the springing of SO₂ from solution.

Ammonia loss from ammonia-based scrubbing systems can be a problem if the process is not controlled quite carefully. Decreasing the absorbent temperature tends to reduce NH₃ losses as well as enhance SO₂ absorption.^{6 8} Absorbent pH is also an important factor. At low pH, there is no SO₂ absorption, while high pH results in an unacceptable level of ammonia loss.⁶ Thus, the absorbent pH must be maintained within a narrow range to result in good SO₂ absorption and reasonably low NH₃ loss. This is achieved at Cominco by adding aqua ammonia to each absorption tower and controlling the absorbent temperature as it is fed to the towers.⁶

Scaling, erosion, and corrosion are generally not problems in ammonia-based scrubbing systems.⁵ Scaling and erosion do not occur because the absorbent is a solution rather than a slurry, and all components tend to remain in solution. Corrosion does not cause problems if the proper materials of construction are used.

A serious problem that has been encountered with most of the ammonia-based scrubbing systems is the formation of an opaque fume in the exit gas stream.^{5 6 8} The fume is partially attributed to gas-phase reactions of ammonia, SO₂, and water forming ammonium sulfite,^{6 8} which due to its small size is not efficiently removed by conventional mist eliminators.⁶ The fume is objectionable as an opacity problem. Wet electrostatic precipitators have been used at some installations in efforts to eliminate this problem. Absorbent temperature and pH have been cited as having the most significant effect on plume formation.⁵ Cominco reported adequate control of the fume when operating with a liquor temperature of 25° C (77° F) and a clean inlet gas stream.⁸ Olin Mathieson operated with a pH control system which reportedly eliminated the plume opacity problem, but the exact pH limitations were not reported.⁸ In the USSR, wet electrostatic precipitators are reportedly used at the top of ammonia absorbers to control the fume.⁸

At the TVA/EPA pilot plant, plume opacity was controlled to 5 percent or less when operating with an absorbent temperature of approximately 49° C (120° F) by using a prewash to remove particulates and SO₃, maintaining a low salt concentration on the top stage of the absorber, and reheating the exit gas stream 6° to 11° C (10° to 20° F) above the temperature required to dissipate the steam plume.⁸ However, a visible plume would often reform outside the absorber on humid days.

4.3.3.5 Survey of Operating Experience. Scrubbing SO₂ from waste gases with ammoniacal solutions has been practiced commercially by Cominco in Trail, B.C., by Olin Mathieson in Pasadena, Texas, and in Romania, Japan, France, Czechoslovakia, Germany, and the USSR.⁸ The systems of "Cominco" design in place at Trail and Pasadena use the sulfuric acid acidulation process. Details of foreign systems are lacking, but it is unlikely that any of the foreign installations utilize the ammonium bisulfite acidulation process. There are no known ammonia-based scrubbing processes that employ ammonia bisulfite acidulation on a large scale; however, the TVA/EPA pilot plant study has provided data on the ammonia bisulfite acidulation scheme.

The "Cominco" type systems in place at Trail, B.C., have been quite successful. These units have processed offgases from a lead sintering plant, a zinc roaster, and a sulfuric acid plant.^{6 8} Performance data on these units are summarized in Table 4-5. As indicated, these systems have achieved SO₂-removal efficiencies of from 91 to 98 percent. The main problem with the Cominco systems has proven to be ammonia loss from the system.⁶ Presently, Cominco converts part of the SO₂ into sulfuric acid while the remainder is converted into ammonium sulfate.

While the ammonium bisulfite acidulation process has not achieved commercial operational status, it merits consideration based upon the fact that the need for an ammonium sulfate market is eliminated. In addition, ammonia and ammonium bisulfite are regenerated for recycle to the absorbent preparation and acidulation steps, respectively.

The TVA/EPA pilot plant has proven to be quite successful in removing SO₂ from boiler offgases. This system has exhibited SO₂-removal efficiencies in excess of 90 percent, with a feed stream concentration of 0.2 to

TABLE 4-5. PERFORMANCE DATA ON THE COMINCO AMMONIA-BASED SCRUBBING UNITS AT TRAIL, B.C.

Feed stream source	Feed stream volumetric flow rate, scfm ⁵	Percent SO ₂ in feed stream ⁵	Percent SO ₂ in cleaned gas stream ⁸	SO ₂ -removal efficiency, percent ^a
Lead sintering plant	150,000 - 200,000	0.3 - 2.5	~0.10	~96
Zinc roaster	0 - 45,000	0.5 - 7.0	~0.10	~98
Sulfuric acid plant	50 - 95,000	0.9 - 1.0	~0.09	~91

^aEstimated based upon the maximum feed stream SO₂ concentration.

0.3 percent SO₂, and an exit gas SO₂ concentration of 200 to 300 ppm.⁸ From this experience, it is evident that desulfurization efficiencies of 90 to 95 percent are technically achievable. As with "Cominco" type systems, however, careful process control is required in order to prevent excessive ammonia loss and the formation of an opaque plume.

4.3.3.6 Applicability to Reverberatory Smelting Furnaces. The Cominco-type process can achieve high SO₂-removal efficiencies over a wide range of SO₂ concentrations. The range of SO₂ concentrations over which these systems will operate efficiently easily encompasses the range of SO₂ concentrations encountered in offgases from reverberatory smelting furnaces.⁶ In addition, applications of this process to metallurgical effluents at Trail, B.C., have demonstrated the system's capability to handle wide variations in feed stream volumetric flow rate and SO₂ concentration. However, ammonia loss from these systems can be a problem. Ammonia volatility may limit the minimum SO₂ emission concentration to the 200-300 ppm range for practical applications.⁶

An additional factor that must be considered in assessing the applicability of the Cominco-type process for control of reverberatory furnace effluents is the possible need for interstage cooling as discussed in Section 4.3.3.3. There would be no technical problems in providing interstage cooling; however, this cooling must be evaluated as an additional cost consideration.

In conclusion, with adequate process control provisions, the Cominco-type system appears to be a technically viable control option for the control of reverberatory furnace effluents. Precise control of the absorbent temperature and pH would be required in order to minimize ammonia loss and eliminate the visible emissions problem; however, neither of these problems appears to be chronic. Pretreatment of the feed stream for the purposes of cooling, humidification, and particulate removal would also be required, but this would present no problems technically as adequate gas conditioning technology already exists.

The feasibility of applying the ammonium bisulfite acidulation scheme for reverberatory furnace effluent control cannot be assessed accurately since no data exist concerning its application to metallurgical offgases.

However, since these systems are identical to the Cominco-type systems with the exceptions of the method of acidulation and the requirement for sulfate decomposition, there is no evidence to suggest that they would not be technically feasible control options. This process is forecasted to be the SO₂-removal system of the future,²⁷ as it provides ammonium bisulfite and ammonia for recycle while simultaneously eliminating the need to market ammonium sulfate.

4.3.4 Magnesium-Based Scrubbing Systems

4.3.4.1 Summary. Magnesium-based scrubbing systems have been the object of a great deal of developmental work during the last decade, especially in Japan, the USSR, and the United States. Most of this developmental work has concentrated on the use of magnesium sulfite/magnesium oxide slurries to effect SO₂ removal from gas streams. Systems of this type are especially attractive since the absorbent can be regenerated.

Commercial demonstration runs on both coal- and oil-fired utility boilers in the United States have demonstrated the ability of the so-called MAGOX process to achieve SO₂-removal efficiencies in excess of 90 percent when operating on utility-related weak SO₂ streams.⁸ Experience obtained from the earliest utility-related applications has also been instrumental in the improvement and optimization of many of the design features of the MAGOX slurry scrubbing process. In addition, the MAGOX scrubbing system currently in place at the Onahama smelter in Japan is said to be a direct transfer of Japanese utility-related scrubbing technology, which suggests that differences in the characteristics of boiler and reverberatory furnace effluents do not constitute serious obstacles to the transfer of utility-related technology.

Perhaps the most significant application of magnesium-based technology to occur over the past few years has been the system installed at the Onahama smelter in 1972. This system produces a concentrated SO₂ stream from a portion of a weak SO₂ stream which is generated by three green-charged reverberatory furnaces, and shows a substantial ability to absorb fluctuations in the feed stream SO₂ concentration.⁶ Sulfur dioxide removal efficiencies are typically in excess of 99 percent. Based upon the successful operation of the Onahama system, it is expected that a similar system could

provide SO₂-removal efficiencies of well over 98 percent in applications to reverberatory furnace effluents of domestic origin,⁶ providing that there is an adequate water supply available to meet the process water requirement. A system of this type would also provide product flexibility, as the concentrated SO₂ stream produced can be used to manufacture liquid SO₂ and elemental sulfur as well as sulfuric acid.

4.3.4.2 General Discussion. A number of magnesium-based scrubbing systems provide effective SO₂ removal; however, U.S. developmental work, as well as related Japanese and Russian work, has concentrated on the use of magnesium sulfite/magnesium oxide slurries to effect SO₂ removal.⁸

A simplified flow diagram for the magnesium sulfite/magnesium oxide slurry scrubbing process, or MAGOX process as it is often called, is presented in Figure 4-7. This process involves operations associated with the following primary areas:

1. Gas cleaning and conditioning
2. SO₂ absorption
3. Slurry handling
4. Solids drying and calcining.

Gas cleaning occurs when the feed stream is passed through a wet scrubber, usually of the venturi type, where it is cooled and residual particulate matter is removed. Undesirable halogens that may be present are also removed in the wet scrubber. A bleed stream from the wet scrubber is thickened to concentrate the particulate matter as a slurry underflow which is transported to a disposal area.

Sulfur dioxide absorption occurs when the cleaned gas stream is vented to a scrubber where it is contacted with the absorbent slurry. The absorption reaction takes place between sulfur dioxide and magnesium oxide (MgO), and results in the formation of magnesium sulfite (MgSO₃). Some of the SO₂ may also react with MgSO₃ in the presence of water to form magnesium bisulfite [Mg(HSO₃)₂], which immediately reacts with excess MgO to yield additional MgSO₃. A small amount of MgSO₄ may be formed by in situ oxidation of a small portion of MgSO₃ and/or by SO₃ absorption into the slurry. The resulting aqueous slurry which exits the absorber contains hydrated crystals

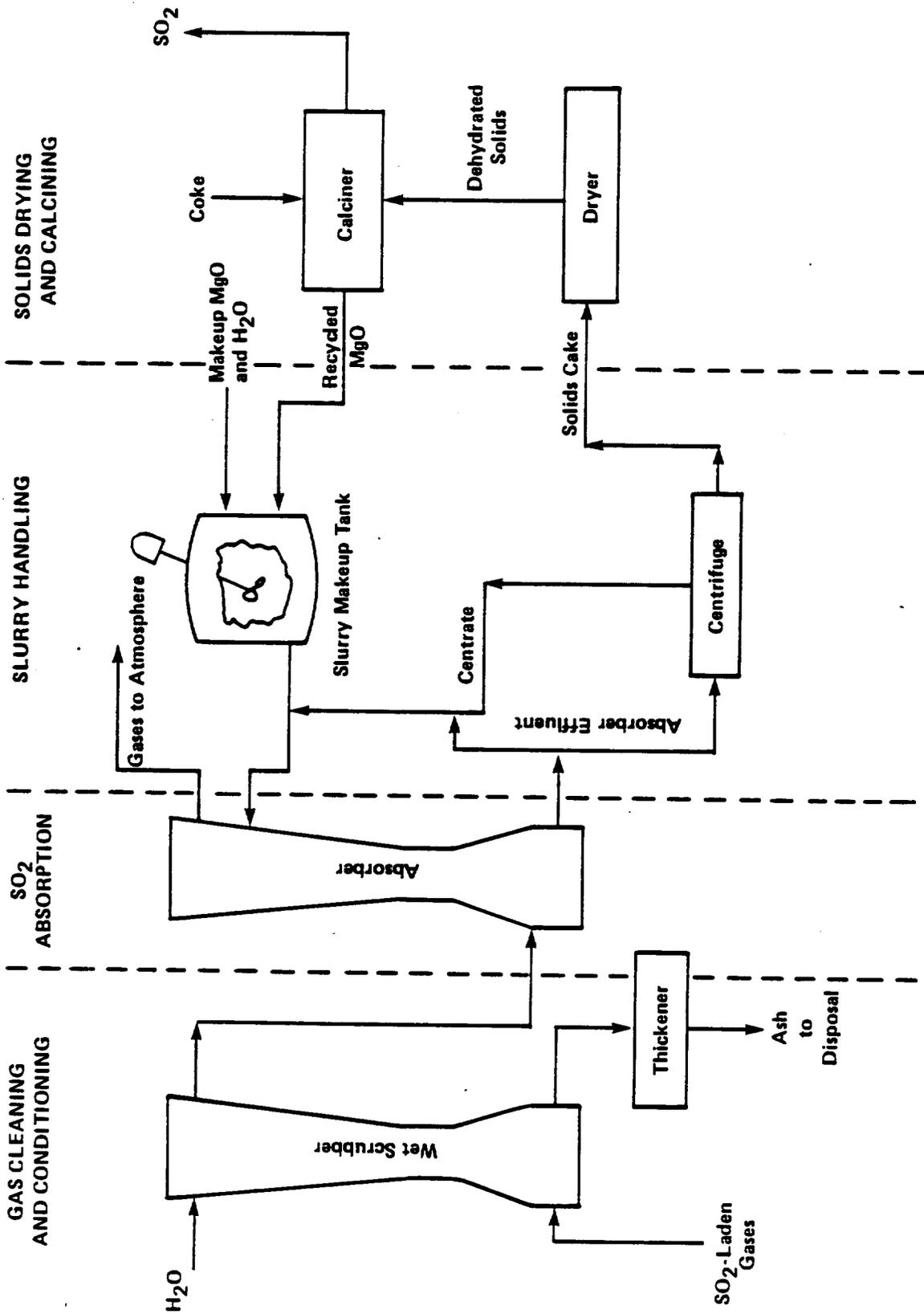


Figure 4-7. Magnesium-oxide (MAGOX) scrubbing process.

of MgSO_3 and MgSO_4 , e.g., $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$, $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, some excess MgO , and a solution that is saturated with each of these components.

Slurry-handling operations involve splitting the slurry after it exits the absorber, routing a portion to a centrifuge for partial dewatering, and recycling the remainder to the absorber. At the centrifuge, a moist cake consisting of crystals of $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$, $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and unreacted MgO is obtained. The clear liquor centrate is then returned to the main recirculating slurry stream together with makeup MgO slurry from the slurry makeup tank, and the resulting stream is recycled to the absorber for further SO_2 recovery. The crystal cake is then conveyed to a dryer where free and bound moisture is removed by using a direct contact drying gas under nonoxidizing conditions. The resulting anhydrous salts are then calcined to MgO , which is reused in the absorption system after having been slaked and slurried in the slurry makeup tank. Coke is added to the calciner in order to convert any MgSO_4 present to MgO .

4.3.4.3 Design and Operating Considerations. The MAGOX process, in common with most aqueous scrubbing systems, requires the feed stream to be at least saturated with water vapor in order to minimize absorbent evaporation and localized high salt concentrations in the absorber(s). With initial gas stream temperatures of between 150°C and 315°C (300°F and 600°F), water quenching in a wet scrubber should provide acceptable cooling and humidification.⁸ A venturi-type scrubber is usually employed for this purpose. Also, since the MAGOX system uses the closed system mode of operation, there is a need to minimize the introduction of particulate matter, most notably oxidation catalyzing metals and sulfuric acid mist, into the absorber. An electrostatic precipitator in series with the wet scrubber should provide adequate cooling, humidification, and particulate matter removal in applications where copper smelter effluents are to be processed.⁸

The most significant operating parameters in the absorption step have been shown to be:

1. Ratio of liquid to gas flow, L/G
2. pH of the absorbent slurry.

The SO₂-removal efficiency of the MAGOX system will increase as L/G is increased;⁸ however, the L/G required to achieve a particular SO₂-removal efficiency will vary depending upon the type of absorber used.

Due to its effect on the SO₂ vapor pressure over the scrubbing solution, the pH of the absorbent slurry has a distinct effect on the SO₂-removal efficiency. Increasing the pH of the absorbent slurry will tend to increase SO₂-removal efficiency.⁸ This is because a high slurry pH will keep the vapor pressure of SO₂ above the solution small in comparison to the SO₂ partial pressure in the gas stream, and thus promote mass transfer.

Temperature exercises little adverse effect on the mass transfer rates if the slurry pH is maintained at 6 or above due to the very low SO₂ vapor pressures which are in evidence at this pH level.

Both venturi and mobile bed absorbers have been evaluated for use in MAGOX systems, and both types have proven capable of attaining SO₂ absorption efficiencies in excess of 90 percent.⁸ However, venturi absorbers require a higher operating L/G to achieve a given SO₂-removal efficiency. In spite of this factor, the venturi absorber appears to provide several operating advantages, and thus has been selected for use in commercial domestic installations. The Japanese have used TCAs almost exclusively in their MAGOX systems; however, they do not feel that TCAs provide any significant operational advantages, and have shown an interest in using venturi absorbers for future applications.⁶

The SO₂ concentration in the gas phase would not be expected to adversely affect the SO₂ absorption rate until the concentration rises above about 3.5 percent.⁸ Therefore, this would not be expected to present any problems in applications to reverberatory furnace effluents, which generally exhibit a maximum SO₂ concentration of 2.5 percent.⁵

In the drying and calcining sections of a MAGOX scrubbing facility, the use of fluid bed equipment offers several advantages, namely lower capital and operating costs, lower heat loss, and better temperature control.⁸ Also, in the case of calciner operation, fluid bed operation would allow for more precise control of oxygen, which in turn could minimize the requirement for coke to reduce the MgSO₄. With regard to oxygen, where the gas stream is likely to contain high levels of O₂, such as would be present

in reverberatory furnace effluents, the use of organic inhibitors may be warranted to reduce the sulfite oxidation rate.

4.3.4.4 Operational Problems. A great deal of information on problems that have been encountered with MAGOX systems of Chemico design was compiled during a commercial-scale test program at Boston Edison's Mystic Power Station. This system processed boiler offgases and produced solid MgSO_3 , which was then sent to Essex Chemical's facility in Rumford, Rhode Island, for calcination. The majority of the problems that were encountered with this system occurred at startup and did not prove to be chronic.

The majority of the problems encountered during startup centered around the dryer.²⁸ The initial problem encountered involved an inability to transfer all of the dried product into the MgSO_3 storage silo due to excessive entrainment of product fines in the countercurrent drying gas stream. Entrainment of this nature ultimately resulted in overloading and plugging of the dryer cyclones. Efforts to alleviate this problem by reducing the draft through the dryers were only partially successful, and the eventual solution involved modifications to the dryer internals.

During the early stages of startup, the changing consistency of the centrifuge cake led to some difficulty in dryer operation. It appeared that, upon startup of the absorption systems, the principal nucleation resulted in the formation of crystals of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$. However, as the system aged and reached an equilibrium temperature of 56°C (132°F), nucleation involving the formation of $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ became more predominant. Since the mature trihydrate crystals were considerably smaller in size than the hexahydrate crystals, they were less efficiently centrifuged and thus resulted in a wetter cake which tended to agglomerate as it passed through the dryer. The formation of large nodules caused shutdown of the conveying system by jamming and ripping the rubber weigh belt. Larger agglomerates also caused some problems in the pneumatic conveying operations. Ultimately, a pulverizer was installed at the dryer exit to alleviate these problems.

The dryer was also unable to operate satisfactorily on high sulfur oil. Burner flameouts were frequent because of the formation of coking deposits, which were later attributed to insufficient oil preheating. With insufficient preheating, the oil did not attain the proper viscosity for

atomization. This problem was resolved by ensuring that the oil was preheated to at least 127° C (260° F).

The calcining system also experienced some problems at startup, the most significant being the difficulty in attaining a nonoxidizing atmosphere in the calciner. This difficulty was overcome by reducing air infiltration through the seals at the firing end of the calciner.

The venturi absorption system at this facility has operated successfully with no evidence of scaling or silting at any points.²⁸ Pluggage of small lines did occur occasionally; however, this problem was easily remedied by back flushing.

The MAGOX process as now commercially defined imposes no unusual problems in terms of corrosion or special processing equipment.⁸ As is normal in slurry systems, the use of elastomer-lined or specially coated equipment and piping in the scrubbing and recirculation system has provided acceptable service in the domestic commercial installations apart from some localized problems.

To avoid downtime for absorber maintenance, the Japanese included a spare TCA absorber in the Onahama system.⁶ Ball wear in the absorbers is controlled by replacement every 2 to 3 months.

In conclusion, there appear to be no chronic operational problems that would hinder the operation and reliability of MAGOX systems that might be employed to control weak SO₂ streams generated by reverberatory smelting furnaces. Although the earlier domestic systems of Chemico design experienced numerous difficulties, all serious problems were eventually alleviated.²⁸

While there does not appear to be a single outstanding reason for the early difficulties encountered, it can generally be said that development and operating experience in Japan was greater than domestic experience at the time the first systems were installed.⁶ The Japanese development work on these systems was a direct transfer utility-related technology and appears to have been considerably more successful than the domestic development work on the same type of system.²⁶ However, domestic experience gained from the earlier systems such as the Boston Edison system has led to numerous improvements in domestic MAGOX system design.

4.3.4.5 Survey of Operating Experience. The MAGOX slurry scrubbing system has been under commercial-scale evaluation in the United States since 1972.⁸ Construction of the first domestic commercial system, the Chemico/Basic MgO sulfur recovery process, was completed in April 1972. The scrubbing and recovery system at Boston Edison's Mystic Station operated on offgases from a 150-MW oil-fired boiler. The regeneration facilities were located at Essex Chemical's facility in Rumford, Rhode Island, where the SO₂ was used to produce sulfuric acid. As noted in Section 4.3.4.4, several difficulties were encountered with this system; however, none proved to be chronic, and all serious operational difficulties were eventually alleviated via design modifications and/or changes in operating procedure. This unit was a prototype trial installation that was built primarily to obtain operating data, and its use was eventually terminated in June 1974. The unit displayed availabilities in the range of 80 percent during the final month of operation.

Another prototype Chemico/Basic unit was installed at Potomac Electric and Power Company's Dickerson No. 3 station in 1973. This scrubbing system processed offgases generated by a 95-MW coal-fired boiler. Performance testing of this system resulted in an average SO₂ removal efficiency of 88.9 percent.²⁴ This unit, like the unit at Boston Edison's Mystic Station No. 6, fulfilled its purpose by indicating areas where improvement was needed. Demonstration runs on the Dickerson unit were completed in August 1975.

Experience obtained from the systems at Boston Edison's Mystic Station and at Potomac Electric and Power Company's Dickerson Station led to several design changes which helped to improve the reliability of the Chemico/Basic system. Chemico subsequently installed a MAGOX scrubbing system at the Chiba refinery in Japan, and this system is apparently working satisfactorily.⁶ While this system provides a concentrated SO₂ stream as feed to a Claus plant, it is essentially the same as the earlier Chemico system except for design modifications which were made to eliminate the previously mentioned operational problems and thus improve system reliability.

In December 1972, the Onahama Smelting and Refining Company, Ltd., began the operation of a MAGOX system designed to produce a strong SO₂

stream from reverberatory furnace offgases. The development and installation of the MAGOX SO₂-concentration system at the Onahama smelter was carried out as a joint effort between the Tsukishima Kikai Company (TSK) and the Mitsubishi Metals Corporation.⁶ The TSK-Mitsubishi MAGOX system is essentially the same as the Chemico/Basic system in as far as major design considerations are concerned, with the only distinct difference being the type of absorber employed. However, as mentioned in Section 4.3.4.3, the Japanese do not feel that the TCAs they use have any distinct advantages over the venturi-style scrubber employed in the Chemico/Basic design. The MAGOX system was chosen to provide a concentrated SO₂ stream for direct acid plant processing because of low energy requirements in comparison to other regenerative systems, particularly the Wellman-Lord system. This system processes approximately 55,000 dry scfm of reverberatory furnace effluent at an SO₂ concentration of approximately 2.5 percent.²⁹ Although the feed stream to the MAGOX system is maintained at about 2.5 percent,^{6 18} the system has shown a considerable capability to handle the fluctuations in the feed stream SO₂ concentration that do occur.⁶ Also, there are no problems with magnesium sulfate buildup, as the turnover ratio and makeup material are sufficient to eliminate this problem. A stream averaging 10 percent SO₂ is produced by the calciner, while the gas stream which exits the absorber generally exhibits an SO₂ concentration of about 20 ppm.⁶ The degree of SO₂ removal associated with the resultant 20 ppm absorber offgas stream is in excess of 99 percent. This system is of particular significance as it demonstrates the ability of a MAGOX system to operate on a weak SO₂ stream generated by reverberatory smelting furnaces.

4.3.4.6 Applicability to Reverberatory Smelting Furnaces.

4.3.4.6.1 Transfer of utility-related scrubbing technology. Commercial demonstration runs on both coal- and oil-fired utility boilers in the United States have demonstrated that the MAGOX slurry scrubbing process is able to achieve SO₂-removal efficiencies of 96 percent or greater on boiler effluents.⁸ Considerable experimental work in recent years has also served to establish, with some assurance, the chemistry, kinetics, and mass transfer relationships that govern the MAGOX process; and suggests that with appropriate adjustment of L/G and the slurry pH, SO₂ removal efficiencies of 90 percent

or greater could be achieved on gas streams containing 3 to 4 percent SO₂. In addition, the MAGOX scrubbing system currently in place at the Onahama smelter is a direct transfer of utility-related scrubbing technology, which suggests that differences in the characteristics of boiler and reverberatory furnace effluents are not serious obstacles to the transfer of utility-related technology.

4.3.4.6.2 Assessment of applicability based upon existing scrubbing systems that process metallurgical effluents. As discussed in Section 4.3.4.5, a MAGOX system has been operated satisfactorily on reverberatory furnace offgases at the Onahama smelter in Japan. Therefore, application of this technology for the control of weak SO₂ streams generated by reverberatory smelting furnaces should be considered demonstrated. Although the MAGOX system at Onahama has shown a considerable capability for absorbing fluctuations in the feed stream SO₂ concentration, the SO₂ concentration in the effluent from the green-charged reverberatory furnaces is kept constant at about 2.5 percent,^{6 12} thus demonstrating the ability to stabilize the SO₂ concentration. The system produces a concentrated stream containing 10 to 13 percent SO₂ which can be processed directly in a dual-stage absorption or single-stage absorption sulfuric acid plant.⁶ Based upon the successful operation of the Onahama system, it is expected that a similar system could provide SO₂-removal efficiencies of well over 98 percent in applications to reverberatory furnace effluents of domestic origin,⁶ providing that there is an adequate water supply available to meet the process water requirement. Furthermore, product flexibility is obtained as the concentrated SO₂ stream produced can be used to make liquid SO₂ and elemental sulfur as well as sulfuric acid.

4.3.5 Citrate Scrubbing Processes

4.3.5.1 Summary. Scrubbing systems that utilize citrate-type absorbents have been the subject of a great deal of developmental work, particularly in the United States and Sweden. The U.S. Bureau of Mines, Salt Lake City Metallurgy Research Center, has sponsored several studies on the absorption of SO₂ in citrate-type absorbents. As a result of these investigations, three pilot-scale studies that utilized process technology developed initially by the Bureau of Mines were conducted.

The feedstocks involved in these studies were effluent gas streams generated by green-charged reverberatory furnaces, coal-fired utility boilers, and a Lurgi updraft lead sintering machine. The results of all three studies were generally inconclusive as various operational problems proved to be chronic in nature, thus preventing long-term reliable operation. It should be noted that most of the operational problems occurred in the SO₂ reduction circuit and not the SO₂ absorption circuit. Consequently, the pilot studies demonstrated that the system has the ability to achieve high SO₂-removal efficiencies while processing weak streams. Removal efficiencies in two of the three applications were in excess of 93 percent.⁶ Thus, with further development and commercial-scale demonstration, the Bureau of Mines process may prove to be a viable control option for weak SO₂ streams of reverberatory furnace origin.

Investigation into the absorption of SO₂ in citrate-type solutions began in Sweden as an effort to improve the SO₂ absorption properties of pure water. The Boliden AB Ronnskarsverken smelter at Skelleftehamn, Sweden, has been removing SO₂ from smelter offgases by absorption in cold water on a commercial scale since 1970. The economic success of this operation depends upon the year-round supply of cold water (5° to 8° C) near the smelter site. The investigations into SO₂ absorption using citrate-type absorbents were prompted by the fact that ample year-round supplies of cold water were not available in all areas where water scrubbing might be used to effect SO₂ removal. Thus, a means to improve the absorption properties of water at temperatures greater than 5° to 8° C (41° to 46° F) was desired.

An absorption process that utilizes a brine of citric acid and sodium citrate was eventually developed as a result of long-range work by the Boliden Company of Sweden, the Norwegian Technical Institute SINTEF, and Svenska Flaktfabrika (Flakt).⁶ A pilot-scale version of the Flakt-Boliden process was used at the Ronnskar smelter in order to establish a design background for the process. Gases from a number of various lead and copper smelting operations were used as feedstocks for the pilot facility. Flakt has reported that the test results look

very promising; however, the actual SO₂-removal efficiencies that were achieved during the tests have not been made readily available.

The Flakt-Boliden process exhibits a very distinct advantage over the Bureau of Mines process; i.e., it is relatively simple. The process utilizes steam stripping of the absorber effluent to produce a concentrated SO₂ stream, while the Bureau of Mines process employs a very complex SO₂ reduction scheme to produce elemental sulfur. Consequently, the Flakt-Boliden process is not likely to involve the numerous operational problems that have been encountered thus far with the Bureau of Mines process. Product flexibility is also obtained with the Flakt-Boliden process, as the concentrated SO₂ stream produced may be liquefied to produce liquid SO₂, fed to a contact sulfuric acid plant to produce sulfuric acid, or fed to a Claus plant to produce elemental sulfur.

The Flakt-Boliden process, like the Bureau of Mines process, has only been applied on a pilot scale. Although the range of feedstream SO₂ concentrations processed by the Flakt-Boliden pilot plant easily encompassed the range of SO₂ concentrations produced by reverberatory smelting furnaces, the system cannot be considered to be a viable control option for reverberatory furnace effluents until it is demonstrated in a commercial-scale application that firmly establishes the achievable range of SO₂-removal efficiencies.

4.3.5.2 General Discussion. The Bureau of Mines citrate scrubbing process was developed as a result of investigations that showed that several organic acids, including acetic, citric, and lactic acid, had a great affinity for SO₂. A mixture of citric acid, sodium citrate, and sodium thiosulfate was finally selected for further development because of its chemical stability. This system was designed to produce elemental sulfur by using manufactured hydrogen sulfide (H₂S) as a reducing agent.

A simplified flow diagram of the Bureau of Mines citrate scrubbing process is presented in Figure 4-8. The principal process steps are as follows:

1. Gas cleaning and cooling

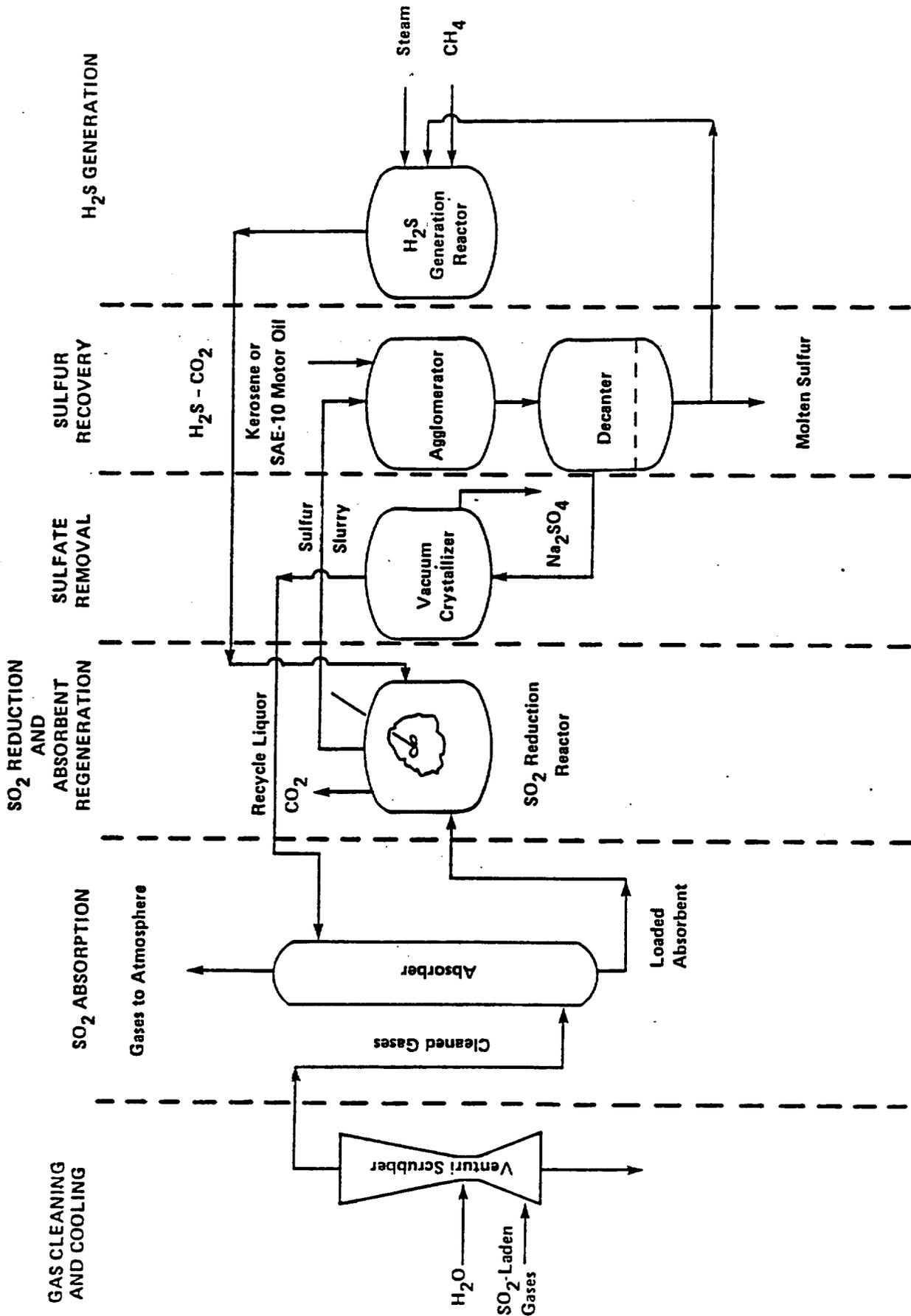


Figure 4-8. Bureau of Mines citrate scrubbing process.

2. Sulfur dioxide absorption
3. Sulfur dioxide reduction and absorbent regeneration
4. Sulfate removal
5. Sulfur recovery
6. H₂S generation.

Gas cleaning and cooling consists of removing particulate matter and acid mist from the gas stream while cooling it to the 46° to 66° C (115° to 150° F) temperature range. The cool, clean gas stream is then vented to an absorber where SO₂ absorption occurs. In the absorber, the gas stream is contacted countercurrently with a sodium citrate-citric acid solution. Gases exiting the absorber are vented to the atmosphere, while the loaded absorbent is pumped to a continuous stirred tank reactor. In the reactor, the SO₂ is reduced to elemental sulfur and the citrate solution is regenerated by introducing H₂S as a reducing agent. Sulfur slurry from the SO₂ reduction reactor is fed to the sulfur separation system. In the sulfur separation unit, the sulfur is agglomerated by flotation with either kerosene or SAE-10 motor oil. The floated sulfur, at 35 to 40 percent solids, is fed to a heater to produce molten sulfur. Liquid phases are then separated in a decanter under a pressure of about 35 psig, resulting in a bottom layer of high quality molten sulfur and a top layer of citrate solution. The molten sulfur is drawn off and the citrate solution is sent to a vacuum crystallizer where sodium sulfate (Na₂SO₄) is removed. Effluent from the vacuum crystallizer is then recycled to the absorber.

The H₂S gas, which serves as the reductant in the SO₂ reduction step, is produced from a portion of the molten sulfur that is drawn off the decanter. Filtered molten sulfur from the decanter is pre-heated by indirect heat exchange with the H₂S reactor effluent before being vaporized and subsequently superheated to 650° C (1200° F). A portion of the resulting sulfur vapor is mixed with a hot natural gas/steam mixture; the resultant stream is routed to a quench-cooled catalytic H₂S generation reactor. The remaining sulfur vapor is mixed with an unpreheated natural gas/steam mixture and injected into the

catalyst bed in order to keep the bed temperature approximately constant. The hot reactor effluent, consisting primarily of H_2S and CO_2 , is then used to preheat the sulfur feed as mentioned above before being used in the production of the steam required for H_2S generation. The reactor effluent is then cooled to approximately $60^\circ C$ ($140^\circ F$) before being fed to the SO_2 reduction reactor. The portion of the molten sulfur that is not used to produce H_2S is generally cast into bricks.

The Flakt-Boliden system has resulted from long-range developmental work carried out by several copper smelters and technical institutes in Scandinavia.⁶ The basic process steps involved in the Flakt-Boliden process are summarized below:

1. Gas cleaning and cooling
2. Sulfur dioxide absorption
3. Stripping and sulfate removal.

The gas stream is cleaned in a high-efficiency particulate collector and then cooled to saturation by direct water injection. In addition, any sulfuric acid mist that may be present is removed in an electrostatic mist precipitator prior to gas stream entry into the absorber. The cool, saturated gases are then vented to the bottom of an absorption tower where they are contacted counter-currently with citrate absorbent. Gases exiting the absorber are passed through a mist eliminator and then vented to the atmosphere, while the loaded absorbent is pumped to a stripping tower. Stripping is accomplished by contacting the loaded absorbent with steam. The concentrated SO_2 stream produced, which contains a small amount of water vapor, is routed to a condenser where most of the water is condensed out. The condensate, which contains only a small quantity of SO_2 , is returned to the stripping column. Absorbent solution containing a small amount of SO_2 is withdrawn from the bottom of the stripper and pumped to a regenerator unit. During regeneration, the sodium citrate and sodium sulfate are separated from solution. This is accomplished by using seed crystals and a cooling unit to recover sodium citrate and remove sodium sulfate. Details of the regeneration system are presented in U.S. patent no. 3,886,069.⁶

The sodium sulfate is discarded, and the recovered sodium citrate solution is recycled back to the absorber.

The concentrated SO₂ stream, which can be as high as 95 percent SO₂ with a water saturation temperature of approximately 30° C (86° F), can be routed directly to (1) a Claus plant for the production of elemental sulfur, (2) a contact sulfuric acid plant for the production of sulfuric acid, or (3) a refrigeration/condensation system for the production of liquid SO₂.

4.3.5.3 Design and Operating Considerations. Proper design and operation of the gas cleaning system is necessary in order to ensure efficient SO₂ removal in citrate-type systems. As with other types of scrubbing systems, the citrate systems require that the feed gas stream be cooled and thus humidified in order to prevent excessive evaporation of the absorbent solution. Because SO₂ absorption is favored by lower temperatures, the optimum feed stream temperature is established as a trade-off between mass transfer considerations and the costs of precooling.⁸ Pilot plant work sponsored jointly by the Bureau of Mines and the Magma Copper Company was conducted at temperatures between 42° C and 52° C (108° F and 125° F) with resulting SO₂-removal efficiencies in the range of 93 to 99 percent.⁸ This particular pilot plant was placed into operation in November 1970 at Magma's San Manuel, Arizona, smelter and processed 300 cfm of gas from a green-charged reverberatory furnace.

In the Bureau of Mines citrate process, adequate gas cleaning can be effected by a baghouse, a packed scrubber, an electrostatic precipitator, or a venturi scrubber.⁶ In the Flakt-Boliden process, gas cleaning and conditioning is accomplished by routing the gas stream through a high-efficiency particulate collector such as an electrostatic precipitator, and then cooling the stream to saturation by direct water injection.⁶ Passing the gas stream through an electrostatic mist precipitator prior to gas stream entry into the absorber is deemed advantageous in both types of processes, as sulfuric acid mist removal prior to absorption minimizes sodium sulfate formation in the absorber and thus minimizes the purge requirements.

The solubility of SO_2 in citrate-type absorbents is a function of the SO_2 partial pressure in the gas phase, the hydronium ion concentration, and the ionization constants of sulfurous acid.⁸ The important process variables in the absorption step can thus be identified as:

1. Absorbent solution pH
2. Absorbent solution composition
3. Feed stream SO_2 concentration
4. Feed stream temperature
5. Ratio of liquid-to-gas flow, L/G.

Sulfur dioxide absorption is increased by maximizing the pH and buffer content of the absorbent solution, maximizing the feed stream SO_2 concentration, and minimizing the feed stream temperature. Under actual operating conditions, the citrate concentration in the absorbent solution is established at the lowest level compatible with the feed stream SO_2 concentration and requisite solution flows. The operating temperature selected balances the advantages of higher absorbent SO_2 loadings at the lower temperatures against the costs of feed stream cooling. The actual absorbent recirculation rate chosen to achieve a specified SO_2 -removal efficiency is dependent upon the absorbent citrate concentration required to effect the specified removal efficiency at a given feed stream SO_2 concentration. In a Bureau of Mines pilot plant program at the Bunker Hill lead smelter in Kellogg, Idaho, the absorbent flow rate used to treat a 1,000 scfm stream from a lead sinter machine containing 0.5 percent SO_2 was about 38 ℓ/min (10 gal/min) of 0.5 M citrate solution.⁸ The resultant SO_2 loading in the absorber offgas stream was approximately $10^7 \text{ mg}/\text{m}^3$. With regard to the Bureau of Mines process, the absorbent solution pH is reported to be limited by factors that concern the SO_2 reduction procedure rather than factors that govern the absorption step.⁶ The pilot-scale work conducted by the Bureau of Mines at the Magma and Bunker Hill smelters has utilized an absorbent pH in the range of 4.0 to 4.6 and a 0.5 M citrate solution with a molar ratio of NaOH to citric acid of

approximately 2.0. Operating temperatures at both installations ranged from 42° to 65° C (108° to 149° F).

The liquid-to-gas flow ratio must be sufficiently high to ensure an adequate rate of SO₂ absorption. In a countercurrent packed scrubber, the type of absorber chosen in both the Bureau of Mines and Flakt-Boliden processes, the L/G required is about 1.3 l/m³ (10 gal/1,000 ft³).⁶

The Bureau of Mines work has also shown that SO₂ absorption is enhanced by the presence of thiosulfate. In practice, thiosulfate is introduced into the system as the regenerated absorbent is returned to the absorption loop.⁸ In the pH range of 4.0 to 4.5, the usual pH range of citrate absorbent solution, thiosulfate, trithionate, tetrathionate, and polythionate are all believed to be formed in the reduction/regeneration step of the Bureau of Mines process. These species, once formed, are thought to react with H₂S to yield elemental sulfur. Studies of the chemistry involved in the reduction/regeneration step have indicated that the reaction of H₂S with thiosulfate is the rate-determining process in this step.⁸ Thus, by allowing the thiosulfate to build up in the system, the reaction rate is increased, which in turn causes a decrease in the size of the reactor required to provide the necessary residence time. For this reason, the presence of the thiosulfate ion in the absorbent solution is deemed essential in the Bureau of Mines process.

As with all closed-loop scrubbing systems, the accumulation of oxidation products, particulates, and other soluble impurities must be controlled by purging a portion of the recirculated absorbent solution. In the Bureau of Mines process, this purge consists primarily of sodium sulfate, and is taken from the vacuum crystallizer as mentioned in Section 4.3.5.2. Soda ash, Na₂CO₃, which is added to the absorbent recirculation loop, produces the sodium sulfate via reaction with the sulfate ion which is present in the system. The resulting sodium sulfate is then readily removed after crystallization and filtration.

In the Bureau of Mines process, the sulfur slurry that is produced in the reduction/regeneration step is vented to a sulfur separation

unit where the sulfur is agglomerated by flotation with either kerosene or SAE-10 motor oil. While the use of kerosene is quite effective in this operation, it can be quite expensive. The use of kerosene and the resultant losses that occur as presently estimated by the Bureau of Mines constitute a major part of the total raw materials cost.⁸ However, laboratory-scale tests have indicated that the use of SAE-10 motor oil should provide results equivalent to those obtained by the use of kerosene. In addition, predicted oil consumption would only be one-fourth that of kerosene.

Very little experience has been gained in the Bureau of Mines pilot plant studies regarding onsite generation of H_2S for use as a reductant. It is imperative, however, that a reliable source of H_2S be available to ensure uninterrupted operation of the Bureau of Mines process. However, due to the locations of the domestic primary copper smelters, onsite H_2S generation would probably be preferred based upon economical considerations, and could conceivably be produced by using a portion of the recovered sulfur, steam, and a reducing agent such as methane. Production of H_2S via this route is exothermic, and the hot product stream that exits the H_2S generation reactor can be used to preheat the sulfur feed to the reactor as well as to generate a portion of the steam required for H_2S generation.⁶

The Flakt-Boliden process utilizes steam stripping to produce a concentrated SO_2 stream from the absorber effluent. Thus, as shown in Figure 4-9, the absorber effluent is routed directly to a stripping tower where it is subjected to steam treatment in a countercurrent fashion. Due to the equilibrium behavior of the SO_2/H_2O system, it is favorable to conduct the stripping process at reduced pressure (down to approximately one-tenth of an atmosphere). The fact that stripping is conducted under a vacuum is favorable with regard to steam consumption, and low pressure steam or hot water can be used.⁶ Equilibrium considerations also dictate the amount of steam required in the stripping process. Consequently, it is highly desirable to operate the stripper at the lowest possible temperature in order to reduce the steam requirement. Steam consumption in the stripper is also directly

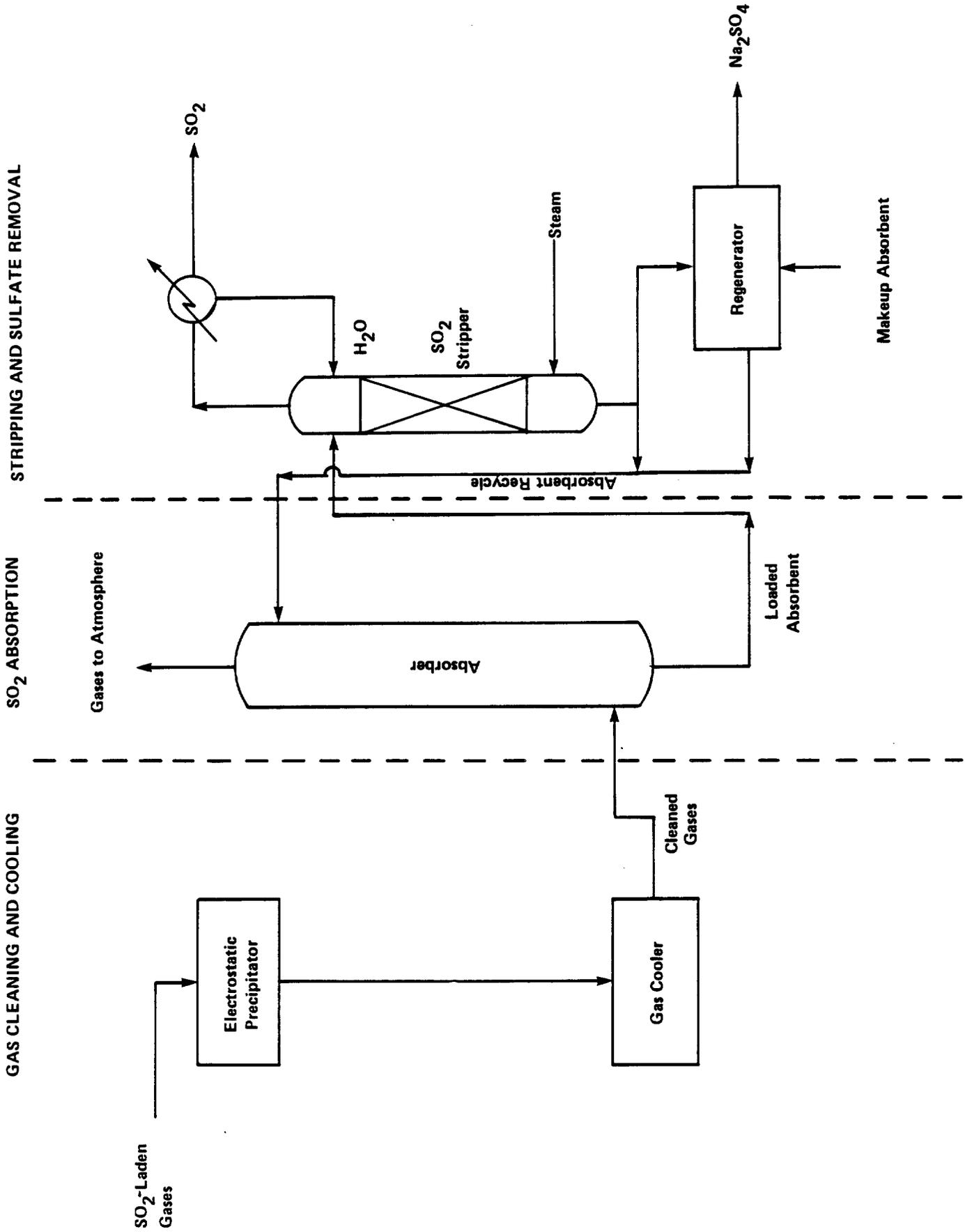


Figure 4-9. Flakt-Boliden citrate scrubbing process.

related to the feed stream SO_2 concentration. In general, the higher the feed stream SO_2 concentration, the lower the specific steam consumption.

There is little information in the literature regarding the design and operating considerations of the absorbent regeneration system that is utilized in the Flakt-Boliden process. Regeneration is accomplished by using seed crystals and a cooling unit to effect separation of sodium citrate and sodium sulfate; the sodium citrate is recycled to the absorber and the sodium sulfate is discarded. The details of the regeneration system are said to be contained in a U.S. patent, as mentioned in Section 4.3.5.2.

4.3.5.4 Operational Problems. A number of actual and potential problems have become evident with regard to citrate-type scrubbing systems as a result of the pilot-scale demonstrations that have been conducted. The Bureau of Mines process is rather complex, and more development work is needed in order to increase the reliability of the process, especially with regard to the H_2S generation and sulfur handling systems.⁶ As currently defined, the Bureau of Mines process utilizes natural gas, normally methane, in the production of H_2S . With the future availability of natural gas in doubt, its use is not very desirable. This consideration is also applicable to the use of kerosene or SAE-10 motor oil in the sulfur flotation step.

Mechanical problems have plagued every pilot-scale effort to date involving the Bureau of Mines process. The majority of these problems have occurred in the SO_2 reduction circuit. The problems experienced include gas cleaning system failures, frequent pump failures, and flow lines plugged with precipitates and melted sulfur.⁶ Due to the frequency of the problems encountered, it was often quite difficult to achieve complete steady-state operation. Many problems did prove chronic and were never eliminated to the extent where system reliability could be increased to acceptable limits. The Bureau of Mines is, however, looking into steam stripping of the loaded absorbent as an alternative to sulfur precipitation by H_2S ,⁶ which would, if adopted, transform the Bureau of Mines process into a process that would be essentially

identical to the Flakt-Boliden process. This alternative would simplify the process significantly and would probably eliminate most of the aforementioned problems.

As suggested above, the Flakt-Boliden process has not involved the numerous problems on the pilot scale that the Bureau of Mines process has encountered. This is primarily due to the fact that the steam stripping procedure utilized by Flakt-Boliden is not nearly as complex as the SO₂ reduction/H₂S generation scheme employed in the Bureau of Mines process. As mentioned previously, the bulk of the problems that were encountered in the Bureau of Mines pilot studies occurred in the SO₂ reduction circuit. Pilot plant experience with the Flakt-Boliden process at the Ronnskar smelter in Sweden has been more successful in terms of demonstrating system reliability.⁶

4.3.5.5 Survey of Operating Experience. Neither the Bureau of Mines citrate scrubbing process nor the Flakt-Boliden citrate scrubbing process has been applied on a commercial scale. However, three pilot-scale studies that involved the Bureau of Mines process have been conducted in the United States, and pilot-scale testing of the Flakt-Boliden system has been conducted at the Ronnskar smelter in Sweden.

The Bureau of Mines, Salt Lake City Metallurgy Research Center, began research on flue gas desulfurization with particular emphasis on the application of scrubbing technology for control of SO₂ emissions from the nonferrous smelting industry. Absorption in an aqueous solution of citric acid and sodium citrate was selected for intensive study due to the chemical stability, low vapor pressure, and buffering capacity of the absorbent.⁶ The purity and physical character of the precipitated sulfur were also considered advantageous.

After promising bench-scale results were obtained, the Bureau of Mines, in conjunction with the Magma Copper Company, constructed and operated a pilot plant to remove SO₂ from reverberatory furnace offgases generated at Magma's facility in San Manuel, Arizona. This pilot plant, constructed in 1970, treated approximately 300 scfm of gas from the reverberatory furnace containing 1.0 to 1.5 percent SO₂ and consistently removed 93 to 99 percent of the SO₂ from the gas

stream. Several problems consistently plagued this system, most of which occurred in the SO_2 reduction circuit as mentioned in Section 4.3.5.4. Pump breakdowns and plugged flow lines were the most frequently encountered problems.⁶ Failure of the gas cleaning system was also quite frequent. Because of the chronic nature of several of the problems encountered, useful data on the consumption of citric acid and other reagents were not obtained. However, as noted above, the system did achieve SO_2 -removal efficiencies of 93 to 99 percent while in operation.⁶

Another pilot plant was constructed by the Bureau of Mines and operated jointly by the Bureau of Mines and the Bunker Hill Company at Bunker Hill's lead smelter in Kellogg, Idaho. This pilot plant had a nominal capacity of 1,000 scfm of gas containing 0.5 percent SO_2 , with a corresponding sulfur production of about 1/3 ton of sulfur per day. The feed stream was taken as a slipstream from a Lurgi updraft sintering machine. Problems with the SO_2 reduction system plagued this pilot facility as well. Problems in maintaining a steady-state feed stream were also encountered. Many problems did prove to be chronic, thus preventing conclusive system tests.

A third pilot plant demonstrating the Bureau of Mines process was independently built and operated by Arthur G. McKee and Company, Peabody Engineering Systems, and Pfizer, Inc., at Terre Haute, Indiana, in 1972.⁶ This facility treated approximately 2,000 scfm of stack gas with an SO_2 concentration ranging from 0.1 to 0.2 percent from a coal-fired steam generating station. After several modifications to arrive at a final equipment configuration, the pilot plant operated from March 15 to September 1, 1974. Although operational difficulties that prevented the steady-state operation of the entire system were encountered, SO_2 -removal efficiencies were consistently in the range of 95 to 97 percent. The longest sustained run was 180 hours.

The Flakt-Boliden process has been applied on a pilot scale at the Ronnskar smelter in Sweden. The major reasons for installing this system were to establish a design background for the absorption/stripping process and to investigate the influences of various components in the raw gas on the oxidation of SO_2 in the absorbent.

The raw gases that comprise the feed stream to the scrubbing system originate in the multihearth roasters, electric furnaces, converters, and various lead smelting operations at the Ronnskar works. As most of the metallurgical processes involved are not continuous, the SO_2 concentration in the effluent streams fluctuates between 0.2 and 6.0 percent by volume; however, the SO_2 concentration does remain approximately constant at one level or another for long enough periods of time to allow steady-state observations.

Flakt has reported that the test results look very promising, with oxidation rates at least an order of magnitude lower than those found in the Bureau of Mines process. Consequently, the requirement for makeup chemicals should be relatively low for the Flakt-Boliden process.⁶ The removal efficiency associated with this pilot facility has not been published extensively in the literature; however, it is thought to be in excess of 90 percent. Similarly, information on operational problems that may have been encountered is scarce.

Flakt is reportedly responsible for a new process development that significantly decreases steam consumption in the stripping step.⁶ This could be especially important where gas streams with low SO_2 concentrations are to be processed since stripper steam consumption is not a linear function of feed stream SO_2 concentration and can increase rapidly at low concentrations. As of this writing, however, no details regarding the specifics of this new development were available.

4.3.5.6 Applicability to Reverberatory Smelting Furnaces. As mentioned in Section 4.3.5.4, the Bureau of Mines process has experienced numerous problems, most of which occurred in the SO_2 reduction circuit; thus, the system was never able to demonstrate adequate reliability. However, when operable, the system did demonstrate the ability to effect SO_2 -removal efficiencies of 93 to 99 percent from a 1.0 to 1.5 percent SO_2 stream that originated in green-charged reverberatory smelting furnaces at the Magma smelter. In addition, the system has proven its ability to handle extremely weak streams as a result of the 95 to 97 percent removal efficiencies achieved by the McKee-Peabody-Pfizer system while operating on coal-fired boiler offgases with an

SO₂ concentration of 0.1 to 0.2 percent. Thus, if system reliability could be improved via the elimination of chronic operational problems, the system could be a viable option for the control of reverberatory furnace effluents. There are no indications that the problems encountered thus far represent fundamental flaws in the application of the theory behind the system operation; however, reliable full-scale operation on either reverberatory furnace effluents or other comparable streams will have to occur before the system can be said to be fully demonstrated for the control of weak streams generated by reverberatory furnaces.

Perhaps the most significant drawback of the Bureau of Mines process is its requirement for kerosene (or SAE-10 motor oil) and natural gas. It has been estimated that the costs of these commodities alone would constitute 25 to 30 percent of the total annual direct operating costs.⁸ In addition, the uncertainty regarding the future availability of these commodities tends to make their use undesirable.

The relative simplicity of the Flakt-Boliden process becomes quite evident in comparison to the Bureau of Mines process when the absence of the SO₂ reduction/H₂S generation steps as well as the other related sulfur handling equipment are considered. In lieu of the problems that are associated with the aforementioned operations, steam stripping of the absorber effluent may be an attractive alternative. The supply of steam at a smelter should not be a critical item since it is normally advantageous to strip at reduced pressure, which allows the use of low quality steam or even hot water. However, this system has not been demonstrated in areas where the supply of water may be a critical item.

Full-scale applications of the cold water scrubbing process at the Ronnskar smelter have resulted in SO₂-removal efficiencies in the range of 98 percent.³⁰ Therefore, since the addition of the citric acid/sodium citrate buffer is known to increase SO₂ absorption efficiency, it would be natural to assume that a full-scale application using the citrate absorbent would be at least equally efficient. However, full-scale application of the system to either reverberatory

furnace effluents or other comparable streams would have to be demonstrated with adequate reliability before the system could be considered to be a technically viable control alternative for weak streams of reverberatory furnace origin.

In summary, both the Bureau of Mines process and the Flakt-Boliden process require further development before they can be considered technically viable weak stream control options. Additional developmental work will be required to eliminate the numerous problems associated with the Bureau of Mines process before a commercial-scale application would be feasible. The Flakt-Boliden process, due to its relative simplicity, has great potential in as far as weak stream control is concerned; however, a commercial-scale application that utilizes the citrate-type absorbent will be required in order to demonstrate that the system can achieve the required level of SO₂-removal efficiency while maintaining good reliability. Furthermore, with the Flakt-Boliden system, product flexibility is obtained because the concentrated SO₂ stream produced can be liquefied to produce liquid SO₂, fed to a Claus plant to produce elemental sulfur, or fed to a conventional sulfuric acid plant to produce sulfuric acid.

4.3.6 Conclusions Regarding Flue Gas Desulfurization Systems

Sections 4.3.2 through 4.3.5 present discussions of six flue gas desulfurization processes based upon four different types of chemical systems. These are summarized in Table 4-6.

Ammonia scrubbing with ABS acidulation and both types of citrate scrubbing systems were eliminated from consideration primarily because of a lack of full-scale demonstration. Of the three systems that remain, two (lime/limestone and magnesium oxide scrubbing) have been applied to reverberatory furnace offgases on a full-scale basis, while the other (ammonia scrubbing with sulfuric acid acidulation) has been applied to metallurgical offgases from several sources on a full-scale basis. These systems, along with their reported SO₂-removal efficiencies and reliabilities, are summarized in Table 4-7.

All of these systems have proven capable of achieving their design SO₂-removal efficiencies. Operating experience suggests that

TABLE 4-6. FLUE GAS DESULFURIZATION PROCESSES ASSESSED FOR APPLICATION TO REVERBERATORY FURNACE OFFGASES

Process	Type of absorbent used
1. Lime/limestone scrubbing	Calcium-based
2. Ammonia scrubbing with sulfuric acid acidulation (the "Cominco" process)	Ammonia-based
3. Ammonia scrubbing with ammonium bisulfite (ABS) acidulation	Ammonia-based
4. Magnesium oxide scrubbing (the MAGOX process)	Magnesium-based
5. Bureau of Mines citrate scrubbing process	Based upon a citric acid-sodium citrate buffer
6. Flakt-Boliden citrate scrubbing	Based upon a citric acid-sodium citrate buffer

TABLE 4-7. FLUE GAS DESULFURIZATION EFFICIENCY AND RELIABILITY DATA FOR THE FGD PROCESSES BEING CONSIDERED
IN THE NSPS REVISION FOR PRIMARY COPPER SMELTERS

Type of FGD system	Origin of the feed gas stream	Reported SO ₂ removal efficiency, %	Reported reliability	Data source(s)
Lime/limestone	Molybdenum ore roaster (.35 to .75% SO ₂)	92-96	Good. Problems with plugging and scaling overcome.	Weisenberg, I. J., T. Archer, F. M. Winkler, and A. Prem. Feasibility of Primary Copper Smelter Weak SO ₂ Stream Control. Prepared for IERL, U.S. Environmental Protection Agency, Cincinnati, Ohio, under EPA Contract No. 68-03-2378. Publication No. EPA-600/2-80-152. July 1980. Background Information for New Source Performance Standards: Primary Copper, Lead, and Zinc Smelters, Volume I: Proposed Standards. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 450/2-74-002a. October 1974.
	Primary copper smelter reverberatory furnace ^a (-2.5% SO ₂)	99.5	Approximately 99.3%. Problems with scaling overcome.	Kohno, H., and Y. Sugawara. SO ₂ Pollution Control with the Lime-Gypsum Process at the Onahama Smelter. (Presented at the AIME Annual Meeting. Chicago. February 22-26, 1981.)
	Coal-fired utility boilers (.04 to 0.4% SO ₂)	90+	In excess of 90%.	Stack, A. V. Application of Flue Gas Desulfurization in the Non-Ferrous Metals Industry. (Presented at the AIME Annual Meeting. Chicago. February 22-26, 1981.) Background information for New Source Performance Standards: Electric Utility Steam Generating Units. Background Information for Proposed SO ₂ Emission Standards. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 450/2-78-007a. July 1978.
Cominco Ammonia	Dwight-Lloyd sintering machines, zinc roasters and sulfuric acid plant tail gases (0.3 to 7.0% SO ₂).	90-98	Good. No plugging or scaling since the absorbent is a solution rather than a slurry.	Background Information for New Source Performance Standards: Primary Copper, Lead, and Zinc Smelters, Volume I: Proposed Standards. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 450/2-74-002a. October 1974. Weisenberg, I. J., T. Archer, F. M. Winkler, and A. Prem. Feasibility of Primary Copper Smelter Weak SO ₂ Stream Control. Prepared for IERL, U.S. Environmental Protection Agency, Cincinnati, Ohio, under EPA Contract No. 68-03-2378. Publication No. EPA-600/2-80-152. July 1980.
				Matthews, J. C., F. L. Bellegia, C. H. Gooding, and G. E. Weant. SO ₂ Control Processes for Nonferrous Smelters. Research Triangle Institute. Research Triangle Park, N.C. Publication No. EPA-600/2-76-008. January 1976.

See notes at end of table.

(continued)

TABLE 4-7. (continued)

Type of FGD system	Origin of the feed gas stream	Reported SO ₂ removal efficiency, %	Reported reliability	Data source(s)
HAGOX	Primary copper smelter reverberatory furnace ^a (-2.5% SO ₂)	99+	--b	Weisenberg, I. J., T. Archer, F. M. Winkler, and A. Prem. Feasibility of Primary Copper Smelter Weak SO ₂ Stream Control. Prepared for IERL, U.S. Environmental Protection Agency, Cincinnati, Ohio, under EPA Contract No. 68-03-2378. Publication No. EPA-600/2-80-152. July 1980.
	Coal-fired utility boilers (-.04 to 0.4% SO ₂)	90+	17-80 ^c	Background Information for New Source Performance Standards: Electric Utility Steam Generating Units. Background Information for Proposed SO ₂ Emission Standards. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 450/2-78-007a. July 1978.
				Maxwell, M. A., and G. R. Koehler. The Magnesite Slurry SO ₂ Recovery Process Operating Experience with a Large Prototype System. (Presented at the AIChE Annual Meeting, New York. November 26-30, 1972.)

^a Located at the Onahama smelter in Japan.

^b No reliability data given.

^c Based on data presented for Boston Edison's Mystic No. 6. System reliability improved steadily as operational problems were alleviated.

the limiting factor is system reliability. However, while all three types of systems have experienced operational problems that hindered system reliability, the most severe problems have been eliminated or minimized to acceptable levels. Consequently, the reliability of these systems should be acceptable. The only possible exception might be the MAGOX system for which reliability data are scarce.

As indicated by the data presented in Table 4-7, the scrubbing systems at the Onahama smelter in Japan are designed to achieve SO₂ removal efficiencies in excess of 99 percent. This is due to the stringent sulfur recovery regulations placed upon the smelter by the local regulatory authority. It is important to note, however, that the incremental cost of achieving a given SO₂-removal efficiency rises quite rapidly when removal efficiencies in excess of 90 percent are considered. Flue gas desulfurization experience in other industries has indicated that the highest design SO₂-removal efficiencies are generally in the neighborhood of 90 percent. Thus, since applications involving SO₂-removal efficiencies in the area of 90 percent are substantially more widespread than applications that require removal efficiencies in excess of 95 to 99 percent, 90 percent has been accepted as a technically feasible SO₂ removal efficiency for each of these systems.

4.4 PARTICULATE MATTER CONTROL FOR REVERBERATORY FURNACES

4.4.1 Introduction

The design of particulate removal equipment is dependent upon a number of factors relating to pollutant gas stream characteristics and process operating parameters. Among the most important data required are the following:

- Physical and chemical characteristics of the particulate
- Range of volumetric flow rates the stream will exhibit
- Range of anticipated particulate concentrations (dust loadings)
- Temperature, pressure, and humidity of the pollutant gas stream

- Nature of the stream, i.e., corrosiveness, solubility, etc.
- Required particulate removal efficiency.

Among the most important physical and chemical characteristics of the particulate are size distribution, shape, hygroscopicity, agglomerating tendency, electrical conductivity, flammability, and toxicity. It is not uncommon for the aforementioned constraints to restrict a designer to one or perhaps two types of equipment.

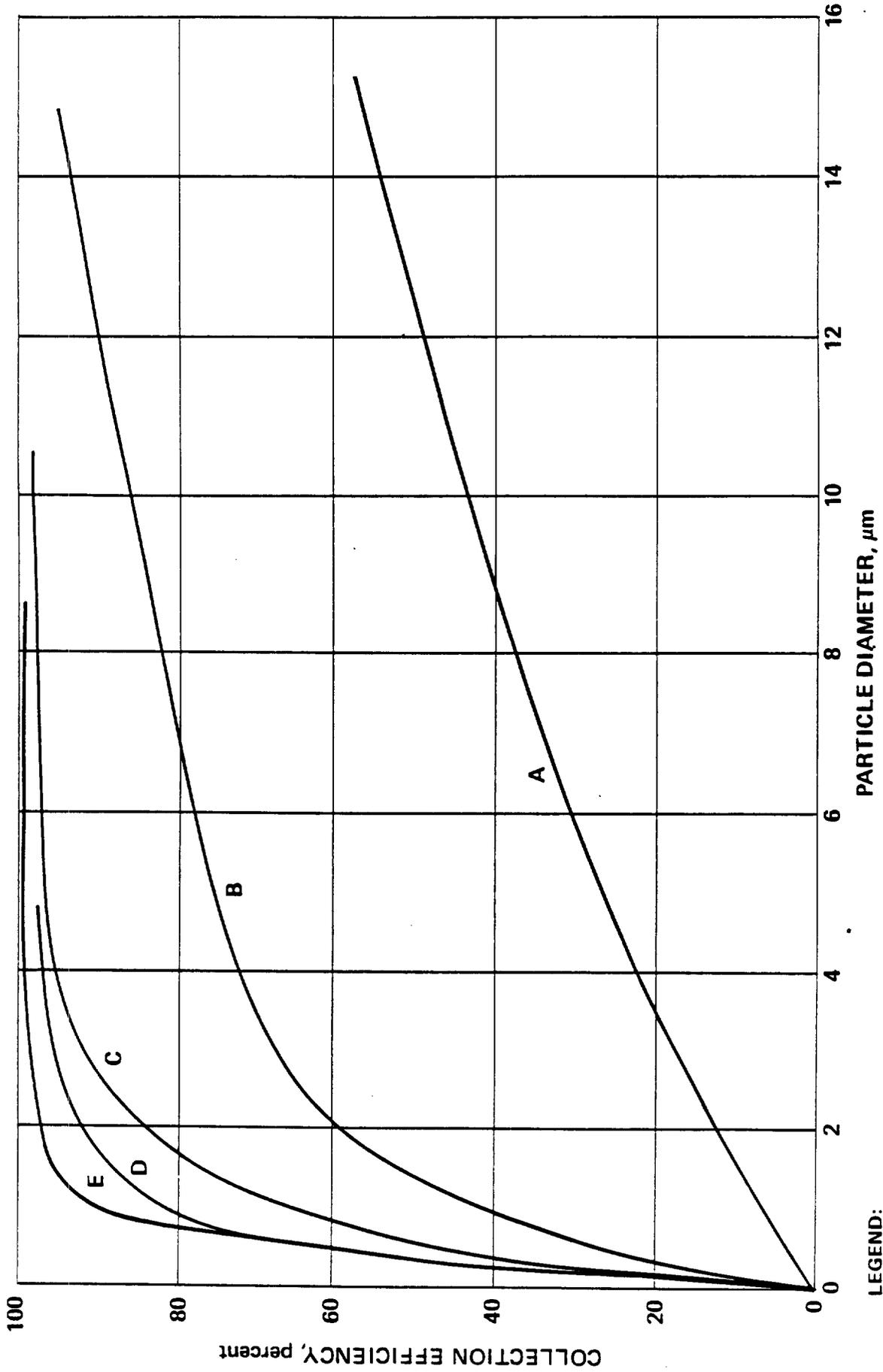
There are currently five basic classes of particulate removal devices in use:²¹

- Gravity separators
- Cyclone separators
- Wet collectors
- Fabric filters
- Electrostatic precipitators.

There may be several types of equipment within each basic class, each of which may bear a different descriptive name.

The nature of reverberatory furnace offgases must be carefully considered before a particular class or type of particulate control device can be specified. Reverberatory furnace effluents are known to contain a substantial quantity of particulate matter less than 10 μm in diameter.³¹ Thus, a control device that efficiently removes particles with a diameter of less than 10 μm is required. For removal of particles in this size range, high-energy scrubbers such as venturi scrubbers, fabric filters, and dry electrostatic precipitators provide the most efficient removal. This fact is illustrated by Figure 4-10, a plot of typical collection efficiency versus particle size for several particulate control devices, and Table 4-8, tabular data relating particulate removal efficiency and particle size for particles less than 10 μm in diameter.

The need to reclaim and reprocess the dusts that are contained in reverberatory furnace offgases is another important factor that must be considered. Recycling of dusts is generally practical to recover valuable



LEGEND:
 A = HIGH-THROUGHPUT CYCLONE D = DRY ELECTROSTATIC PRECIPITATOR
 B = HIGH-EFFICIENCY CYCLONE E = VENTURI SCRUBBER
 C = SPRAY TOWER

Figure 4-10. Typical collection efficiency curves for several types of particulate removal devices.

TABLE 4-8. TYPICAL FRACTIONAL COLLECTION EFFICIENCIES OF PARTICULATE CONTROL EQUIPMENT²¹

	Efficiency at given size (percent)		
	5 μm	2 μm	1 μm
Medium-efficiency cyclone	30	15	10
High-efficiency cyclone	75	50	30
Electrostatic precipitator	99	95	85
Fabric filter	99.8	99.5	99
Spray tower	95	85	70
Venturi scrubber	99.7	99	97

metals contained in the dusts. Consequently, particulate control methods that facilitate dust reclamation are preferable.

4.4.2 Venturi Scrubbers

4.4.2.1 General Discussion. Like other wet collectors, venturi scrubbers operate at variable collection efficiencies directly proportional to the amount of energy expended.⁵ It is possible, however, to effectively remove particles in the 0.1 to 20 μm range with venturi scrubbers.²¹

Venturi scrubbers use a rectangular or circular flow conduit that converges to a narrow throat section and diverges back to its original cross-sectional area. When the gas stream enters the convergent section, its linear velocity begins to increase and eventually reaches a maximum in the throat area. The high-velocity gas stream tends to atomize the liquid (usually water in the case of particulate removal), which is injected into the stream via nozzles in the throat area. The liquid droplets produced serve as targets for inertial impaction of the particles. Thus, good atomization is essential in providing sites for inertial impaction. A typical venturi scrubber is illustrated in Figure 4-11.

The typical water circulation rate to a venturi scrubber varies from 0.3 to 1.6 $\ell/\text{m}^3/\text{min}$ (2 to 12 gal/10³ cfm) of gas treated,²¹ which is comparable to the water circulation rate required for other wet particulate collectors. However, as compared with other dry and wet collectors, pressure losses in venturi scrubbers can be quite large. Venturi scrubbers are capable of attaining high removal efficiencies of submicron particles at the expense of high pressure drops. Pressure drops vary from 0.007 to 0.25 atm (3 to 100 in H₂O), depending upon the collection efficiency desired;²¹ however, collection efficiencies as high as 99 percent for submicron particles may be attained. Figure 4-12 depicts a typical relationship between fractional collection efficiency²¹ and particle size for venturi scrubbers.

4.4.2.2 Application of Venturi Scrubbers to Reverberatory Smelting Furnaces. As noted previously, analysis of the particle size distribution of particulate matter entrained in reverberatory furnace

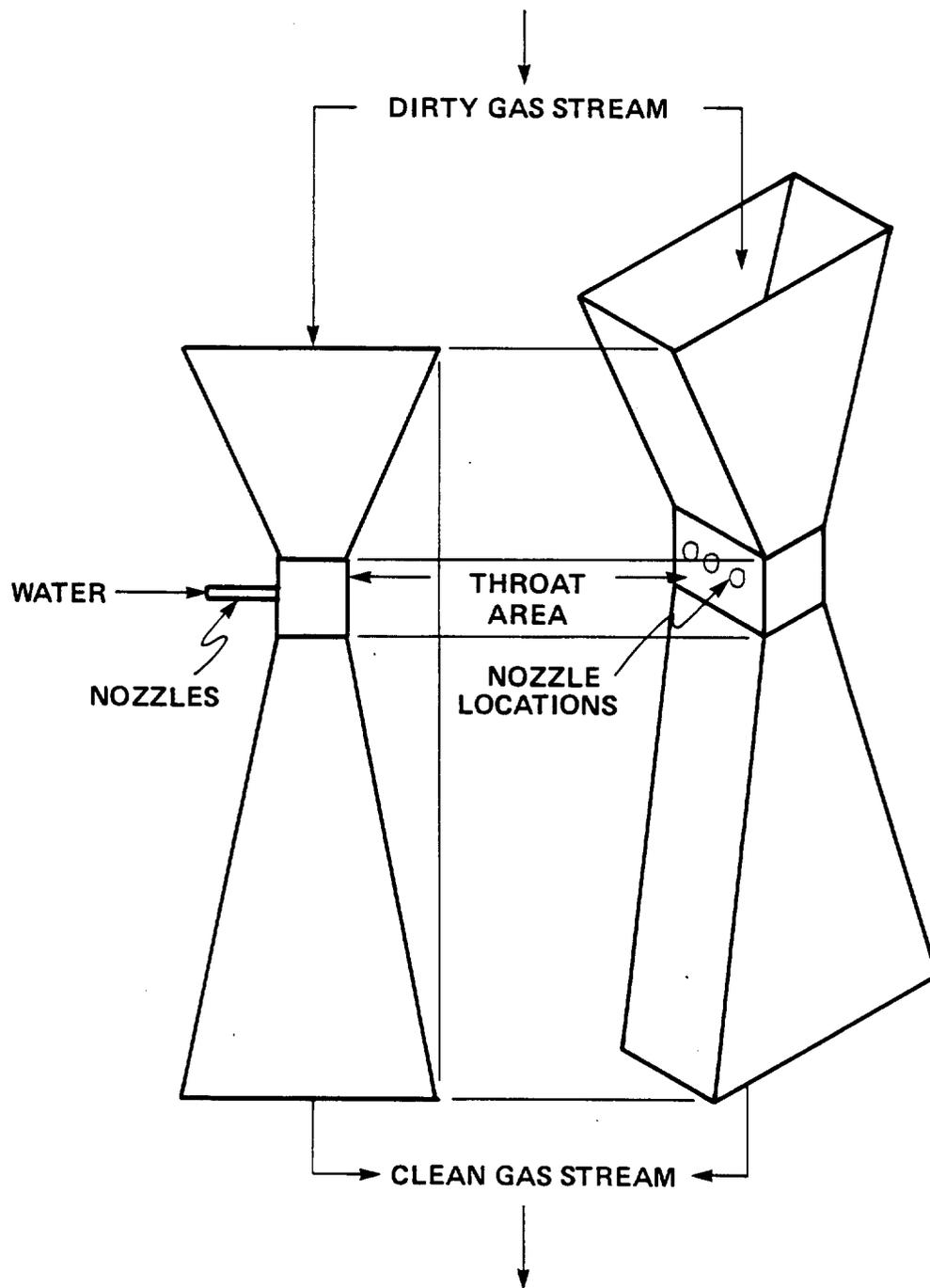


Figure 4-11. Venturi scrubber.

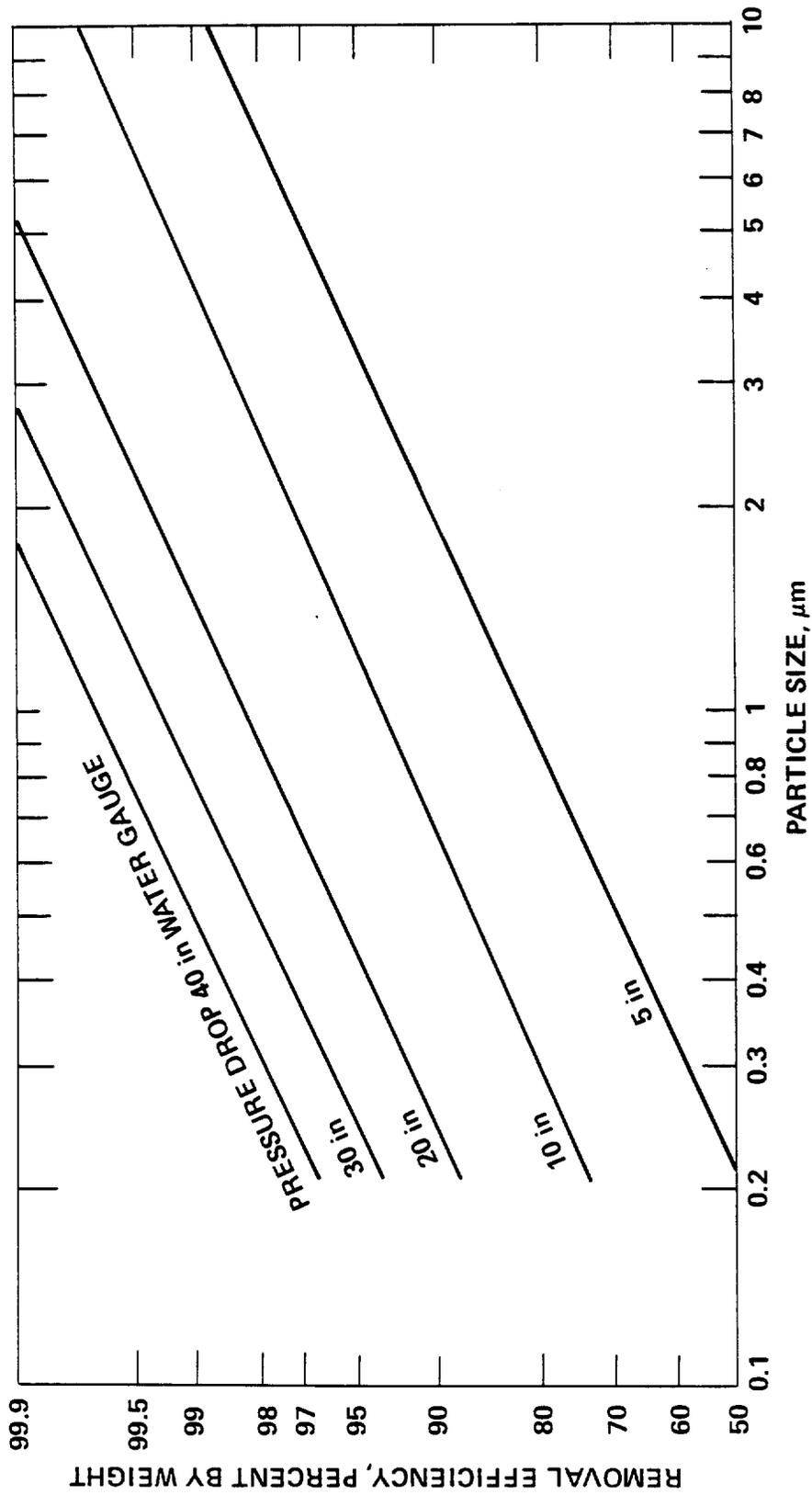


Figure 4-12. Typical relationship between fractional collection efficiency and particle size for venturi scrubbers.²¹

effluents indicates that the majority of the particles are less than 10 μm in diameter.³¹ While a venturi scrubber can achieve efficient removal of these particles, high pressure losses will be required (see Figure 4-12). Consequently, because energy requirements are proportional to the pressure losses incurred, energy costs may be high.

The treatment of the liquid effluent from venturi scrubbers must also be considered. When dust reclamation is considered, venturi scrubbers, by virtue of being wet collectors, would not prove to be as convenient as dry collectors. This fact, coupled with potentially high energy requirements, is probably the major reason why venturi scrubbers have not found wide-spread application in the smelting industry. When they have been applied, their primary function has been to remove particulate matter from gas streams bound for sulfuric acid plants.

4.4.3 Fabric Filters

4.4.3.1 General Discussion. Fabric filtration is one of the oldest and most commonly used methods of effecting particulate removal from gas streams.^{5 21} Fabric filters are typically used for high efficiency (>99 percent) particulate removal.

Filters must be constructed of materials compatible with characteristics of both the carrier gas and the particulate to be collected. A wide range of filtering materials, including woven or felted fabric, is used. Fabrics may be natural or synthetic, depending upon the nature of the gas stream to be treated. Among the materials currently in common use are wool, cotton, nylon, fiberglass, polyesters, and aromatic polyamides.²¹

Particulate matter is removed from the gas stream by impingement on or adherence to the fibers. The filter fibers are normally woven with relatively large open spaces, sometimes 100 μm or larger in diameter. Consequently, the filtering process is not one of simple fabric sieving, as evidenced by the fact that high collection efficiencies have been achieved for dust particles with a diameter of 1 μm or less. 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.

One of the major disadvantages of fabric filters is the requirement that they be cleaned frequently to prevent excessive pressure drops. Several means of cleaning the filter bags have been devised, and filters are generally designed with ease of cleaning in mind. The most common methods of cleaning are mechanical vibration or "shaking," pulse jets, and reverse air flow. Figures 4-13, 4-14, and 4-15 present schematics of baghouses with each of the above-mentioned cleaning systems. Cleaning is responsible for a major portion of the filter degradation that occurs over time. Thus, the frequency of cleaning must be determined as a tradeoff between higher operating costs resulting from increased pressure drops and filter replacement costs resulting from more frequent cleaning.

In general, fabric filters must provide a large surface area per volume of gas to be cleaned. The reverse of this ratio is known as the air-to-cloth ratio. Optimum values normally range from 0.5 to 4 cm/s (1 to 8 ft/min).²¹ The air-to-cloth ratio required for a given application may in turn require that the baghouse be quite large. Thus, one inherent disadvantage of fabric filters becomes evident; namely, the overall size of the required equipment is quite large in comparison to other particulate removal devices.

4.4.3.2 Application of Fabric Filters to Reverberatory Smelting Furnaces. With regard to smelters, baghouses are generally chosen as the control device when the SO_3 concentration and chloride content of the effluent gases are low.⁵ High SO_3 concentrations are known to produce corrosion and deterioration of both the baghouse structure and the filter fabric. If chlorides are present in the effluent gases, they will tend to produce hygroscopic effects on the fabric filters. Copper, zinc, and lead chloride act as desiccant materials and can produce a sticky material that tends to blind and eventually tear the filter fabric. Reverberatory furnace effluents may contain any of the

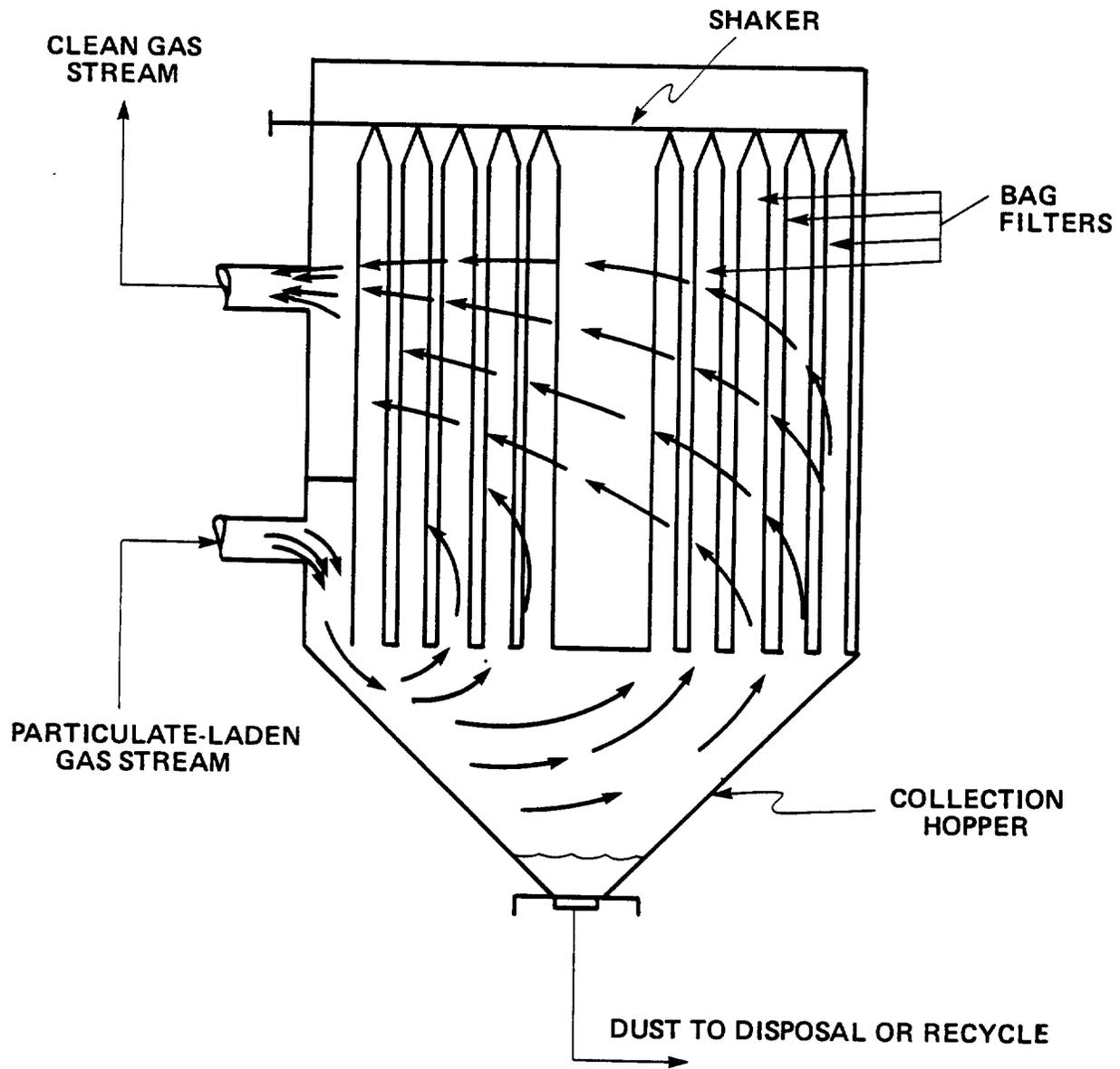


Figure 4-13. Baghouse with mechanical shaking.

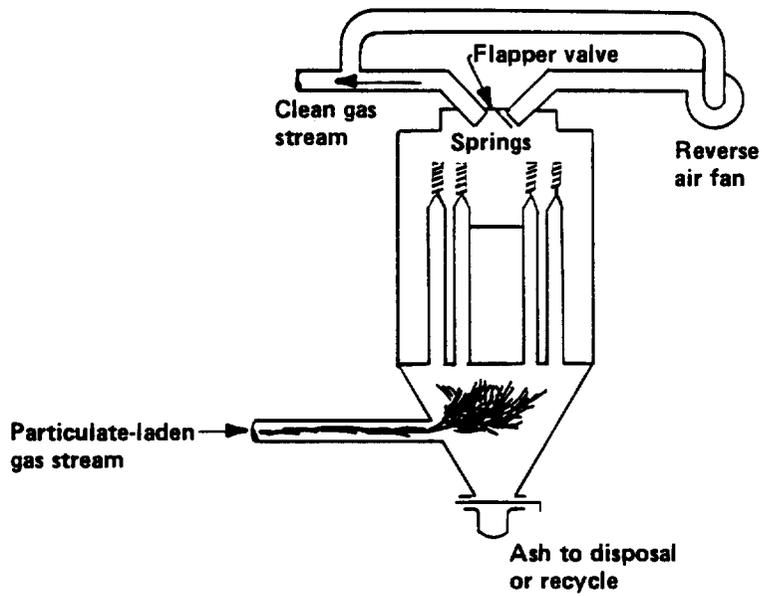


Figure 4-14. Baghouse with reverse flow cleaning.²¹

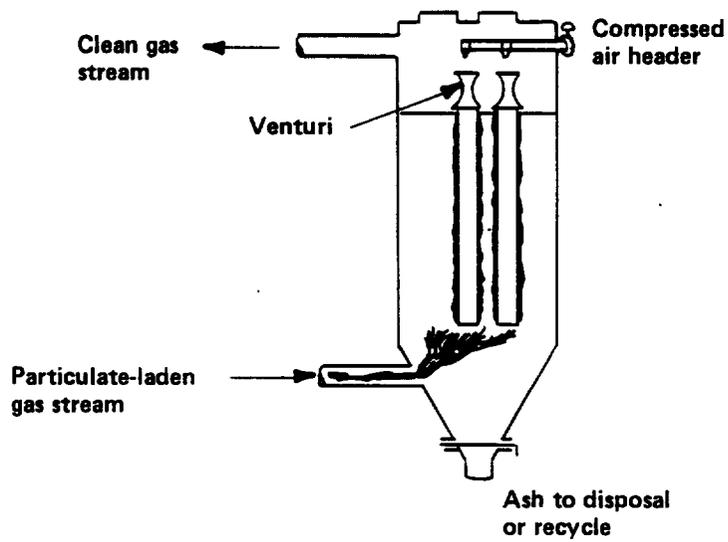


Figure 4-15. Baghouse with cleaning by jet pulse.²¹

above-mentioned chemical species. The gas stream temperature is the factor that governs the extent to which these species are formed in the gas stream.⁵ With careful control of the gas stream temperature, the formation of potentially troublesome chemical substances such as acid mists and metal chlorides can be minimized to acceptable levels;⁵ however, there is a practical limit to the degree that temperature can be controlled. Excessive gas stream cooling is usually not practical; however, the gas stream temperature must not exceed the upper limit as defined by the type of filter material being used. Filters made of glass fibers are more suitable for higher temperatures, i.e., 260° to 270° C (500° to 518° F). The current temperature ceiling for the application of fabric filters is about 288° C (550° F).²¹

Thus, for the application of fabric filters to reverberatory furnace effluents to be technically feasible, the following criteria would have to be met:

1. The gas stream temperature would have to be carefully monitored to prevent the excessive formation of SO₃ and metal chlorides; however, the gas stream temperature could not be decreased to the point where the stream reaches its dew point.
2. The gas stream temperature would have to be below the current ceiling temperature of approximately 288° C (550° F).

Gases generated in a reverberatory furnace exit the furnace at approximately 1300° C (2372° F). Thus, it is evident that they would have to be cooled prior to being routed through any type of fabric filtration device. Reverberatory furnace offgases are generally passed through waste heat boilers to effect heat recovery, which in turn decreases the gas stream temperature to about 316° to 427° C (600° to 800° F). As indicated above, gases in this temperature range would be too hot for treatment by fabric filtration. Additional cooling would be required to ensure that the filters would not be damaged. The amount of cooling required could be provided by dilution with ambient air; however, this would increase the volume of gases to be handled, which would in turn increase the capital and operating costs of the filtra-

tion device. Evaporative cooling may, however, be an acceptable means by which to further cool the gases.

Fabric filtration has never been used by the domestic primary copper industry to control particulate matter emissions from reverberatory furnaces. Fabric filters have, however, been used to control particulate matter emissions from gases that originate in fluid-bed roasters, multihearth roasters, electric furnaces, and converters. EPA has tested a fabric filter that was used to remove particulate matter from a gas stream composed of effluents from a fluid-bed roaster, an electric furnace, and several converters. These tests were conducted at the Anaconda Smelter in Anaconda, Montana, which subsequently shut down in 1980. Evaporative cooling was used to cool the gases prior to their entry into the baghouse. This was accomplished by routing the gases through a spray chamber. The fabric filter was tested at approximately 102° C (216° F) and processed about 4,670 dscm/min (~164,920 dscf/min) of gas.³² Test results indicated that this device was achieving a particulate removal efficiency of 99.7 percent, which resulted in a mass emission rate of 13.1 kg/h (~29 lb/hr) to the atmosphere.

4.4.4 Electrostatic Precipitators

4.4.4.1 General Discussion. Electrostatic precipitation has played an important role in industrial gas cleaning since the original development work by F. G. Cottrell in 1910. Electrostatic precipitators are capable of achieving high collection efficiencies on particles that range from 0.05 to 200 µm in diameter;²¹ thus, use of electrostatic precipitators (ESP's) could be advantageous in applications where the majority of the particles to be collected are in the submicron range. Generally, electrostatic precipitators are employed when the major portion of the particulate matter to be collected is less than 20 µm in mean diameter and when temperature constraints preclude the use of fabric filters.

Particulate matter collection by electrostatic precipitation is based upon the fact that particles of one electrical charge experience an attraction to an electrode of opposite polarity. Separation of

suspended particulate matter by electrostatic precipitation requires three basic steps:⁵

1. Electrical charging of the suspended matter.
2. Collection of the charged particles on a grounded surface.
3. Removal of the collected matter to an external receptacle.

A charge may be imparted to the particulate matter prior to gas stream entry into the ESP by either 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. Particulate matter that passes through the corona is subject to an intense bombardment of negative ions that flow from the high-voltage electrode to the grounded collecting surface. The particles thereby become highly charged within a fraction of a second and migrate toward the grounded collection surface. A typical ESP is illustrated in Figure 4-16.

After the particulate matter deposits on the grounded collecting surfaces, adhesive, cohesive, and primary electrical forces must be sufficiently strong to resist any action or counter-electrical forces that would cause reentrainment of the particulate matter. The particulate matter is dislodged from the collecting surfaces by mechanical means such as vibrating with rappers or flushing with liquids. The collected materials fall to a hopper, from which they can be reclaimed for recycle or disposal.

Perhaps one of the most important properties of the particulate matter in relation to electrostatic precipitation is the electrical resistivity of the material to be collected. The resistivity of industrial dusts may vary from 10^{-3} to 10^{14} ohm · cm.²¹ If the resistivity of the material to be collected is too low ($<10^4$ ohm · cm), collected particles may not retain an electrostatic charge sufficiently high to keep them firmly attached to the collecting surfaces, thus allowing some of the collected material to become reentrained in the gas stream. On the other hand, particulate matter with a resistivity

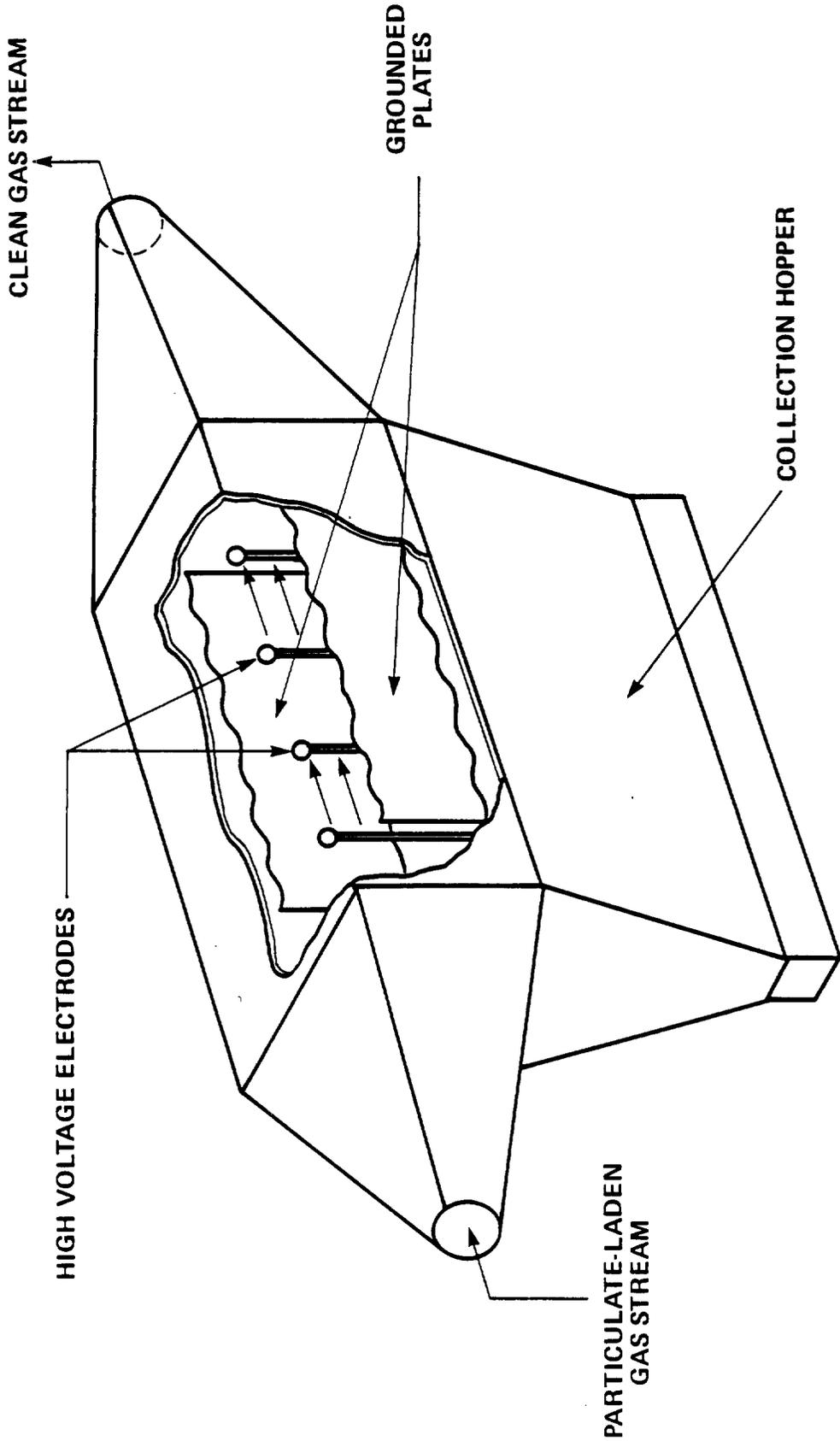


Figure 4-16. Electrostatic precipitator.

of greater than 10^{10} ohm · cm can cause precipitator collection efficiency to suffer.²¹ When dust resistivity is high, a large portion of the total voltage drop between the high-voltage electrodes and the collecting plates actually occurs across the dust layer, which in turn reduces the total corona power available to ionize and drive the charged particles to the collecting plates. Electrostatic precipitation is most effective in collecting dusts that exhibit resistivities in the range of 10^4 to 10^{10} ohm · cm.

When the resistivity of the dusts to be controlled is not appropriate for electrostatic precipitation, means exist by which to alter the resistivity in such a way that the dusts become amenable to removal by electrostatic precipitation. Resistivity is a strong function of both gas stream temperature and humidity; thus, by appropriate manipulation of these parameters, the resistivity of some dusts can be altered so that efficient removal by electrostatic precipitation becomes feasible.

Another means by which to achieve electrical resistivities in the desired range is the addition of conditioning agents to the gas stream. Currently, SO_3 and NH_3 are the only conditioning agents that are technically and economically feasible in commercial practice.²¹ Ammonia or SO_3 , when added to a gas stream in small amounts, act as electrolytes when adsorbed on the deposited dust particles. This in turn causes a marked reduction in resistivity.

4.4.4.2 Application of Electrostatic Precipitators to Reverberatory Smelting Furnace Effluents. Electrostatic precipitators have been used by the domestic primary copper industry for several years now to control effluents from reverberatory furnaces as well as effluents from roasters, converters, fugitive gas collection systems, and sulfuric acid plants. In some cases, ESP's are used to remove particulate matter from gas streams that are composed of effluents from several of the aforementioned sources.

(ESP's have several characteristics that make them particularly attractive for the reclamation of smelter dusts.) ESP's are capable of handling very large volumes of gas and can also easily reclaim valuable dusts. The ability of ESP's to exhibit high collection efficiencies

on fine particles is also quite attractive, especially where the control of reverberatory furnace effluents is considered.

It should be noted, however, that ESP's will only remove materials that exist as solids at the gas stream temperature. Some species, most notably metallic oxides, may remain in the vapor phase until the gas stream is vented to the atmosphere, at which point they condense and become particulate. Thus, particulate control efficiencies may be lowered substantially when the escape of condensable materials downstream of the control device is considered. This fact is supported by in-stack/out-of-stack test data obtained at several copper smelters.³²

For example, in-stack measurements on the reverberatory furnace ESP at Phelps Dodge-Ajo showed that, at 315° C (600° F), the ESP was achieving a 96-percent particulate removal efficiency. However, out-of-stack measurements obtained at 120° C (250° F) indicated that this ESP is less than 50 percent efficient because of the vaporized metallic oxides that pass through the ESP and subsequently condense. A summary of in-stack/out-of-stack test data from ESP outlets at three primary copper smelters is presented in Table 4-9. The data in this table indicate that a substantial portion of the emissions generated remain in the vapor phase at the temperature of the gas stream and thus are not removed by the ESP. For instance, at the Magma Smelter in San Manuel, Arizona, the data indicate that only about 18 percent of the emissions generated exist as solids when the gas stream passes through the ESP. Consequently, the other 82 percent escapes to the atmosphere.

There are several demonstrated methods of particulate control involving ESPs that can be applied to reverberatory furnace offgases. These may be summarized as follows:

1. A "hot" ESP to recover copper-containing dusts, with the treated gases vented to the atmosphere.
2. A "hot" ESP (to reclaim copper-rich dusts), followed by a "cold" ESP to reclaim the condensible out-of-stack emissions (e.g., metallic oxides), followed by venting to the atmosphere.

TABLE 4-9. SUMMARY OF IN-STACK/OUT-OF-STACK PARTICULATE MATTER TEST RESULTS AT REVERBERATORY FURNACE ESP OUTLETS³²

Smelter/test contractor	No. of test runs	Temperature, °C	In-stack particulate loading, mg/dscm ^a	Out-of-stack particulate loading ^b at 120° C, mg/dscm	Total particulate loading ^c at 120° C, mg/dscm
Magma, San Manuel, ^d AZ/ EPA, NEIC	4	280	230	1,030	1,260
Phelps Dodge, ^e Ajo, AZ/ Radian	3	315	95	2,335	2,430
Phelps Dodge, Ajo, AZ/ Aerotherm	2	290	70 ^f	1,730 ^g	1,800
Kennecott, Hayden, AZ/ Aerotherm	1	145	30 ^f	30 ^g	60

^aIncludes nozzle wash and in-stack filter.

^bIncludes probe wash, back half of the in-stack filter holder wash, front half of the out-stack filter holder wash, and the out-stack filter.

^cIncludes in-stack and out-of-stack particulate (does not include impinger catch).

^dSingle-point sample.

^eIncomplete traversing.

^fDoes not include nozzle wash. Therefore, these results are somewhat lower than the actual loading.

^gIncludes nozzle wash. Therefore, these results are somewhat higher than the actual loading.

3. Gas cooling (by evaporative water cooling) to approximately 121° C (250° F), followed by a "cold" ESP or fabric filter to collect all particulates, followed by venting to the atmosphere.

As evidenced by the in-stack/out-of-stack test results presented in Table 4-9, Option 1 would allow a substantial portion of the generated emission to escape. Options 2 and 3, however, would capture essentially all of the particulate matter in the furnace offgases. If, for metallurgical reasons, the copper-containing dusts to be recycled cannot tolerate substantial quantities of metallic oxides, e.g., As_2O_3 , "hot" and "cold" ESPs in series (Option 2) would be preferable. However, if the metallurgy involving the dusts to be recycled is not sensitive to the level of impurities, Option 3 would be preferred, especially since it appears to be less expensive than Option 2.

In addition to the in-stack/out-of-stack tests mentioned above, EPA has simultaneously tested the inlet and outlet streams of an ESP at the ASARCO smelter in El Paso, Texas. The gas stream subjected to particulate matter removal was composed of gases from multihearth roasters and a reverberatory furnace, with a corresponding flow rate of 4,670 dscm/min (165,000 dscf/min). The estimated removal efficiency, based on the in-stack measurements, was 96.7 percent, with about 37.2 kg/h (82 lb/h) of particulate matter emitted to the atmosphere.³² The concentrations in the inlet and outlet streams were 5,100 mg/dscm (0.0003 lb/dscf) and 1,127 mg/dscm (0.0001 lb/dscf), respectively.

In a study conducted by Nichols et al.,³¹ actual test data were compared to theoretically generated data to determine if ESP's were capable of operating at design efficiency while removing particulate matter from reverberatory furnace offgases. Actual in-stack test data involving a Joy-Western precipitator indicated that approximately 96.7 percent of the particulate matter in the furnace offgases was removed. The result compared quite favorably with the 96.8-percent theoretical removal efficiency that was predicted by computer simulation.

In summary, ESP's appear to be very effective in removing particulate matter from reverberatory furnace offgases. It is crucial to

note, however, that an ESP can only remove material that exists as particulate matter at the temperature of operation. Consequently, measures to control out-of-stack particulate emissions must be taken. Control options consist of the use of hot and cold ESP's in series or gas cooling followed by a cold ESP or fabric filter. The most appropriate option will depend upon the sensitivity of the dusts to be recycled to impurities such as metallic oxides.

4.5 INCREASING THE SO₂ STRENGTH OF REVERBERATORY FURNACE OFFGASES

The quantity of sulfur emitted from reverberatory furnaces as SO₂ averages about 22 percent (by weight) of the total sulfur entering the smelter, but can be as high as 34 percent for green charge or as low as 9 percent for calcine charge produced by a fluid-bed roaster.⁶ The concentration of SO₂ in the offgases is typically in the range of 1.0 to 1.5 percent for green-charged furnaces, and 0.5 to 1.0 percent for those using calcine feed. As noted previously, these concentrations are too low for processing autothermally in conventional contact sulfuric acid plants.

Options to be considered for facilitating the control of reverberatory furnace offgases fall into two major categories. The first group includes control systems that are applied directly to the weak SO₂ stream. These are discussed in Section 4.3. The second group includes furnace operating modifications, which can lead to an increase in the concentration of SO₂ in the offgases and thus facilitate acid plant control. Such operating modifications include the following:

- Elimination of converter slag return
- Sealing leakage points
- Preheating combustion air
- Operation at lower air-to-fuel ratio
- Predrying wet charge
- Oxygen enrichment of combustion air.

Each of these techniques is discussed in subsequent subsections. Although these techniques have been used at various smelters, in most

cases they have been applied not to obtain control-related benefits but rather to improve operating conditions and/or increase production. Discussion of the first five operating techniques mentioned here is based primarily on information in Reference 6.

4.5.1 Elimination of Converter Slag Return

As discussed in Section 3.2.2.1, converter slag is typically returned to reverberatory furnaces to recover copper. These slags are charged while molten by pouring them into a chute or launder leading to an opening in the furnace wall. Fifty or more ladles of converter slag can be returned in a 24-hour period, depending upon the number of converters and the smelter throughput rate.

The converter slag, in contrast to reverberatory furnace slag, is high in magnetite content--normally 17 to 35 percent.⁶ To some extent, the magnetite reacts with iron sulfide in the bath to release SO₂. However, each time converter slag is returned, a large volume of air enters the furnace. The net effect is a reduction in the average SO₂ concentration. An additional disadvantage to converter slag return to reverberatory furnaces is that the addition of converter slag can lead to magnetite buildups on the furnace bottom.

An alternative to processing converter slag in reverberatory furnaces directly is to use the flotation process to recover the copper content of this material. To do so requires slow cooling of the slag to allow the growth of crystalline particles of sufficient size to be amenable to flotation. Cooling requirements are on the order of 1 to 2 days. Following cooling, the slags are ground to liberate the copper-containing mineral particles. Grinding to at least 85 percent minus 200 mesh is not uncommon.⁶ Most flotation treatment is performed using a circuit separate from that used for ore treatment because of the different reagents and techniques required, although a few plants simply add the slag to the incoming ore at the concentrator crusher without noticeable detrimental effects.

4.5.2 Sealing Leakage Points

In addition to the converter slag return opening, numerous other openings exist that allow air to infiltrate into reverberatory furnaces,

thereby increasing the offgas volume and decreasing the SO_2 concentration. Such openings exist primarily because heretofore there has not been any great need for extensive sealing of reverberatory furnaces in the United States. In addition to SO_2 -control-related advantages, reducing infiltration would also result in higher temperature offgases, which would in turn enhance the heat recovery in the waste heat boilers. Furthermore, the reduced offgas volume would allow for the use of smaller gas-handling equipment.

Sources of infiltration include openings associated with charge slingers, Wagstaff-type feeders, and, in the case of furnaces employing silica refractory, furnace repair ports (through which personnel spray silica slurry to increase the thickness of brick in the roof and sidewalls). Infiltration also occurs around burners and through spaces between bricks in the furnace wall. Concerning spaces between bricks, there has been as much as 100-mm (4-in) expansion allowed in a 9-m (30-ft) length. When hot, the refractories theoretically expand and seal these openings, although some gaps inevitably result.

Infiltration can be greatly reduced by careful maintenance practices. Cracks, crevices, and gaps can be hand sealed. Although in some cases infiltration is allowed to prevent excess refractory temperatures, the furnace must, upon sealing, be operated in such a way that overheating will not occur. It may be necessary to use a different refractory material or readjust burner location and operation.

The most extensive work performed to seal reverberatory furnaces specifically to facilitate SO_2 control was conducted at the Onahama smelter in Japan. At this furnace, air infiltration was reduced from a level of approximately 50 percent of the furnace gas at the uptake to less than 15 percent by eliminating air leaks through crevices, clearances, openings in the furnace roof, sidewalls, fettling chutes, damper slots, expansion joints, peep holes, cleaning doors, and, especially, dust-discharging hoppers of the boilers and the Cottrell treaters.⁶ Ongoing maintenance at Onahama includes repairing and replacing portions of the furnace roof every 6 months to minimize inleakage.

4.5.3 Preheated Combustion Air

Preheating the furnace combustion air can increase the concentration of SO_2 in the exhaust gases. The increase results because the sensible heat content of the air serves to decrease the fuel requirement, which in turn results in a smaller volume of combustion products.

The use of preheated air for natural gas combustion is usually required to increase the flame temperature, which, in turn, increases the rate of heat transfer to the melt by radiation and convection. The use of preheated air for oil and coal combustion can, however, produce furnace control and durability problems because of the higher flame temperatures.

At the Onahama smelter, preheating of the secondary air to the oil burners has increased the smelting rate and consequent release of combined sulfur. The resulting increase in SO_2 strength has been estimated at 0.1 to 0.2 percentage points.⁶

4.5.4 Operation at Lower Air-to-Fuel Ratio

The quantity of combustion air supplied to the burners has a direct effect on the SO_2 concentration in the furnace offgases. Introducing less air will result in higher offgas SO_2 concentrations.

The theoretical amount of air required to combust a given amount of fuel is that necessary to complete the oxidation of all of the carbon, hydrogen, and sulfur contained in the fuel. In most cases, however, excess air (more than the theoretical amount) is supplied to ensure complete combustion, because the air and fuel are not perfectly mixed. The quantity of excess air supplied should not exceed the level at which the heat lost to the additional air exceeds the heat gained from the combustion of additional fuel.

The quantity of excess air used in firing reverberatory smelting furnaces varies depending upon the type of fuel burned. Since gaseous fuels mix with air easily, natural gas burners can achieve essentially complete combustion using a relatively small amount of excess air (between 0 and 10 percent). Thorough mixing of liquid fuels with air is more difficult to achieve, and, as a result, oil burners require up to 18 percent excess air. Solid fuels, such as ground coal, are the

most difficult to combust completely and require from 12 to 50 percent excess air.

The average SO_2 concentration of 2.6 percent in the offgases from the Onahama reverberatory furnaces (see Section 4.3.1.5) is partially attributed to operation at a low air-to-fuel ratio.⁶ These furnaces, which are fired with oil, operate at approximately 10 percent excess air.⁶ The air entering at the burner end of each furnace is actually less than the theoretical requirement--the balance being supplied by infiltration.

While operation of the Onahama furnace with a fuel-rich mixture does not provide maximum heat release within the furnace, it does (in addition to increasing the SO_2 concentration) increase furnace durability and reduce the formation of NO_x .

4.5.5 Predrying Wet Charge

Ore concentrates processed in green-charged reverberatory furnaces typically contain from 5 to 15 percent moisture. As the moisture is eliminated in the furnace offgases, it contributes to the dilution of SO_2 .

Processing green charge in concentrate dryers allows some increase in the concentration of SO_2 from the reverberatory furnace by eliminating the dilution effect of the moisture. Other advantages also result. Concentrate drying results in an overall decrease in fuel consumption since the temperature of the moisture is raised to only about 82°C (180°F) in the dryer, as compared to $1,288^\circ \text{C}$ ($2,350^\circ \text{F}$) in the furnace. Also, by eliminating moisture, the possibility of steam-induced pressure surges or destructive steam explosions in the furnace is greatly reduced. This affords the additional advantage of providing added capability for furnace sealing to reduce the diluting effect of infiltration air.

4.5.6 Oxygen Enrichment Techniques

Oxygen enrichment techniques involve the substitution of pure oxygen for a portion of the combustion air fed to a piece of smelting equipment. A number of techniques related to the use of oxygen enrichment of the combustion air for reverberatory furnaces have been devel-

oped and continue to be used by the smelting industry worldwide. These techniques result in an increase in the concentration of SO_2 in the exhaust gases and can lead to the production of an acid-plant-strength gas. The primary reason for the increased concentration is the elimination of the nitrogen that is associated with air when it is used for combustion. Since air contains 79 percent nitrogen and only 21 percent oxygen, the dilution effect associated with the nitrogen in the air is evident. The decrease or elimination of nitrogen also results in a reduction in the size and cost of all downstream gas handling and processing equipment. Other major advantages associated with oxygen-enrichment include increased furnace capacity, or a decrease in fuel usage for a fixed furnace capacity. These aspects are discussed in Section 3.5.3.4.

The extent of the increase in SO_2 concentration when using oxygen enrichment depends upon numerous factors, including the composition of the feed, charging rate, degree of enrichment, and the level of air infiltration. The composition of the feed determines the availability of pyritic sulfur for SO_2 formation under a given set of operating parameters, two of which are the charge rate and the degree of enrichment. Naturally, the infiltration that occurs has an effect on the SO_2 concentration.

4.5.6.1 Survey of Experience with Oxygen Enrichment. The advantages of oxygen enrichment in a reverberatory furnace from the production and pollution control standpoints have been emphasized by numerous authors.^{29 33-49} All of the theoretical and experimental studies on oxygen enrichment in reverberatory furnaces show that the SO_2 concentration in the flue gas stream increases with oxygen enrichment. Thus, the use of oxygen enrichment to alleviate the weak stream control problem is a real possibility.

Various methods of introducing oxygen into the reverberatory furnace have been used to date. These may be categorized as follows:

1. Oxygen introduced directly with fuel in separate oxygen-fuel burners.

2. Oxygen mixed with primary air and introduced into the existing burner system.
3. Undershooting the flame with oxygen-enriched air.
4. Oxygen lancing of the molten furnace bath.
5. Oxygen sprinkle smelting.

Illustrations of these alternative methods of oxygen introduction are presented in Figure 4-17.

Itakura et al.³⁴ and Goto³⁵ report using oxygen-fuel burners at the Onahama smelter and refinery. The result was a 0.3-percent increase in the flue gas SO₂ concentration per oxy-fuel burner utilized.³⁵ The maximum oxygen consumption per burner was 1,190 m³/h (42,000 ft³/h).

The work at the Caletones smelter⁴² with oxy-fuel burners indicated that an SO₂ concentration of over 7 percent (on a dry basis) could be attained with a full-scale, green-charged reverberatory furnace. This was accomplished by burning 100 percent of the fuel with industrial grade oxygen (97 percent pure) in individual oxygen-fuel burners located in the roof of the furnace. Processing of a nickel-copper calcine charge by the same technique at the Inco Copper Cliff smelter indicated that offgas SO₂ concentrations of 5 to 6 percent could be achieved.⁵¹

A number of smelters have conducted studies involving oxygen enrichment of the combustion air. Pluzhnikov et al.³⁷ report oxygen enrichment of primary combustion air using roof-mounted burners at Noril'sk Ore-Mining Combine. Kupryakov et al.³⁸ report using oxygen-enriched primary air in burners at the Almalyk copper smelter. Achurra et al.⁴² report on limited tests made with oxygen enrichment of the primary burner air at the Caletones smelter. Wrampe et al.³⁹ report Linde's experience with oxygen enrichment of the combustion air in domestic reverberatory furnaces.

As mentioned previously, all of the theoretical and experimental studies on oxygen enrichment indicate that the SO₂ concentration in the flue gas stream increases with oxygen enrichment. Wrampe et al.³⁹ present a model that correlates the flue gas SO₂ concentration with

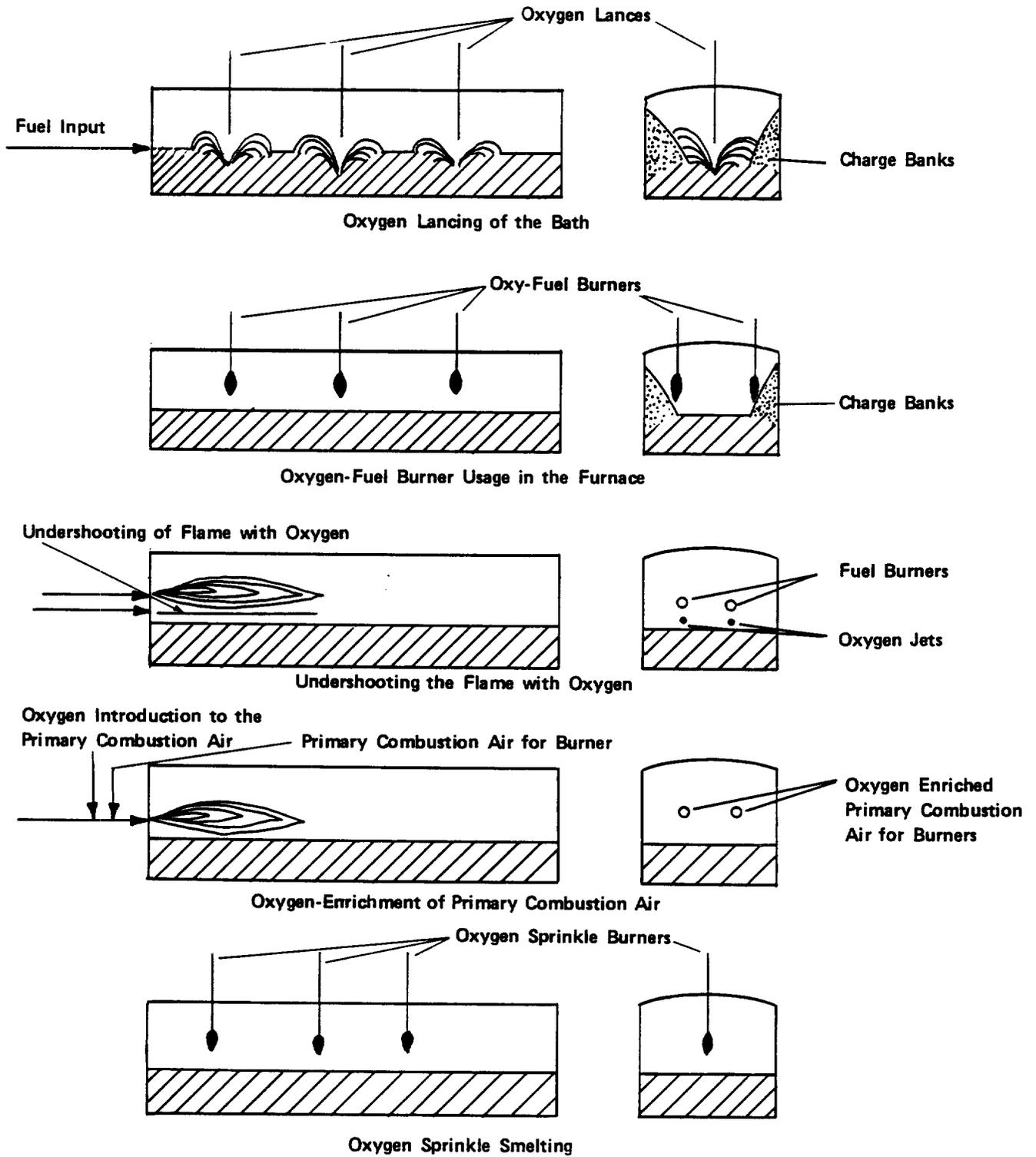


Figure 4-17. Methods of oxygen addition.

the degree of oxygen enrichment. This model shows the flue gas SO_2 concentration to be primarily dependent upon the smelting rate and the degree of oxygen enrichment. The relationship between the flue gas SO_2 concentration and the degree of oxygen enrichment as given by Linde's model³⁹ and the results of studies conducted by Kupryakov were compared and found to be in reasonable agreement. At a constant fuel rate with 21 and 25 percent oxygen content in the combustion air, Linde's model projects flue gas SO_2 concentrations of 3.55 and 5.5 percent, respectively. For the same levels of enrichment, Kupryakov's investigations yielded offgas SO_2 concentrations of 3.8 and 5.8 percent. Theoretical investigations at the Rokana smelter have predicted that, with 30 percent enrichment of the primary combustion air, reverberatory furnace offgas SO_2 concentrations could be increased from 1.0 to 1.6 percent.³⁶

Undershooting the flame with oxygen or oxygen-enriched air has been studied at several smelters. Kupryakov³⁸ and Saddington³³ report that studies of this nature have been performed at the Almalyk and Inco Copper Cliff smelters. Data on the offgas SO_2 concentrations obtained in these ventures have not been published. Eastwood et al.³⁶ report on experience accumulated at the Rokana smelter.

Beals et al.⁴⁰ report SO_2 concentrations as high as 18 percent with oxygen lancing of the bath. These data resulted from tests conducted in a pilot-scale furnace. Beals currently has a patent assigned to Kennecott for using oxygen lancing of the melt to increase production and to obtain a high SO_2 concentration in the flue gases. Achurra et al.⁴² report on limited investigations made with roof-mounted oxygen lances at the Caletones smelter.

Oxygen sprinkle smelting has been largely developed by Queneau and Schuhmann.⁴⁹ This method involves retrofitting existing reverberatory furnaces with oxygen sprinkle burners as illustrated in Figure 4-18. Theoretically predicted values of flue gas SO_2 concentrations associated with this process have been in the neighborhood of 42 percent.⁴⁹

Detailed discussions of the most significant applications of oxygen-related technology are presented in the following sections.

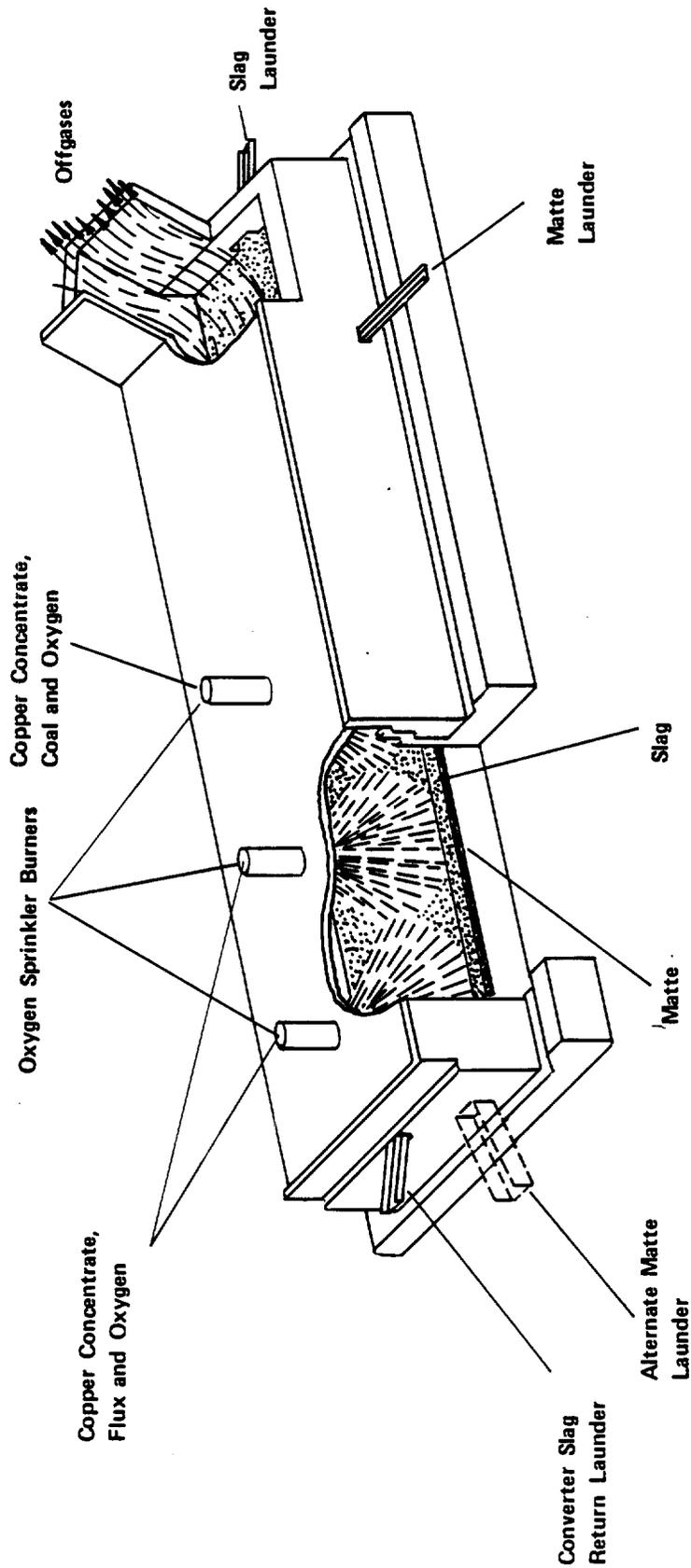


Figure 4-18. Conventional copper reverberatory smelting furnace that has been converted to an oxygen sprinkle smelting furnace.⁴⁹

4.5.6.1.1 Use of oxygen at the Caletones smelter. Development work involving the combustion of fuel with pure oxygen in oxygen-fuel burners began at the Caletones smelter in Chile during 1971.⁴³ Up to 12 oxy-fuel burners were installed on a green-charged reverberatory furnace. The positions of these burners in the furnace roof are shown in Figure 4-19. A top view of the furnace is illustrated in Figure 4-20. Oxy-fuel burner dimensions and operating data are presented in Table 4-10.

The matte grade is approximately 49 percent with full oxygen usage (all fuel burned with pure oxygen), while the copper content of the slag is 0.7 percent. It was determined that the use of calcium carbonate as flux could be discontinued due to higher slag temperatures that resulted from the use of 100 percent oxygen. The increase in matte temperature also minimized magnetite buildup on the furnace bottom. In addition, refractory wear on a per-ton-of-copper produced basis was either less or the same as previously encountered.

The production rate of reverberatory furnace No. 3 at the Caletones smelter was increased from 622 dry Mg/day (686 dry tons per day) to 1,380 dry Mg/day (1,520 dry tons per day) with the use of the oxy-fuel burners. Energy consumption was reduced from approximately 1.82×10^6 kcal/ton of material smelted (7.22×10^6 Btu/ton of material smelted) to 0.806×10^6 kcal/per ton smelted (3.20×10^6 Btu/ton smelted). The oxygen rate in evidence at the elevated production level was 345 Mg/day (380 tons/day).

The most significant result from a pollution control standpoint is the SO_2 concentration in the offgases, which has been in the range of 5.8 to 7.3 percent. The increase in SO_2 concentration was primarily due to the elimination of inert nitrogen along with the increase in smelting rate, which increases the availability of pyritic sulfur within the furnace. A gas stream that exhibits SO_2 concentrations in the 5.8 to 7.3 percent range can easily sustain autothermal operation in a conventional dual-stage absorption sulfuric acid plant.

4.5.6.1.2 Use of oxygen at the Onahama smelter. In 1971, oxygen-oil burners were installed in a green-charged reverberatory furnace at

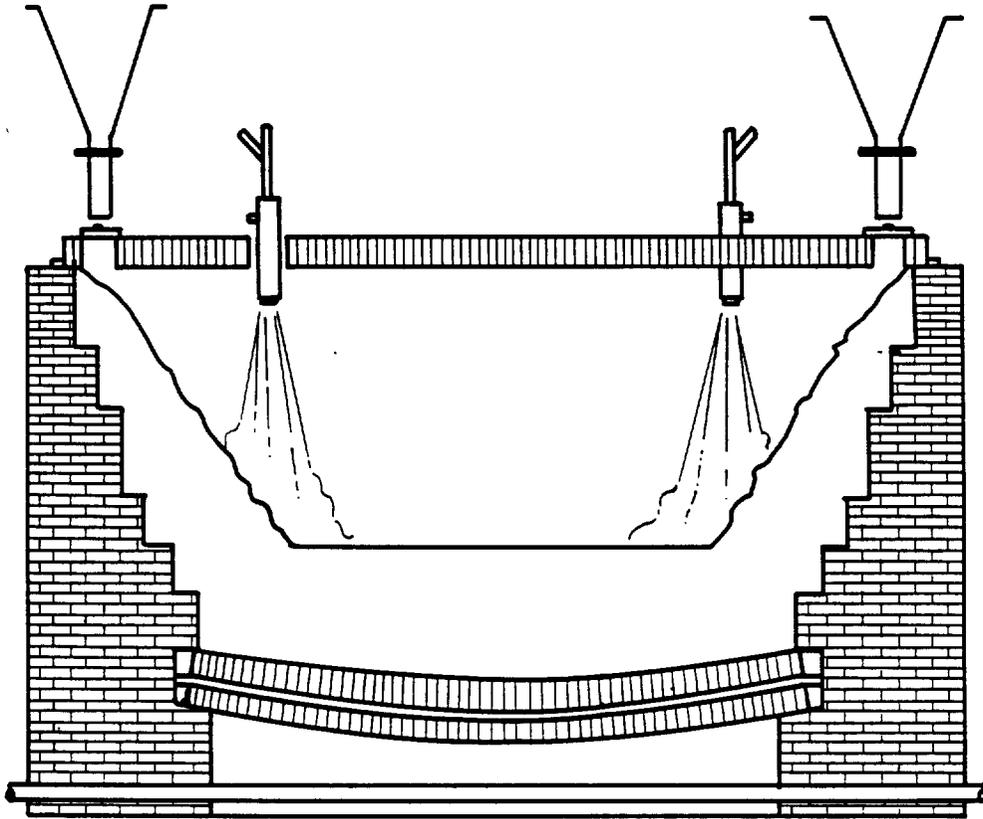


Figure 4-19. Oxy-fuel burner locations in Reverberatory Furnace No. 3 at the Caletones smelter.

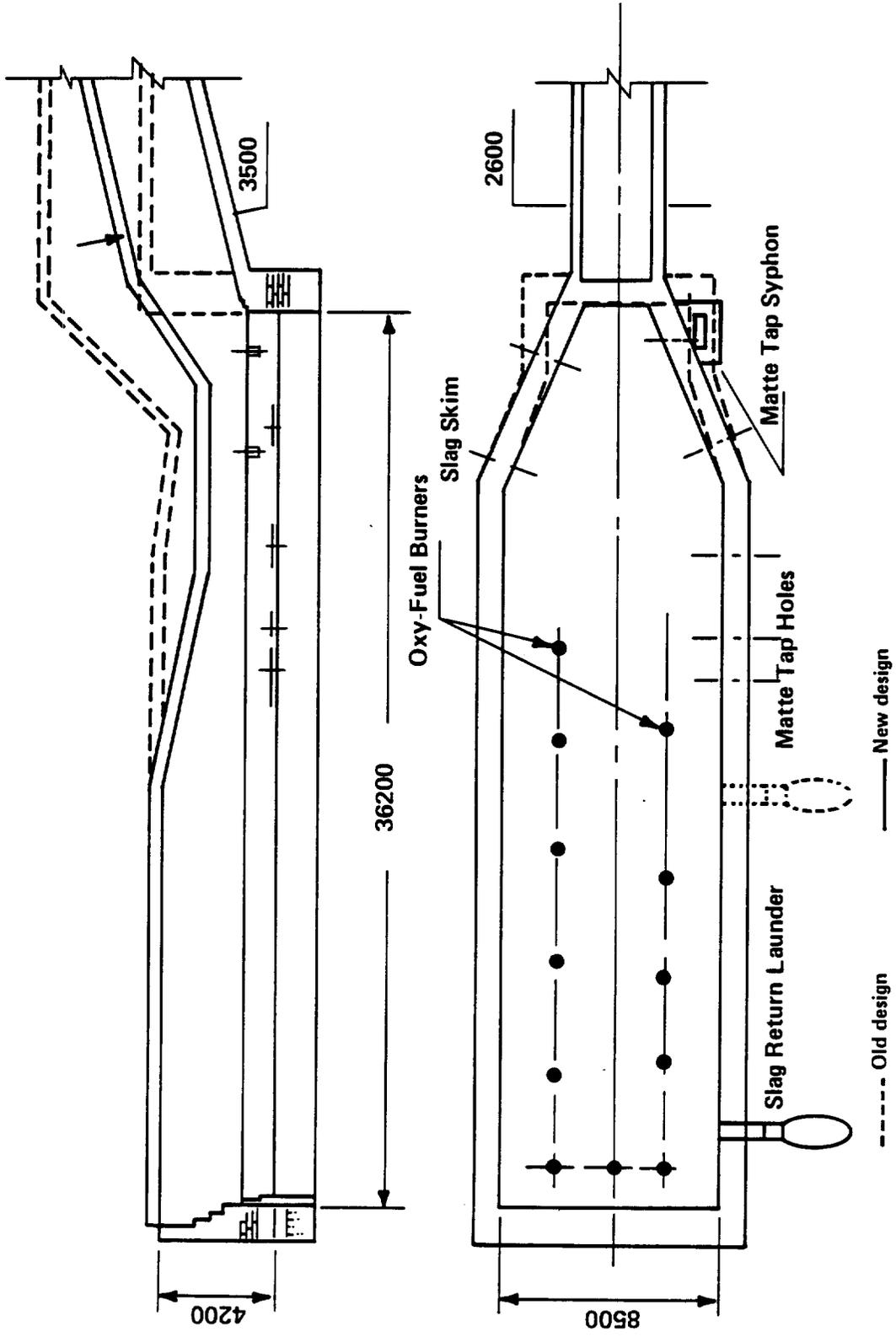


Figure 4-20. Plan and elevation of Reverberatory Furnace No. 3 (in-plan view oxy-fuel burner location is shown).

TABLE 4-10. OXY-FUEL BURNER DIMENSIONS AND OPERATING DATA AT MAXIMUM FIRING CAPACITY

Burner dimensions	
Length	94 cm (37 in.)
Outside diameter	15.2 cm (6 in.)
Fuel rate ^a	12 l/min (3.17 gpm)
Oxygen rate	35.0 Nm ³ /min (1,236 ncfm)
Oxygen pressure	2.04 atm (30 psi)
Oil pressure	6.80 atm (100 psi)
Cooling water rate	11.5 l/min (3.04 gpm)
Noise level	90 dB

^aFuel type: ENAP-6 oil, with a heating value of approximately 10,200 Kcal/kg.

the Onahama smelter in Iwaki City, Japan. Table 4-11 presents the general specifications of the type of burner employed at Onahama. Two burners were installed and are presently being used when furnace capacity must be increased. The two burners penetrate the roof vertically at the center line.

Table 4-12 summarizes reverberatory furnace operating data for two time periods--one prior to the installation of the oxy-fuel burners and one during oxy-fuel burner use. As indicated, the charging rate was increased from 22,470 Mg per month (24,769 tons per month) to 27,142 Mg per month (29,919 tons per month) with the use of the two oxy-fuel burners. The corresponding oxygen consumption rate was 667,058 Nm³/month (2.4×10^7 scf/month). The fuel consumption rate increased only slightly at the elevated production rate. Fuel consumption during conventional operation (no oxygen) at the original charging rate was approximately $4,723 \times 10^3$ l/month (167×10^3 ft³/month), while consumption at the increased production rate (with oxy-fuel burner operation) was $4,870 \times 10^3$ l/month (172×10^3 ft³/month).

The use of oxy-fuel burners at Onahama did result in an increase in the flue gas SO₂ concentration. The results indicated that the flue gas SO₂ concentration could be increased by 0.3 percentage point per oxy-fuel burner used.

4.5.6.1.3 Use of oxygen at Inco's Copper Cliff smelter. The Inco Copper Cliff smelter in Ontario, Canada, processes nickel-copper calcines in two reverberatory furnaces fitted with roof-mounted oxy-fuel burners.

Nickel-copper concentrates containing about 22 percent sulfur are first roasted in Herreshoff multihearth roasters. Conveyers then deliver calcine and crushed nickel converter slag to the reverberatory furnaces. The calcine is sidewall-charged using a drag conveyor/fettling pipe feed system. Both furnaces are fired with Bunker C fuel oil and measure 35 m (114 ft) long by 9 m (30 ft) wide. One of the furnaces burns all of the fuel oil in ten roof-mounted oxy-fuel burners, while the other burns fuel oil in two conventional air/fuel end-wall burners and four roof-mounted oxy-fuel burners.

TABLE 4-11. GENERAL SPECIFICATIONS OF THE OXY-FUEL BURNER
EMPLOYED AT THE ONAHAMA SMELTER

Burner dimensions	
Length	193 cm (76 in.)
Diameter	15.2 cm (6 in.)
Maximum fuel rate ^a	6.6 l/min (1.8 gpm)
Maximum oxygen rate	20 Nm ³ /min (707 cfm)
Oxygen pressure	4.8 atm (71 psi)
Type of cooling system	Water jacket

^aFuel type: Bunker C oil.

TABLE 4-12. REVERBERATORY FURNACE OPERATING DATA BEFORE AND AFTER
THE USE OF OXY-FUEL BURNERS AT THE ONAHAMA SMELTER

Parameter	Time period	
	December 1970 ^a	January 1972 ^b
Concentrate smelted	22,470 Mg	27,142 Mg
Silicious flux smelted	2,966 Mg	3,663 Mg
Limestone smelted	1,868 Mg	1,970 Mg
Reverts smelted	518 Mg	707 Mg
Total solid charge	27,822 Mg	33,482 Mg
Fuel oil consumed	4,723 × 10 ³ ℓ	4,870 × 10 ³ ℓ
Oxygen consumed	--	667,058 Nm ³ /min
Matte produced	18,465 Mg	22,843 Mg
Matte grade	34.5 percent Cu	34.4 percent Cu
Slag produced	18,546 Mg	23,530 Mg
Slag copper content	0.46 percent	0.47 percent

^aRepresentative of reverberatory furnace operation without the use of oxy-fuel burners.

^bRepresentative of reverberatory furnace operation with the use of oxy-fuel burners (combustion of the fuel oil with industrial grade oxygen).

Without the use of oxygen, the offgas flow rates from each furnace varied from 1,400 to 1,700 Nm³/min (50,000 to 60,000 scfm) and contained 1.0 to 1.5 percent SO₂. With full oxy-fuel operation, the furnace offgas flow rates vary from 570 to 850 Nm³/min (20,000 to 30,000 scfm) and contain 5 to 6 percent SO₂ (measured at the furnace outlet). During conventional operation (without oxygen), 23 percent of the sulfur in the charge was removed in the roasters, while 16 percent was eliminated in the reverberatory furnaces. The result was a matte grade of about 25 to 30 percent Ni + Cu + Co. With full oxy-fuel operation, sulfur elimination in the furnace increased somewhat as a result of the hotter flames which transferred heat directly to the bath. To compensate for increased desulfurization in the furnace, a lighter roast is used, so that presently 17 percent of the feed sulfur is eliminated in the roasters and 24 percent is eliminated in the furnace. This scheme produces approximately the same matte grade with oxy-fuel operation. Also, with full oxy-fuel operation the charging rate increased from 1,270 to 1,830 Mg per day, and the fuel requirement was reduced to 45 percent of the operating value in evidence during conventional operation without oxygen.

The increase in the sulfur dioxide concentration in the reverberatory furnace offgases was accomplished by the following:

1. A 50-percent reduction in the offgas volumetric flow rate as a result of eliminating the nitrogen present when air was used.
2. An increase in production rate, which in turn provided a greater availability of pyritic sulfur within the furnace.
3. A reduction in the amount of sulfur eliminated in the roasters, with a corresponding increase in the amount of sulfur eliminated in the reverberatory furnaces.

Tonnage oxygen has been used in the Copper Cliff smelter since 1945, when Inco began piloting the flash smelting of copper and nickel concentrates. Commercial application of this technology started in 1952. Air blast to the nickel converters has been enriched to 30 percent oxygen by weight since 1958; by the mid-50's, the reverberatory furnace combustion air was being enriched with oxygen, and chalcocite

concentrates were smelted in Peirce-Smith converters using an oxygen-enriched blast. Development work on the oxy-fuel burners continued until June 1978. The resulting Inco-designed oxy-fuel burners produce a good flame pattern and acceptable noise levels operating at firing rates of 3.8 kg (8.4 lb) of oil per minute and 7 to 27 kg (15 to 33 lb) of oxygen per minute. Oxygen is supplied to the burner for 70 to 100 percent of stoichiometric requirements. The burners are fed oxygen at 25 psi and oil at 500 psi pressure. The oil is introduced at 116° C (240° F).

For the furnace using only oxy-fuel burners, smelting started at the beginning of October 1979 using 12 oxy-fuel burners and continued for the next 13 months with only minor interruptions. During this time, 652,000 Mg (718,700 tons) of dry solid charge were smelted, and only minor repair delays were experienced. Overall, refractory consumption and fuel efficiency compared favorably with those for conventional operation; roof refractory consumption of about 0.76 kg/Mg of dry solid charge has been lower than initially anticipated. The only major problem after startup involved difficulty with slag temperature control. This problem was resolved by removing two of the burners at the skimming end, resulting in the current 10-burner operation.

Green charge furnace operation with oxy-fuel burners at Onahama involved the practice of impinging the burner flame directly on the charge banks to (1) protect the furnace wall, (2) produce concentrated heat directly on the material to be smelted, (3) increase available heat by molecular recombination and, of course, (4) eliminate the sensible heat loss associated with nitrogen. Thus, impinging the flame on the base of the charge banks as Inco does represents a different methodology than that practiced at Onahama. The end of the flame just touches the calcine charge banks in the Inco furnaces. The optimum flame pattern for processing the calcine charge was determined by adjusting the amount of oxygen supplied to the burner, which is currently 90 percent of the stoichiometric requirement.

The angle of repose for calcine is considerably smaller than that of green charge. Protection of the side walls is still provided by

the charge banks, however. The operator must be especially careful to maintain the proper feed distribution along the full length of the furnace to prevent localized wall heating and severe refractory erosion. Such overheating can occur if the charge banks are allowed to disappear, because the furnace does not employ sidewall cooling.

The higher heat transfer capability and improved heat distribution made possible with oxy-fuel burners has led to better control of furnace bottoms and minimized the height of the charge banks. As a result, the matte-holding capacity of the oxy-fuel furnace is about 400 Mg (441 tons) instead of the 150 Mg (165 tons) during conventional operation. The increase in active furnace volume coupled with the higher heat transfer rates has substantially increased the ability of the furnaces to adapt to changes in feed rates and compositions. Improvement in the ability to recover from furnace slow-downs arising from maintenance or from environmental requirements has also been accomplished.

Essentially one-half of the fuel requirement per unit mass of dry solid charge is used with the oxy-fuel operation as compared to conventional. When considering the overall energy requirement including oxygen manufacture, only 67 percent is used, resulting in a 33-percent savings.

The two reverberatory furnaces equipped with oxy-fuel burners have over 27 combined months of smelting experience and over 1.27 million Mg (1.4 million tons) of charge smelted. Furnace smelting rates have increased by 45 percent for full oxy-fuel operation.

Slag compositions, metal losses, and dust carryovers have remained essentially constant over 16 months of operations and are the same for the conventional and oxy-fuel furnaces.

4.5.6.1.4 Use of oxygen at the Phelps Dodge-Morenci smelter.

The Phelps Dodge smelter at Morenci, Arizona, is currently undertaking a development program for the "sprinkle" oxygen enrichment system. This development program involves one of the reverberatory furnaces at the Morenci facility.

The oxygen sprinkle process involves closing all unnecessary openings in an existing reverberatory furnace and fitting the furnace

with three sprinkle burners. These burners are designed to accomplish several important functions within the confines of the existing structure. The two most critical functions of the burners are the following:

1. To provide intimate mixing of finely divided concentrates with the oxygen-rich gas phase.
2. To sprinkle the feed uniformly over most of the molten bath surface.

Queneau and Schuhmann⁴⁹ report that the use of sprinkle burners transforms existing reverberatory furnaces into oxygen flash smelting units. Figure 4-18 shows a reverberatory furnace that has been converted for oxy-sprinkle smelting via the installation of three oxy-sprinkle burners.

In addition to providing for the flash oxidation of sulfides, the oxy-sprinkle burners optimize the interphase heat and mass transfer and facilitate the control of heat and mass distribution within the furnace. This in turn improves the efficiency of the reverberatory furnace and makes it more flexible as a chemical reactor.

Queneau and Schuman⁴⁹ have predicted that a reverberatory furnace converted to the oxy-sprinkle system can produce offgas streams with SO₂ concentrations in the 38 to 44 percent range, depending upon the desired matte grade. As suggested above, tests have been conducted using one of the reverberatory furnaces at the Phelps Dodge-Morenci facility. However, detailed results of these tests have not been made available. In addition, the slag cleaning feature of the process has not been tested. Consequently, oxygen sprinkle technology is not considered by EPA to be a fully demonstrated means by which to alleviate the weak stream control problem:

4.5.6.2 Refractory Wear with Oxygen Usage In Reverberatory Furnaces.

A possible constraint on the use of oxygen in reverberatory smelting furnaces is the increased potential for excessive refractory wear. To some extent, the method of oxygen introduction to the furnace dictates the amount of increase in the roof and side wall temperatures. For example, when oxygen-fuel burners are used, they can release the heat close to the charge and the roof temperature is not significantly

increased. The Inco experience⁴⁶ with the calcine-charged reverberatory furnace indicated that when the burners were placed in the roof but close to the side wall, deterioration of the wall occurred. When the burners were moved toward the center line of the furnace, however, the refractory deterioration was better controlled.

When undershooting the flames with oxygen, high temperatures are created in the vicinity of the charge, but the furnace roof tends to be protected by the air-fuel flame itself. Oxygen enrichment of primary air is very easy to control but results in lower thermal efficiencies and also tends to increase the roof temperatures when compared to oxy-fuel burner operation. Preliminary investigations by Saddington et al.³³ indicate that refractory cost per ton of output in a reverberatory furnace should not increase when oxygen is introduced. By introducing the oxygen below the fuel nozzles, the hottest zone of the flame was found to be at the bottom next to the bath. Figure 4-21 shows the roof temperature variation along the length of two different furnaces with and without oxygen enrichment. The maximum temperature at the furnace roof did not increase with oxygen enrichment. However, the temperatures were higher along the entire length of the furnace.

The recent work with oxy-fuel burners at Inco⁴⁶ indicates that overall refractory consumption compared favorably with conventional operation. The roof refractory consumption was about 0.76 kg/Mg DSC (dry solid charge) (1.52 lb/ton DSC). Operation of the furnaces with oxy-fuel firing has required an increased operator's awareness of proper feed distribution along the full length of the furnace. Improper fettling can easily lead to localized wall heating and severe refractory erosion. Localized heating trends are monitored for this reason.

Kupryakov et al.³⁸ indicated that during a development period, where operating conditions varied markedly with various concentrations of oxygen, the average wear of the furnace roof reached a rate of 0.2 mm/24 h (0.008 in./24h). Taking into account the accuracy of measurement and the frequent changes in the operating conditions within the furnace, the wear of the furnace roof during reverberatory furnace operation with an oxygen-enriched blast did not differ markedly from wear when operating with conventional air blast.

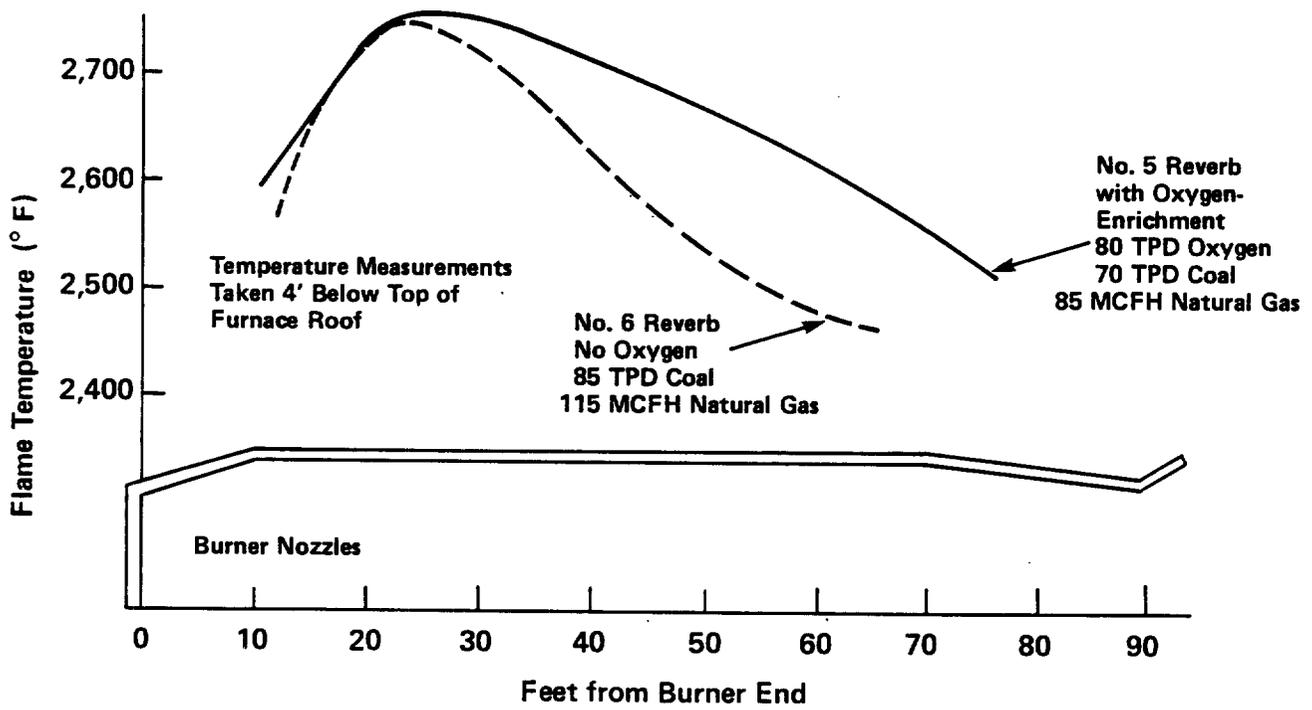


Figure 4-21. Reverberatory furnace temperatures in the vicinity of the furnace roofs with and without oxygen-enrichment at Inco smelter.

Itakura et al.³⁴ reported that using oxygen-fuel burners in a reverberatory furnace did not increase the lining wear. They postulated that this probably was due to the heat being released close to the charge rather than the lining.

Wrampe and Nollman³⁹ reported during their work on oxygen enrichment at reverberatory furnaces at various U.S. smelters that the overall refractory temperatures increased by approximately 0.28° C (0.5° F) per 28.3 Nm³/min (1,000 scfm) of oxygen. During their test, excessive roof temperatures did not become a problem until production increases exceeded 50 percent.

The Caletones smelter experience⁴³ indicated that it was necessary to use a bottom ventilation system, but roof refractory wear was in the range of 10 percent over a 6-month operating period. Maximum temperatures were no higher than for "normal" operation, and a more uniform temperature distribution was obtained.

Bohlin et al.,⁴⁴ while using a furnace configuration different from the normal reverberatory furnace, experienced charging door burnout, soot formation in the cooler door area, and low production capability. These problems were resolved by reducing the number of burners from eight to six, modifying the burner outlets and atomizing nozzles, and changing the angle of the burners.

4.5.6.3 Summary of Oxygen Enrichment Techniques. A summary of the commercial demonstrations involving the use of oxygen in reverberatory furnaces is presented in Table 4-13. As indicated, the use of oxygen in reverberatory furnaces can increase production substantially while simultaneously increasing the offgas SO₂ concentration. The largest reported increases in full-scale demonstrations have resulted from the use of oxygen-fuel burners that combust the fuel with industrial grade (97 percent pure) oxygen. Oxy-fuel burners can be adapted to both green- and calcine-charged furnaces. Calcine-charged furnaces which use Wagstaff gun charging systems are expected to be capable of adopting oxy-fuel burners readily, as these furnaces employ sidewall cooling by design and would therefore not require sidewall charging to protect the sidewall refractory from excessive erosion.

TABLE 4-13. SUMMARY OF COMMERCIAL DEMONSTRATIONS INVOLVING THE USE OF OXYGEN IN REVERBERATORY SMELTING FURNACES

Type of technology applied	Smelter	Nature of application	Reported increase in production	Reported increase in offgas SO ₂ concentration
Oxygen-fuel burners	Onahama	Full-scale demonstration	~ 21 percent ^a	0.3 percent per burner. (2.6 percent to 3.2 percent for a two-burner configuration)
Oxygen-fuel burners	Caletones	Full-scale demonstration	~ 122 percent ^b	As high as 5.8 to 7.3 percent for a 12-burner configuration
Oxygen-fuel burner	Inco Copper Cliff	Full-scale demonstration	~ 44 percent ^c	From 1-1.5 percent to 5-6 percent
Oxygen-enriched primary combustion air (25% O ₂ to 30 percent O ₂)	Almalyk	Full-scale demonstration	21-27 percent	From 3.8 to 5.8 percent
Oxygen-enriched primary combustion air (with roof mounted burners)	Noril'sk Ore Mining Combine	Pilot and full-scale demonstration	--e	--e
Undershooting the air-fuel flame with pure oxygen or oxygen-enriched air	Almalyk	Full-scale demonstration	--e	--e

See footnotes at end of table.

(continued)

TABLE 4-13. (continued)

Type of technology applied	Smelter	Nature of application	Reported increase in production	Reported increase in offgas SO ₂ concentration
Undershooting the air-fuel flame with pure oxygen or oxygen-enriched air	Inco Copper Cliff	Full-scale demonstration	~ 36 percent ^b	-- ^e
Undershooting the air/fuel flame with oxygen	Rokana	Full-scale demonstration	~ 18 percent ^a	From 1.0 to 1.6 percent ^d
Oxygen lancing of the furnace bath	--	Pilot scale demonstration	-- ^e	As high as 18 percent
Oxygen-sprinkle smelting	Phelps Dodge-Morenci	Full-scale demonstration of a retrofitted reverberatory furnace	-- ^e	As high as 38-44 percent

^aCalculated based upon the increased production obtained in 1 green-charged reverberatory furnace.

^bCalculated based upon the increased production obtained in 1 calcine-charged reverberatory furnace.

^cCalculated based upon the increased production obtained in 2 calcine-charged reverberatory furnaces fitted with oxy-fuel burners. Each furnace had a slightly different burner configuration.

^dActual values from demonstration run are not available. Values presented here are theoretical.

^eNo data available.

^fSlag cleaning feature of this technology not demonstrated.

The adoption of oxy-fuel burners by domestic smelters may lead to somewhat increased sulfur elimination in the reverberatory furnace, which could in turn lead to increases in matte grade. The extent of any increased desulfurization would be dependent upon the positioning of the flame relative to the charge, and the quantity of labile sulfur within the charge. It should be noted, however, that the furnace matte grade can be maintained at its former value by lightening the roast, as was demonstrated by Inco.

The maximum increase in SO_2 concentration that can be realistically obtained by any oxygen enrichment technique will depend upon the amount of sulfur that can be eliminated without adversely affecting the matte grade. Matte grades in the 40 to 45 percent range are deemed desirable as they allow for the longer converter blowing times needed for adequate impurity elimination. (Impurity elimination is discussed in more detail in Section 3.5.) Consequently, the amount of sulfur that can be eliminated in a reverberatory furnace, a factor that has a direct effect on the offgas SO_2 concentration, is dependent upon the composition of the furnace charge. For instance, a furnace charge with a low copper-to-sulfur mass ratio could be subjected to more sulfur elimination than a charge with a high copper-to-sulfur ratio before the matte grade would be driven too high. Thus, the degree of sulfur elimination must be controlled to ensure the proper matte grade.

The theoretical model presented in Appendix __ has been used to estimate the increase in SO_2 concentration that results from the application of oxygen enrichment techniques to reverberatory furnaces that process feeds comparable in composition to the feeds that are currently processed by domestic smelters. This model is based upon a rigorous material balance that accounts for such factors as the required energy input, the level of enrichment, and the desired capacity increase. The concentrate assays used as bases for each smelter configuration are arithmetic averages indicative of current industrial practice. Only oxygen enrichment of the primary combustion air and oxy-fuel burner operation with industrial grade oxygen are considered since

they are by far the most extensively demonstrated techniques. Estimates of reverberatory furnace offgas SO₂ concentrations obtained from this model reflect a furnace matte grade low enough (≤ 46 percent Cu) to allow for adequate blowing times in the converters. Table 4-14 summarizes the theoretical estimates for the use of oxygen accompanied by an increase in production. The increases in production utilized here were arrived at as indicated in Section 3.4.3.4.4. As suggested, direct acid plant control of such streams may be impractical where existing acid plants are involved. Table 4-15 presents analogous theoretical estimates for the use of oxygen at a new smelter that processes high impurity ore concentrates. It is important to note that no increase in production accompanies the use of oxygen in as far as these estimates are concerned. As shown, estimates indicate that using oxygen enrichment of the primary combustion air would result in an increase of 0.20 percentage points, while the use of oxy-fuel burners would result in an increase of 0.6 percentage points.

In summary, it appears that adopting oxygen enrichment of the primary combustion air or oxy-fuel burners will not result in a strong reverberatory furnace offgas stream in as far as applications to domestic ores are concerned. However, the use of these techniques will enhance an operator's ability to control SO₂ when weak gas stream blending is considered. This topic is discussed fully in Section 4.6.

4.6 GAS BLENDING

4.6.1 Assessment of Weak Stream Blending as Applied to a New Smelter That Processes High Impurity Ore Concentrates

Gas stream blending as applied to a new smelter that processes high impurity concentrates might involve any of the following scenarios:

1. Blending the entire weak stream with the strong streams produced by the roasters and converters, with subsequent treatment in a dual-stage absorption sulfuric acid plant.
2. Blending a portion of the weak streams with the strong streams produced by the roasters and converters, with subsequent treatment in a dual-stage absorption sulfuric acid plant.
3. Implementation of oxygen enrichment of the primary combustion air accompanied by blending the entire weak stream with the

TABLE 4-14. SUMMARY OF THEORETICAL ESTIMATES ASSOCIATED WITH THE EXPANSION OF REVERBERATORY SMELTING FURNACES VIA OXYGEN ENRICHMENT OF PRIMARY COMBUSTION AIR AND THE USE OF OXY-FUEL BURNERS

Smelter configuration	Technique employed	Reverberatory furnace offgas SO ₂ concentration prior to oxygen usage (percent)	Reverberatory furnace offgas SO ₂ concentration during oxygen usage (percent)	Associated production increase (percent)
Multihearth roaster-reverberatory furnace-converter ^a	Primary air enrichment	0.8	1.1	20
	Use of oxy-fuel burners	0.8	1.6	40
Reverberatory furnace-converter ^b	Primary air enrichment	1.4	2.0	20
	Use of oxy-fuel burners	1.4	3.0	50
Fluid bed roaster-reverberatory furnace-converter	Primary air enrichment	0.4	0.6	20
	Use of oxy-fuel burners	0.4	0.8	40

^aEstimates for this configuration are based upon a concentrate composition of 21.9 percent copper, 20.4 percent iron, and 24.8 percent sulfur.

^bEstimates for this configuration are based upon a concentrate composition of 22.4 percent copper, 24.8 percent iron, and 28.4 percent sulfur.

^cEstimates for this configuration are based upon a concentrate composition of 19.6 percent copper, 23 percent iron, and 28.9 percent sulfur.

TABLE 4-15. SUMMARY OF THEORETICAL ESTIMATES ASSOCIATED WITH THE OXYGEN ENRICHMENT OF PRIMARY COMBUSTION AIR AND THE USE OF OXY-FUEL BURNERS AS APPLIED TO A NEW SMELTER THAT PROCESSES HIGH IMPURITY ORE CONCENTRATES

Technique employed	Reverberatory furnace offgas SO ₂ concentration prior to oxygen usage (percent)	Reverberatory furnace offgas SO ₂ concentration during oxygen usage (percent)
Enrichment of the primary combustion air ^a	1.3	1.5
Use of oxygen-fuel burners ^a	1.3	1.9

NOTE: A new smelter of this type would consist of multihearth roasters, reverberatory furnaces, and converters.

^aEstimates are based upon a concentrate composition of 25.8 percent copper, 17.3 percent iron, 25.8 percent sulfur, 0.87 percent antimony, 0.70 percent lead, 1.01 percent zinc, and 3.18 percent arsenic.

roaster and converter strong streams, with subsequent treatment in a dual-stage absorption sulfuric acid plant.

4. Implementation of oxy-fuel burners accompanied by blending the entire weak stream with the roaster and converter strong streams, with subsequent treatment in a dual-stage absorption sulfuric acid plant.

An analysis of Case 1 (defined by the model plant in Figure 6-1) as outlined above indicates that there would be several periods of time over a 24-hour period when the blended stream SO_2 concentration would fall below 4.0 percent. Estimates show that the cumulative (not continuous) time during which the blended stream concentration would be below 4.0 percent SO_2 is about 17.3 hours per 24-hour period. Consequently, supplemental heat would have to be supplied to the acid plant.

As noted in Section 4.2.3, it is possible, however, to design a dual-stage absorption sulfuric acid plant to operate autothermally at gas stream SO_2 concentrations below 4.0 percent. Since a new acid plant would be required at a new smelter, a design for autothermal operation at 3.5 percent SO_2 would be a sensible and technically viable option. Estimates indicate that decreasing the autothermal operating requirement from 4.0 percent SO_2 to 3.5 percent SO_2 would result in a 9 to 12 percent increase in the installed capital cost of a metallurgical dual-stage absorption sulfuric acid plant (see Appendix ___ for supporting calculations).

Thus, as outlined above, Case 2 (partial weak stream blending) is considered at a level that would allow autothermal processing of a portion of the reverberatory furnace offgases in a dual-stage absorption acid plant designed to operate at 3.5 percent SO_2 .

A material balance indicates that, if approximately 45 percent of the reverberatory furnace offgases are blended with the strong streams from the roasters and converters, the blended stream SO_2 concentration will not fall below 3.6 percent. Consequently supplemental heat would not be required at any time to process the blended stream autothermally. Sulfur dioxide control under this scenario would result in an estimated 153 tons/day SO_2 emission rate to the atmosphere.

Estimates show that oxygen enrichment of the primary combustion air (Case 3, as outlined above) would not allow the entire reverberatory furnace offgas stream to be blended. There are several periods of time (cumulative time of about 4 hours) when the blended stream SO_2 concentration would be approximately 3.4 percent, which is less than the 3.5 percent that would be required to run the new acid plant autothermally. Thus, supplemental heat would have to be provided to ensure that the temperature in the catalyst beds remains at the appropriate level ($\sim 438^\circ \text{C}$).

With oxy-fuel burner operation, however, estimates indicate that the blended stream should not exhibit an SO_2 concentration below 4.9 percent. Thus, a dual-stage absorption acid plant designed to operate autothermally at either 3.5 or 4.0 percent SO_2 could maintain autothermal operation while blending the entire reverberatory furnace offgas stream. The resultant SO_2 emission rate to the atmosphere would be approximately 23.2 tons/day.

4.6.2 Assessment of the Technical Feasibility of Partial Weak Stream Blending

Existing facilities that undergo physical or operational changes to achieve greater production capacity would not become subject to NSPS requirements provided that postchange or postexpansion emission levels at an existing facility do not exceed preexpansion emission levels. For expanded reverberatory smelting furnaces that produce a weak SO_2 offgas stream, one approach available to maintain post-expansion SO_2 emissions at preexpansion levels is partial weak stream blending. Partial weak stream blending would consist of blending a sufficient portion of the postexpansion weak SO_2 stream with the strong SO_2 streams produced by the roasters and/or converters, and the subsequent treatment of the resultant blended stream in a sulfuric acid plant. Depending upon the scale of the expansion, the upgrading of existing acid plant capacity or the installation of new acid plant capacity may be required.

The technical feasibility assessment involved identifying all of the expansion scenarios (as reported in Table 6-8) that require partial

blending and analyzing each one with a rigorous material balance procedure to determine if postexpansion SO₂ emissions could be reduced to the preexpansion SO₂ emission level via partial weak SO₂ stream blending while simultaneously producing a blended stream with a high enough SO₂ concentration to operate the appropriate sulfuric acid plant autothermally. The details of the partial blending feasibility model developed and used for this assessment are presented in Appendix _____.

The feasibility of partial weak stream blending has been assessed for two types of reverberatory furnace expansions: (1) oxygen enrichment of the primary combustion air and (2) expansion via the use of oxy-fuel burners.

4.6.2.1 Assessment of Partial Blending as Applied to Reverberatory Smelting Furnaces That Are Expanded Via Oxygen Enrichment. Model Plant 1 (see Table 6-8) depicts expansion at the reverberatory furnace for a typical smelter that processes a calcine charge produced by multihearth roasters. Application of the partial blending feasibility model indicates that partial blending is feasible only with a single-stage absorption sulfuric acid plant. Estimates indicate that the blended stream will not exhibit SO₂ concentrations below 3.0 percent over a given 24-hour period.

Model Plant 18 depicts a reverberatory smelting configuration that processes a calcine charge produced by a fluid-bed roaster. This model represents an expansion of 20 percent via oxygen enrichment of the primary combustion. Application of the partial blending feasibility model indicates that partial blending is feasible with a single-stage absorption sulfuric acid plant. Once again, estimates indicate that the blended stream will not exhibit SO₂ concentrations below the 3.0 percent level over a given 24-hour period.

Model Plant 9 (see Table 6-8) depicts expansion at the reverberatory furnace for a typical green-charged smelter. Application of the feasibility model to this configuration indicates that partial blending is feasible with a single-stage absorption sulfuric acid plant. Material balances indicate that the blended stream will not

exhibit an SO₂ concentration below 3.8 percent over a given 24-hour period.

4.6.2.2 Assessment of Partial Blending as Applied to Reverberatory Smelting Furnaces That Are Expanded Via the Use of Oxy-Fuel Burners.

Model Plant 5 (see Table 6-8) depicts a 40-percent expansion of a typical smelter that processes a calcine charge produced by multihearth roasters. Conversion to oxy-fuel burners results in a significant decrease in the volume of gases generated by the reverberatory furnaces, which is accompanied by a marked increase in the weak stream SO₂ concentration. However, application of the partial blending feasibility model to this scenario indicates that partial blending is not technically feasible with the specified dual-stage absorption sulfuric acid plant. Estimates indicate that the blended stream would never exhibit the 4.0 percent SO₂ concentration required to maintain autothermal operation in the acid plant.

Model Plant 22 (see Table 6-8) depicts a 40-percent expansion of a reverberatory smelting configuration that processes a calcine-charge produced by a fluid-bed roaster. The expansion is accomplished by the installation of oxy-fuel burners. Application of the partially blending feasibility model (see Appendix ___) to this configuration indicates that partial blending is feasible with the specified dual-stage absorption acid plant. Estimates indicate that the blended stream SO₂ concentration never drops below 4.0 percent.

Analysis of a 50-percent expansion of the green-charged configuration illustrated by Model Plant 13 yielded similar results. It was determined that partial blending is feasible with the specified single- and dual-stage absorption acid plants.

4.7 CONTROL OF FUGITIVE EMISSIONS FROM PRIMARY COPPER SMELTERS

4.7.1 General

Fugitive emissions may be characterized as emissions from material transfer operations, process vessel leakage, and primary flue leakage that escape directly to the atmosphere. Capture of fugitive emissions is effected by either local or general ventilation techniques. Once captured, fugitive emissions may be routed directly to a control

device, or they may be combined with primary process effluents prior to treatment in a control device. In many cases, they are simply routed to a stack for dispersion without any type of prior particulate or vapor removal. It should be noted, however, that even though captured fugitive emissions may not be subjected to particulate matter or SO₂ removal, high-level dispersion of these emissions will result in lower ambient concentrations of these pollutants at the ground level near the smelter. Consequently, the ambient air quality would be improved even though mass emissions of particulate matter and SO₂ to the atmosphere would remain the same.

Fugitive emissions from some sources may be minimized or eliminated by minor process changes and/or good operating and maintenance practices. In other cases, add-on controls are required. A detailed discussion of the sources of fugitive emissions within a primary copper smelter is presented in Section 3.3.

4.7.2 Local Ventilation

Local ventilation systems consist of localized hoods or enclosures that are designed to confine and capture fugitive emissions at the source. These systems utilize induced air currents to divert fugitive emissions into an exhaust duct.

In this discussion, the term "hood" is used in a broad sense to include all suction openings regardless of shape or physical characteristics. The design of a local exhaust hood involves the specification of its shape and dimensions, its position relative to the emission point, and its rate of air exhaust. In the design of local exhaust hoods, an attempt is made to create a controlled air velocity that will prevent the escape of fugitive emissions from the controlled area to the surrounding atmosphere. The rate of exhaust at the hood entrance is dependent upon the air velocity required to prevent the escape of emissions. The air velocity that will just overcome the dispersive motion of the contaminant(s), plus a suitable safety factor, is called the "capture velocity." The capture velocity must be high enough so that particles at the most distant null point will be captured. Emissions are generally released from the source with a considerable

velocity; however, momentum is soon lost, which results in a rapid decrease in velocity. The position at which the fume velocity is approximately zero is called the null point. Figure 4-22 illustrates the formation of null points as the fume rises from the emission source. If an adequate velocity toward the hood is provided at the most distant null point from the hood, the majority of the fume will be captured.

Wark and Warner²¹ report that a velocity of less than 30 m/min at a null point seldom can be tolerated without a marked loss in capture hood effectiveness. The optimum capture velocity depends upon the following factors:²¹

1. The size and shape of the hood,
2. The position of the hood relative to the emission source,
3. The nature and quantity of the fume to be captured.

For an exhaust hood to be effective, the rate of exhaust across the space between the emission source and the hood must be sufficient to entrain all of the emissions. Proper hood design must incorporate allowances for indoor air currents that could deflect the emissions away from the hood. A capture hood that is designed to work in a still atmosphere may be completely ineffective in the presence of indoor air currents. In addition, the design should be such that the exhaust rate is as uniform as possible over the entire plane of the hood inlet.⁵²

In the case of fugitive emissions from hot sources associated with primary copper smelters, the hood design and the specified ventilation rate must account for the thermal draft that results from heat transfer from the source to the surrounding air. The hood design must accommodate not only the volume of fugitive gases to be collected but also surrounding air set into motion by convective currents. In addition, hoods should be placed as close to the emission source as practical to enhance pollutant recovery.

Air curtains can be used to complement local ventilation systems. A detailed discussion of air curtains is presented in Section 4.6.6.3.

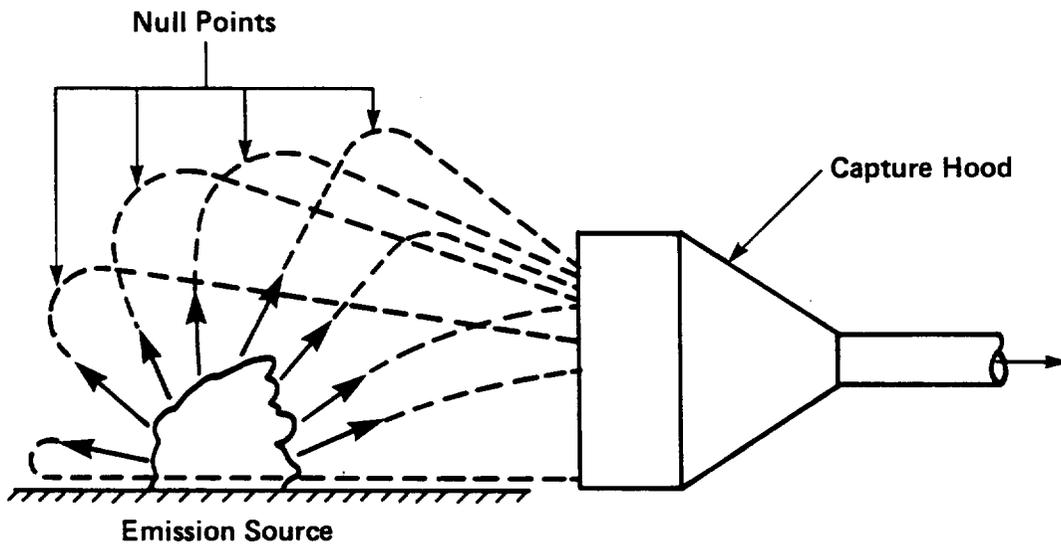


Figure 4-22. Illustration of null point formation.

Several fugitive emission sources associated with primary copper smelters can be controlled by local ventilation methods. Among these sources are:⁵²

1. Calcine discharge and transfer from multihearth roasters,
2. Matte tapping,
3. Slag tapping,
4. Converter operations,
5. Anode furnace operations.

4.7.3 General Ventilation

General ventilation is generally required when it is not possible or expedient to use local exhaust hoods. Local hoods may handicap the operation, maintenance, or surveillance of a process or a piece of process-related equipment, in which case general ventilation would become the preferred method of fugitive emissions control.

General ventilation has historically taken the form of either natural air change due to wind and possibly convective air currents or mechanically assisted air change. Natural changes of air throughout a building can occur by either of two mechanisms:

1. The force of natural wind currents through windows or other openings in the building,
2. The force of convective air currents that occur due to temperature gradients that exist between the inside of the building and the surrounding environment.

Mechanical ventilation is induced by motor-driven fans and is used when the emissions cannot be removed by natural ventilation.

Ventilation requirements for buildings are generally defined in terms of the number of air changes required per unit of time. Although essential in determining the ventilation requirements, the air change rate, also referred to as the ventilation rate, is not the only factor that must be considered. The rate of evolution of emissions within a building must also be considered as well as other site-specific characteristics such as sources of heat, the configuration of the building (number of spans and the form

and shape of the roof), and the arrangement of ventilation openings (windows, roof bays, etc.). Proper ventilation entails a delicate balance between mechanical and naturally occurring forces within a structure.

4.7.4 Control of Fugitive Emissions From Roasting Operations

As suggested by the discussion of fugitive emission sources in Section 3.3, calcine discharge and transfer are the only significant sources of fugitive emissions from multihearth roaster operations. Fluid-bed roasters are designed in such a manner that fugitive emissions are virtually eliminated;⁵² therefore, this discussion will primarily address the control of fugitive emissions from calcine discharge and transfer operations associated with multihearth roasters.

Four domestic copper smelters currently utilize multihearth roasters. These facilities are:

1. ASARCO-El Paso
2. ASARCO-Hayden
3. ASARCO-Tacoma
4. Phelps Dodge-Douglas.

Calcine produced at these smelters is normally discharged from the bottom of the multihearth roaster into a hopper, which in turn distributes the calcine to a transfer vehicle (larry car) for transportation to the smelting furnace(s). Calcine hoppers are discharged intermittently rather than continuously. More than one hopper may be discharged during the transfer of calcine to the larry cars for transport to the smelting furnace(s). The frequency of discharge for any one hopper may vary from zero to 30 times per hour.⁵² Typically, the duration of discharge is approximately 30 to 60 seconds per hopper. Large quantities of dust are generated as a result of material movement and pressure changes within the transfer vehicle. Consequently, local ventilation is needed to control emissions at the transfer point, and the transfer vehicle feed opening must be covered to prevent the escape of emissions during transport.

The design and effectiveness of these systems vary from smelter to smelter. Generally, the captured fugitive emissions are routed to existing process control systems for particulate removal.

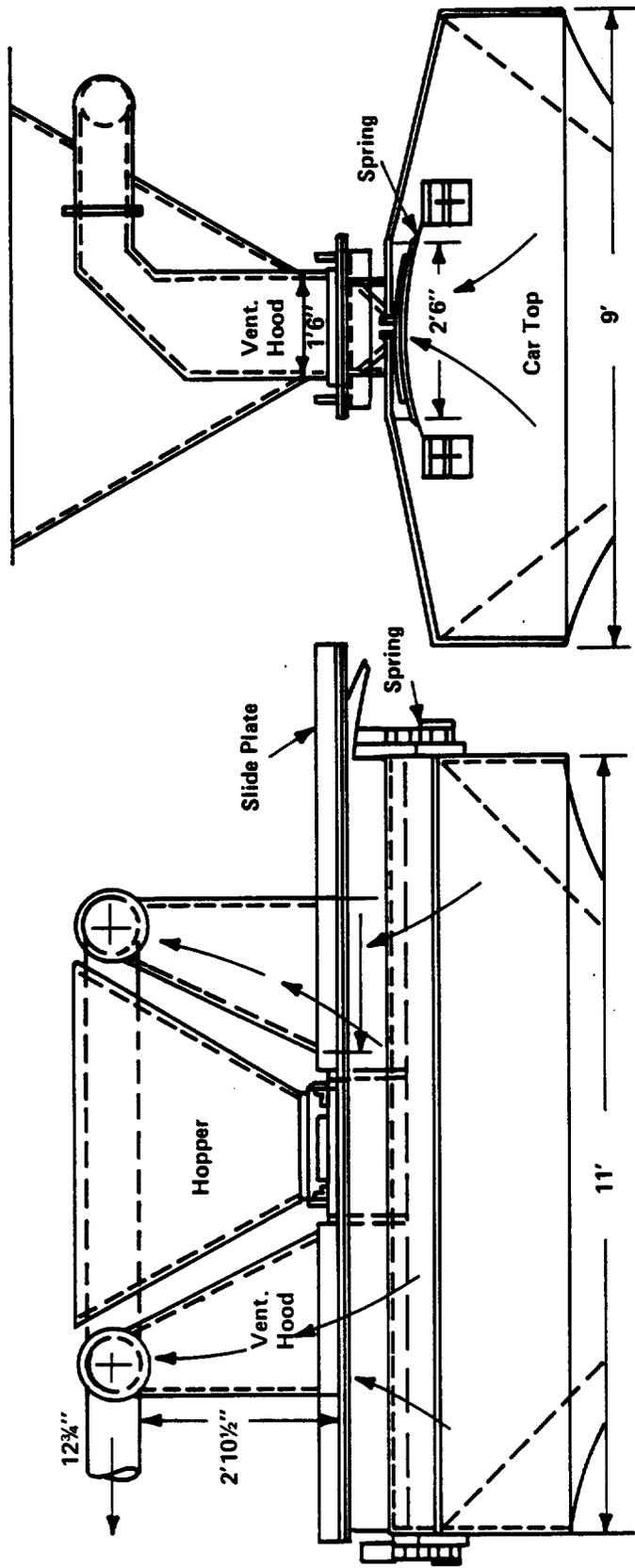
Figure 4-23 presents a schematic of the calcine transfer/fugitive emissions control system at ASARCO-Hayden. A similar system is used at ASARCO-Tacoma. A continuous flat apron strip nearly 0.6 m (2 ft) wide is mounted directly below the row of multihearth roasters at the hopper discharge gate. In the apron below each hopper there are two ports connected to a duct 0.5 m (1.5 ft) wide. A matching leaf spring-loaded flat apron is mounted on the larry car. When the larry car is driven beneath the roaster, it is positioned so that the matching apron on the car is directly aligned with the apron on the bottom of the roaster hopper. Consequently, the ports in the hopper apron are perfectly aligned with ports on the larry car apron. One port is used for transferring the calcine to the larry car, while the other two ports are used for ventilation. Each port has its own individual fan* rated at approximately 142 Nm³/min (5,000 scfm). Emissions captured by this system are routed to the roaster primary offgas flue.

At ASARCO-Tacoma, the calcine hopper area is enclosed in a tunnel-like structure into which larry cars are driven and loaded. This ventilated enclosure is very effective in capturing fugitive emissions that escape capture at the transfer point. No fugitive emissions were observed to escape during a visual evaluation of this system.⁵²

At El Paso, calcine transfer occurs in a long shed. The shed is open at one end for larry car entry and an exhaust duct is located at the opposite end. The captured emissions are exhausted into the spray chamber system that handles the primary process emissions from the reverberatory smelting furnaces. A visual inspection of this facility indicated that about 50 percent of the visible emissions are captured.⁵²

At Phelps Dodge-Douglas, hooding with canvas flaps is provided around the roaster discharge area into which the larry cars are driven. Captured emissions are routed to a baghouse for particulate removal. The average volumetric flow rate at the inlet of the baghouse used to treat these emissions has been measured to be approximately 990 Nm³/min (35,000 scfm). A visual inspection indicated that about 70 percent of the visible emissions are captured by this system.⁵²

*Only a single fan is used at ASARCO-Tacoma.



NOTE: Car Top and Hood — 18 Ga. C.R.S.

FRONT ELEV.

SIDE ELEV.

Figure 4-23. Spring-loaded car top and ventilation hood, ASARCO-Hayden. 52

From an alternative control standpoint, the ASARCO system applied at Tacoma and Hayden seems to be the most viable since this system is very effective in controlling visible fugitive emissions. This determination has been made based upon visible observations of the various systems now in use for the control of fugitive emissions from calcine discharge operations (see Table 4-__).

Although visible emissions from calcine discharge operations are effectively controlled as discussed above, emissions from calcine transfer operations are generally poorly controlled. Visible emissions from larry cars at ASARCO-El Paso and ASARCO-Hayden were evident.^{60 61} In addition, the odor of SO₂ was easily detected from the larry car emissions observed at the El Paso smelter.⁶⁰ Larry car covers should be used while the cars are in transit to minimize fugitive emissions from calcine transfer operations.

4.7.5 Control of Fugitive Emissions From Smelting Furnace Operations

A complete discussion of the fugitive emissions sources associated with various types of smelting furnaces is presented in Section 3.3. From this discussion, it becomes evident that matte tapping and slag skimming operations are the most significant sources of fugitive emissions from smelting furnaces. Consequently, this discussion addresses the control of fugitive emissions from tapping and skimming operations only.

4.7.5.1 Control of Fugitive Emissions from Matte Tapping Operations.

Matte tapping is the operation by which matte is removed from the smelting furnace for transport to the converters. Matte is removed (tapped) from the furnace through tapping ports, which are generally located on the sides of the furnace. The number and location of the tapping ports will vary from furnace to furnace depending upon the size and type of smelting furnace; however, the tapping procedure is generally the same. Normally, matte is tapped from one port at a time and conveyed through launders into ladles. The ladles vary in volume from 4.9 to 9.2 m³ (175 to 324 ft³). A single matte tap may last from 9 to 15 minutes, with emissions in evidence from the point at which the matte exits the furnace to the point where it settles into the ladle.

Most smelters employ local exhaust hoods at the points where the matte exits the furnace. In addition, launder covers are used at most facilities.

Tap port exhaust hoods may be of any shape as long as they are designed to evacuate as much of the emission area as possible. Hoods of this type are generally affixed to the side of the furnace. Observations indicate that, when operated properly, hoods of this nature are quite effective in capturing fugitive emissions that are generated in the area of the tapping port. In addition, these hoods are quite effective in capturing heavy emissions that occur during the lancing that is required to open the ports. A typical hood of this type is illustrated in Figure 4-24.

A schematic of a typical matte tapping fugitive emissions control system is presented in Figure 4-25. The system illustrated is employed at the ASARCO-Tacoma smelter. The actual matte tap hoods are 1.2 m by 1.2 m (4 ft by 4 ft) in cross section and are located less than 0.9 m (3 ft) above the tapping port.⁵² Each matte tap hood is connected to the main fugitive emissions duct as shown. The ducts, which connect each hood to the main fugitive emissions duct, are 0.6 m (2 ft) in diameter; the main duct is 1.2 m (4 ft) in diameter. During a tap, approximately 283 Nm³/min (10,000 scfm) are exhausted from a given matte tap hood.

Launder covers are usually made of metal and are mounted on the launders in sections to allow manual removal for launder cleaning. A typical section of a launder hood is 1.2 to 1.5 m (4 to 5 ft) long.⁵² Launder covers of this type are depicted in Figure 4-26. A great deal of the emissions that are generated by the molten matte as it flows down the launder can be captured by launder covers if the covers are well maintained and in place during tapping operations. Due to the incline of the launder, hot fumes captured by the launder covers will generally rise back to the tapping port area where they are captured by the tap port hood.

An effective type of launder hood has been developed by the Phelps Dodge Corporation and is currently in use at Phelps Dodge's Morenci smelter. This type of hood, as depicted in Figure 4-27, is movable and is placed over the launder during tapping operations. Visible observations yielded an estimated capture efficiency of ___ percent. A summary of the visible emissions data obtained for this hood is presented in Table 4___. This type of hood can be effective if the surrounding atmosphere is calm; however, if the air currents within the furnace building are strong, a major portion of the emissions will be blown out from under the hood.

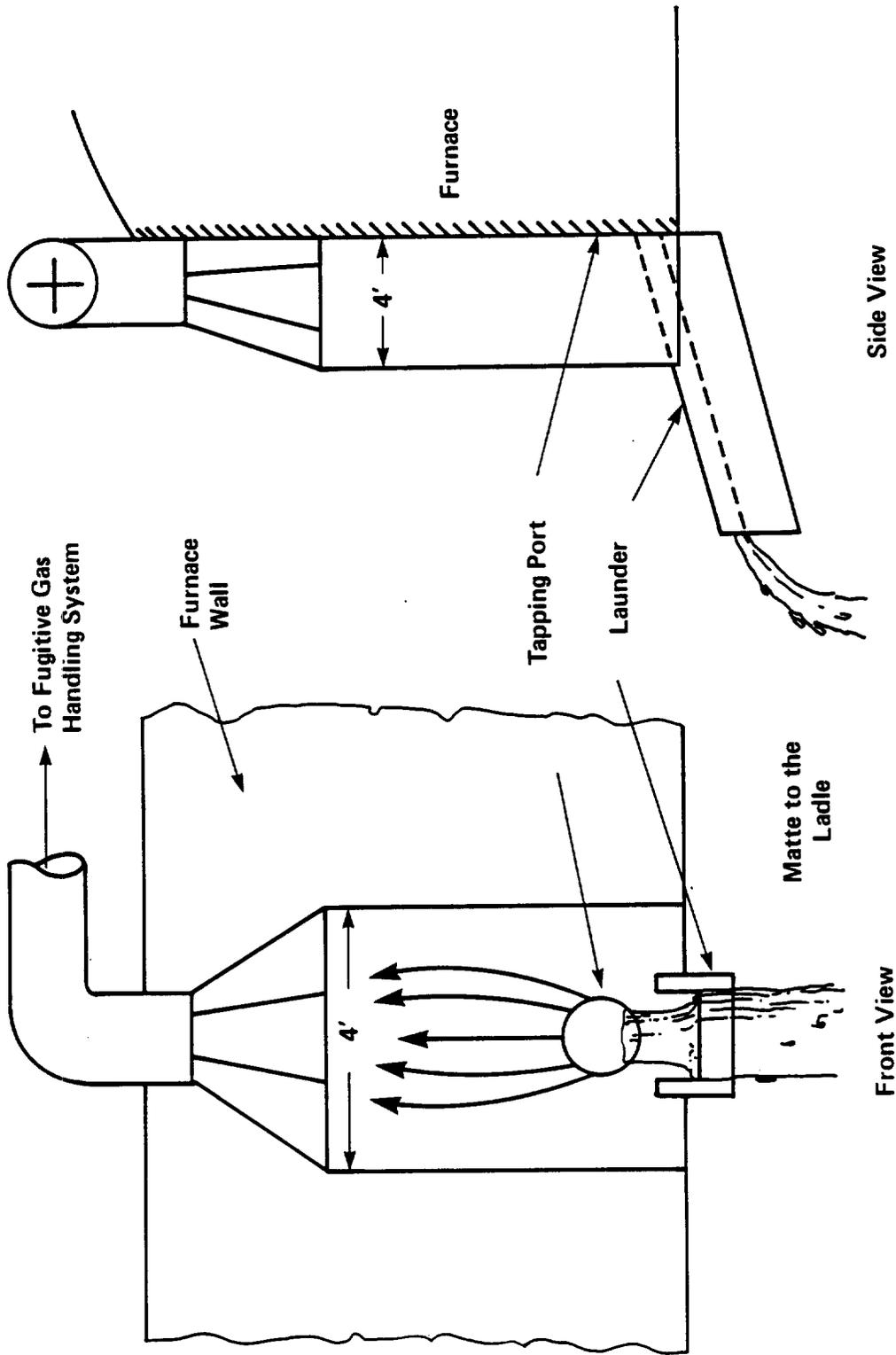


Figure 4-24. Typical hooding for a matte tapping port.

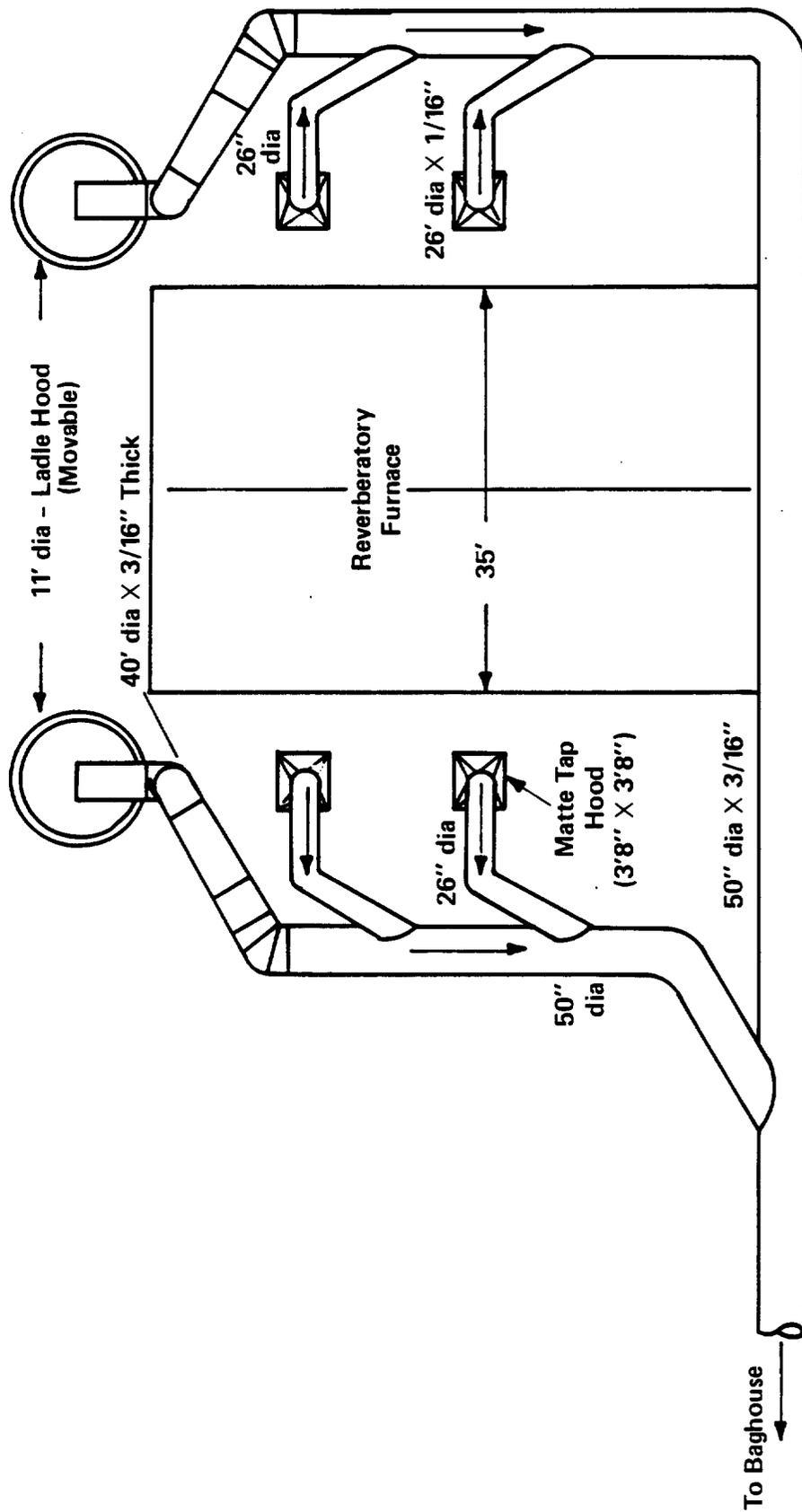


Figure 4-25. Schematic of a typical fugitive emissions control system for matte tapping operations.⁵²

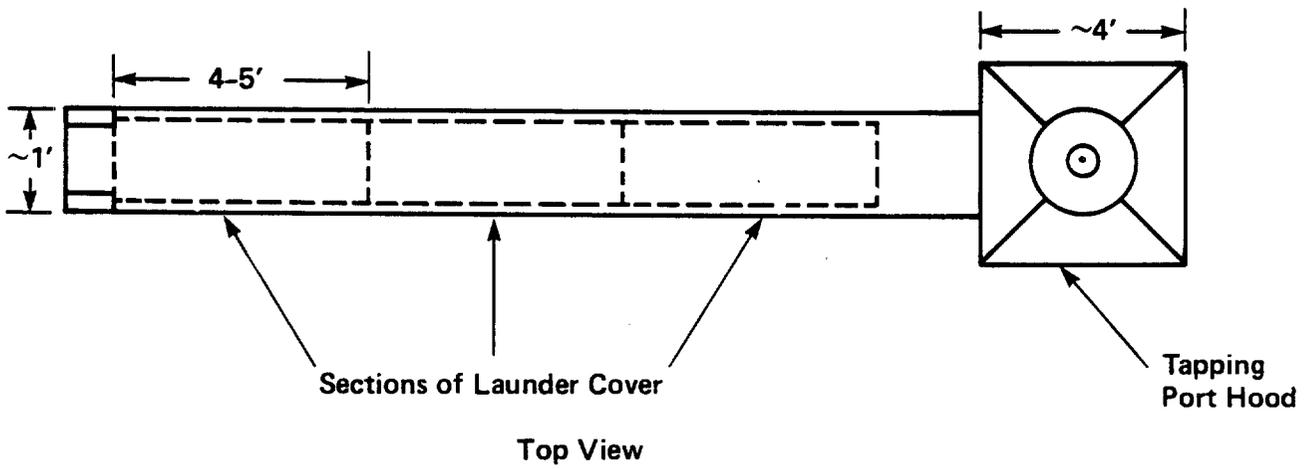
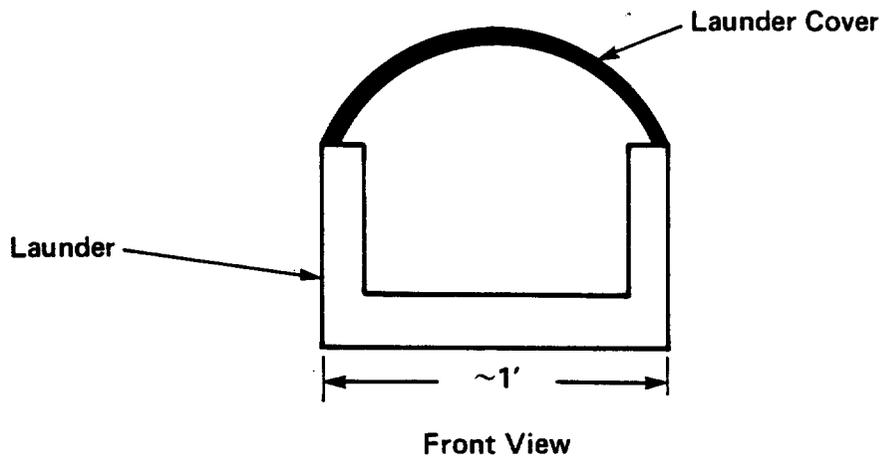


Figure 4-26. Typical sectional launder covers.

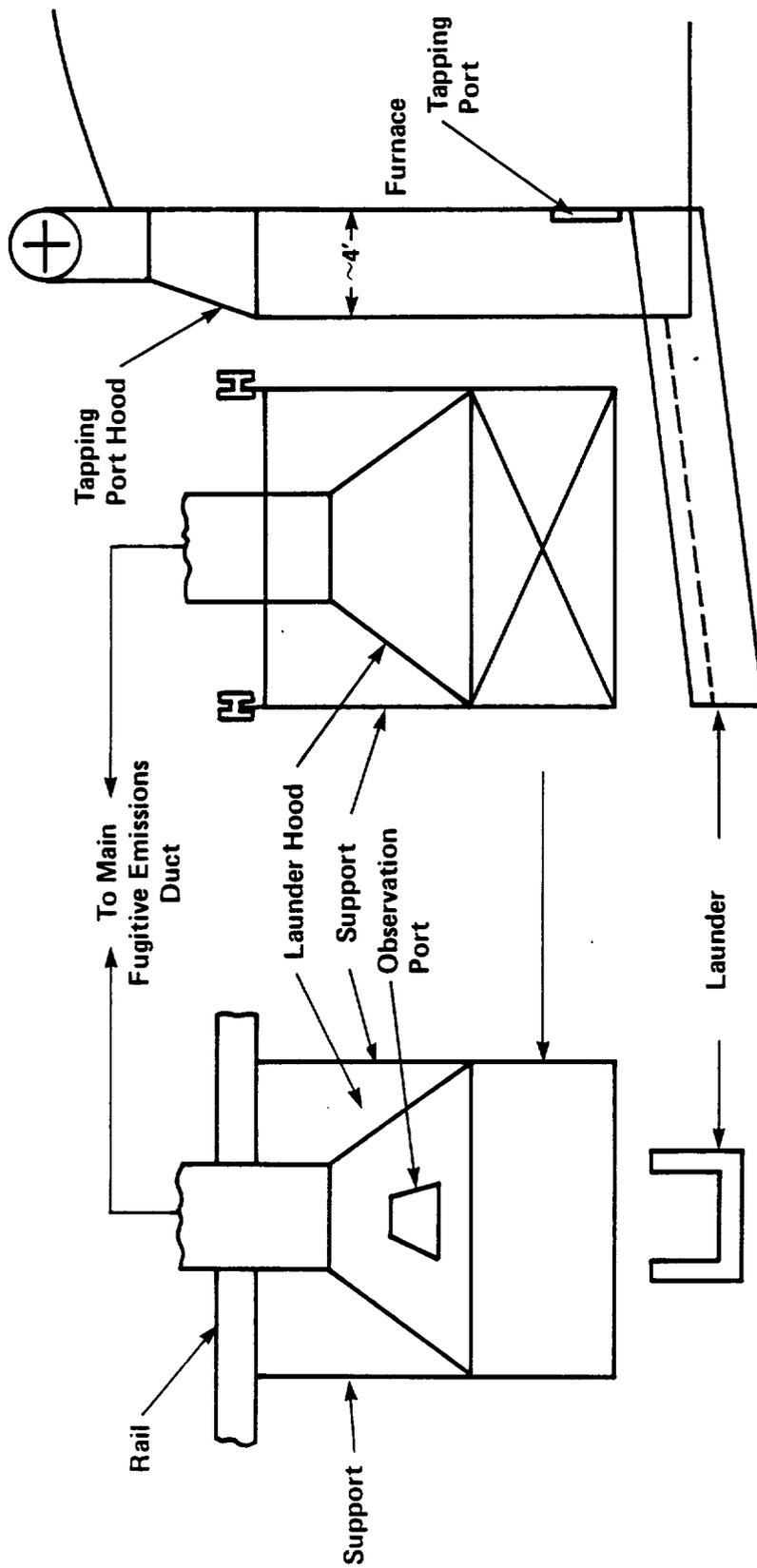


Figure 4-27. Launder hoods utilized at the Phelps Dodge—Morenci Smelter for the capture of fugitive emissions generated during matte tapping operations.

As suggested by Figure 4-25, movable hoods can be employed to capture emissions that occur at the ladle. Figure 4-28 illustrates the type of ladle hood that is used at the ASARCO-Tacoma smelter. The dimensions of the matte tap hoods used at the Tacoma facility are also presented in Figure 4-28. Emissions that are captured by the ladle hooding are evacuated to the main fugitive emissions duct via the 102-cm (40-in) diameter offtake, as illustrated. The ladle hood is retractable and is lowered into place over the ladle just prior to tapping. The ladle hood is lowered and raised via use of a cable and winch.

As indicated by Figure 4-25, the matte tapping fugitive emissions capture system at the ASARCO-Tacoma facility employs both tap port hoods and a ladle hooding system. Emissions testing and visual observations (see Section 4.7.7.1) conducted by the EPA at the Tacoma smelter indicate that this capture system is quite effective in capturing fugitive emissions generated during matte tapping operations. Visual observations indicate that the capture efficiency of this system is probably in excess of 90 percent.⁵² Consequently, from an alternative control standpoint, the Tacoma system seems to be the most viable alternative for the capture of fugitive emissions generated during matte tapping operations.

4.7.5.2 Control of Fugitive Emissions From Slag Skimming Operations.

Slag skimming is the process by which molten slag is removed from the smelting furnace for disposal. Slag is skimmed from the furnace through skim bays that may be located on the sides or at one end of the furnace. As with matte tapping ports, the number and location of the skim bays will vary depending upon the size and type of furnace. Normally, slag is skimmed from one bay at a time and conveyed through launders into one or several slag pots (ladles). Slag pots may range in capacity from 2.8 to 17 m³ (100 to 600 ft³). A single slag skim may last from 10 to 20 minutes.

Because slag skimming is very similar to matte tapping, the fugitive emissions capture technology used for both operations is quite similar. Local exhaust hoods are employed over skim bays and slag launders are either partially or completely covered. Design rates for skim bay hoods vary from smelter to smelter; however, they normally range from 566 to 850 Nm³/min (20,000 to 30,000 scfm).⁵²

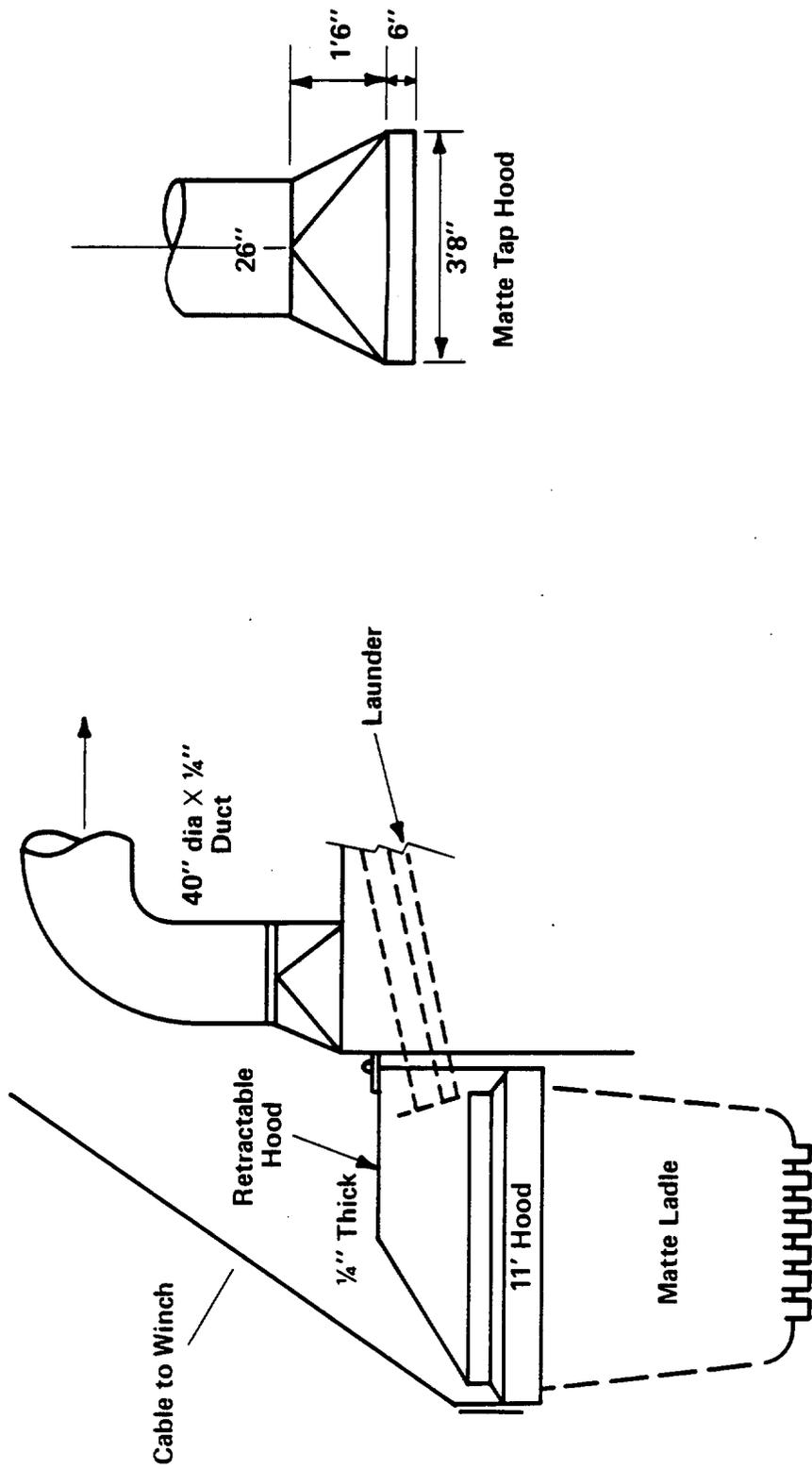


Figure 4-28. Schematic of the matte tapping and ladle hoods at the ASARCO-Tacoma Smelter.

A schematic of the slag skimming fugitive emission control system used at the ASARCO-Tacoma smelter is presented in Figure 4-29. The slag skim hoods are pyramidal in shape with a 1.2 m by 2.4 m (4 ft by 8 ft) rectangular cross section, and they are less than 0.9 m (3 ft) above the skim port. A larger exhaust hood with a 2.4 m by 4.3 m (8 ft by 14 ft) rectangular cross section is situated directly above the slag pot transfer point. In addition, each launder is covered with a fixed hood. During skimming, the slag skim hood operates at about 142 Nm³/min (5,000 scfm), while the hood above the slag pot operates at approximately 566 Nm³/min (20,000 scfm). Emissions that are captured by the launder hooding are vented to either the slag skim hood or the slag pot hood.

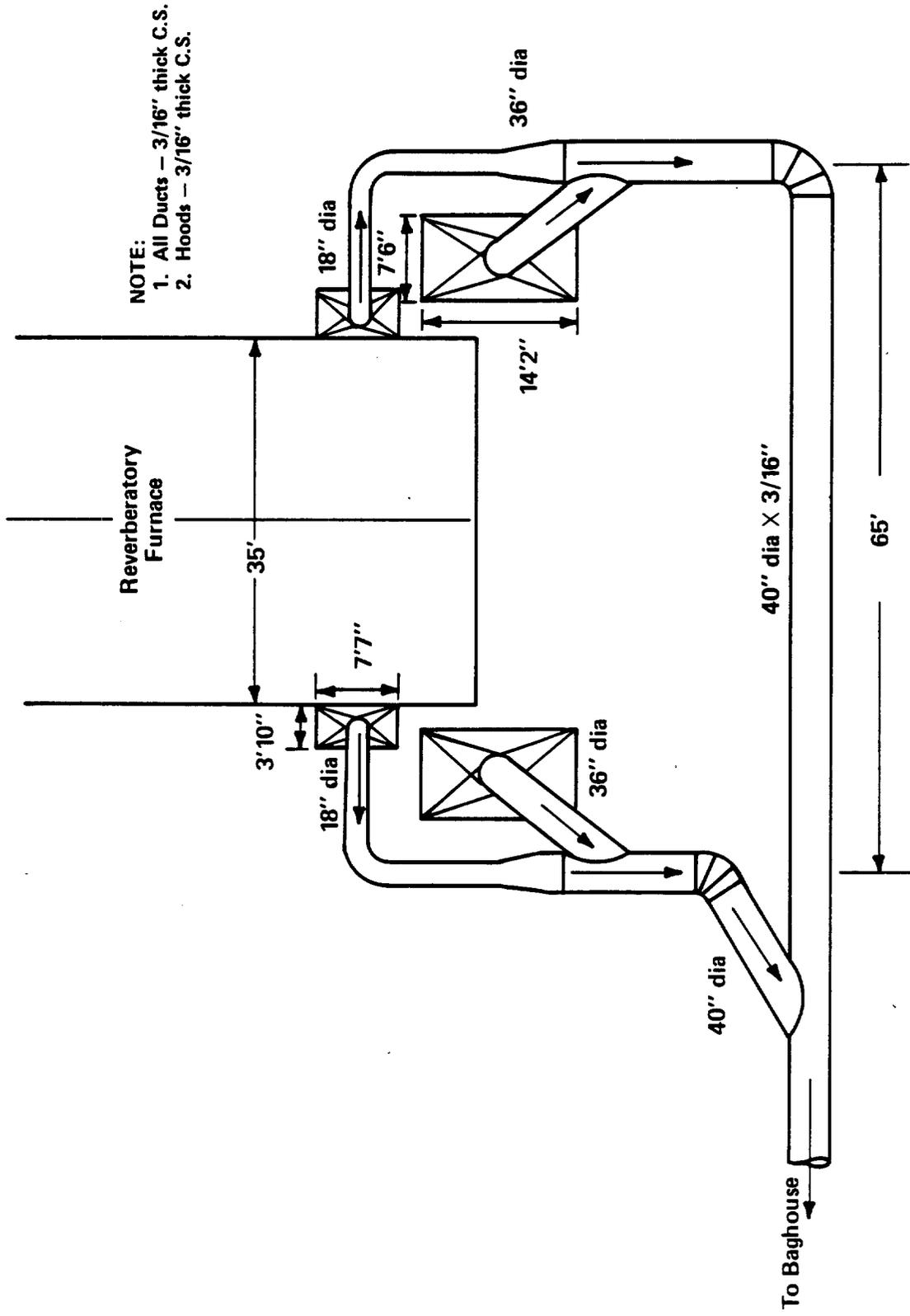
From visual observations made by the EPA at the Tacoma smelter (see Table 4-20), it was determined that this type of hooding system achieves a capture efficiency of approximately 90 percent.⁵² Consequently, the Tacoma system is considered to be the most viable alternative for the control of fugitive emissions generated during slag skimming operations.

4.7.6 Capture of Fugitive Emissions From Converter Operations

Primary converter hoods capture the majority of the process emissions generated during converter blowing operations with the exception of some emissions that escape due to primary hood leakage. However, during converter charging, skimming, and pouring operations, the mouth of the converter is no longer under the fixed primary hood, thus significant quantities of fugitive emissions escape capture by the primary hood. Fugitive emissions are also quite extensive during the converter holding mode as discussed in Section 3.3.2.4.

Previously conducted emissions testing by EPA has indicated that converters are the most significant sources of fugitive particulate and SO₂ emissions within primary copper smelters (see Tables 3-5 and 3-6). There are, however, three basic alternative control techniques that can be used to capture fugitive emissions from converter operations: (1) general ventilation, i.e., building evacuation; (2) secondary mechanical hoods; and (3) air curtains with fixed enclosure hoods.

4.7.6.1 General Ventilation as a Means of Capturing Fugitive Emissions Generated by Converter Operations. Building evacuation has historically



NOTE: The dimensions indicated are those of a system of this type currently utilized at the ASARCO-Tacoma facility.

Figure 4-29. Schematic of the slag tapping (plan view) fugitive emissions control system at the ASARCO-Tacoma Smelter. 52

taken the form of either natural air changes due to wind and atmospheric density differences or mechanically assisted air changes. However, some engineering considerations must be made before applying a simple rate of air change method for designing an industrial ventilation system. The rate of air change method estimates are based on room volume only and do not consider the rate of evolution of the contaminant, the number of heat sources, or the natural draft due to building configuration. For example, a general ventilation installation designed by the rate of air change method can, under some conditions, actually cause the contaminant to be spread throughout the building, thus increasing the volume of dilution air required to maintain hygienic conditions. This situation occurs when the distribution of the ventilation air supply is poorly controlled. Uncontrolled airflows into a building due to negative pressure in the building or because of poorly designed air supply distributors may not only cause recirculation of the contaminant, but may also upset the local ventilation systems. It is therefore important that the amount of air, its location of entry into the building, and its direction be controlled. For example, Figure 4-30 shows a convective flow from a heat source (such as a ladle of molten metal) rising to be exhausted through a roof ventilator. Figure 4-31 shows an uncontrolled air supply that results in a disrupted rising plume and recirculation of the contaminant throughout the building.

Natural air changes take place when hot air from the ground level heat sources rises due to its buoyancy. If, however, there exists a point within the building where the temperature of the surrounding air is equal to that of the rising column of hot air, buoyancy is lost. Therefore, natural air changes will take place only if the temperature of the rising column of hot air is high enough to maintain the buoyancy of the column until it is discharged through the roof monitors. However, in most hot metal workshops, this is not the case. Hot pools of contaminated air are formed under the building roofs. As a result, clean air entering the building will at times mix turbulently with pools of contaminated air and transport it downward to the occupied levels near the floor.

Increasing the rate of ventilation is the most commonly used method of correcting such an air contamination problem. Increasing the rate of

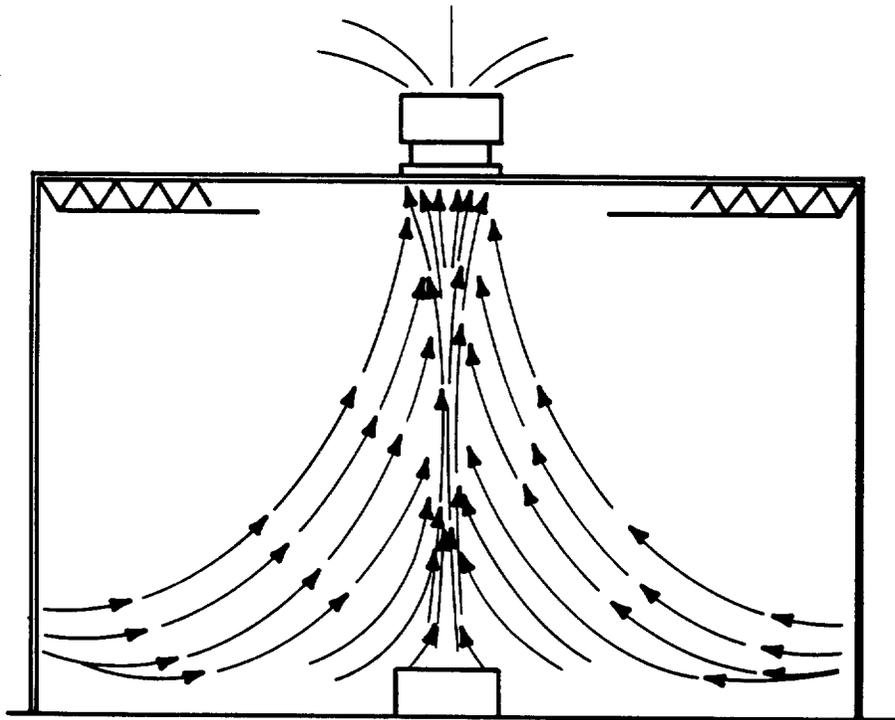


Figure 4-30. Controlled airflow from a heated source.⁵²

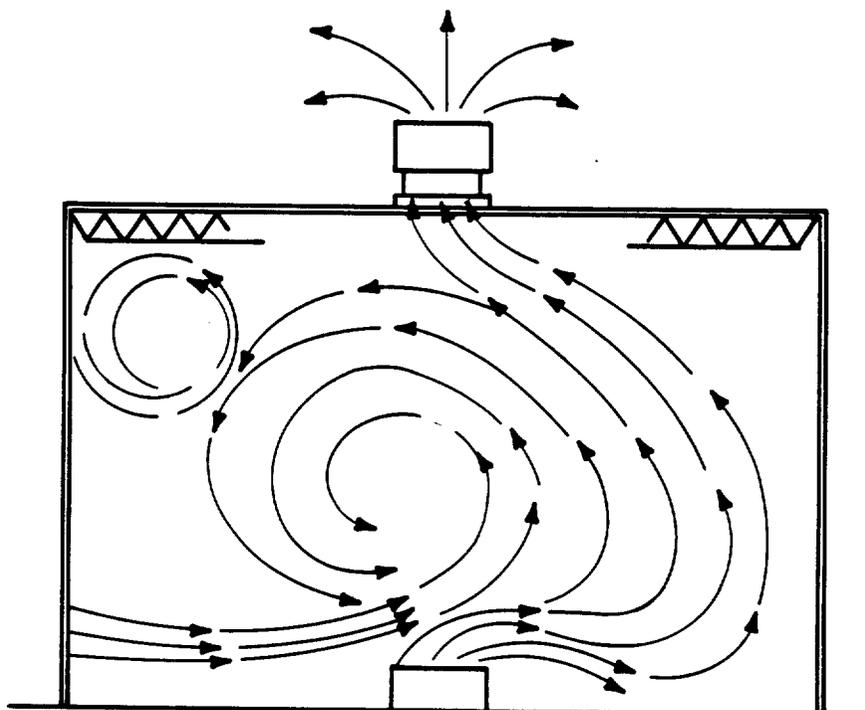
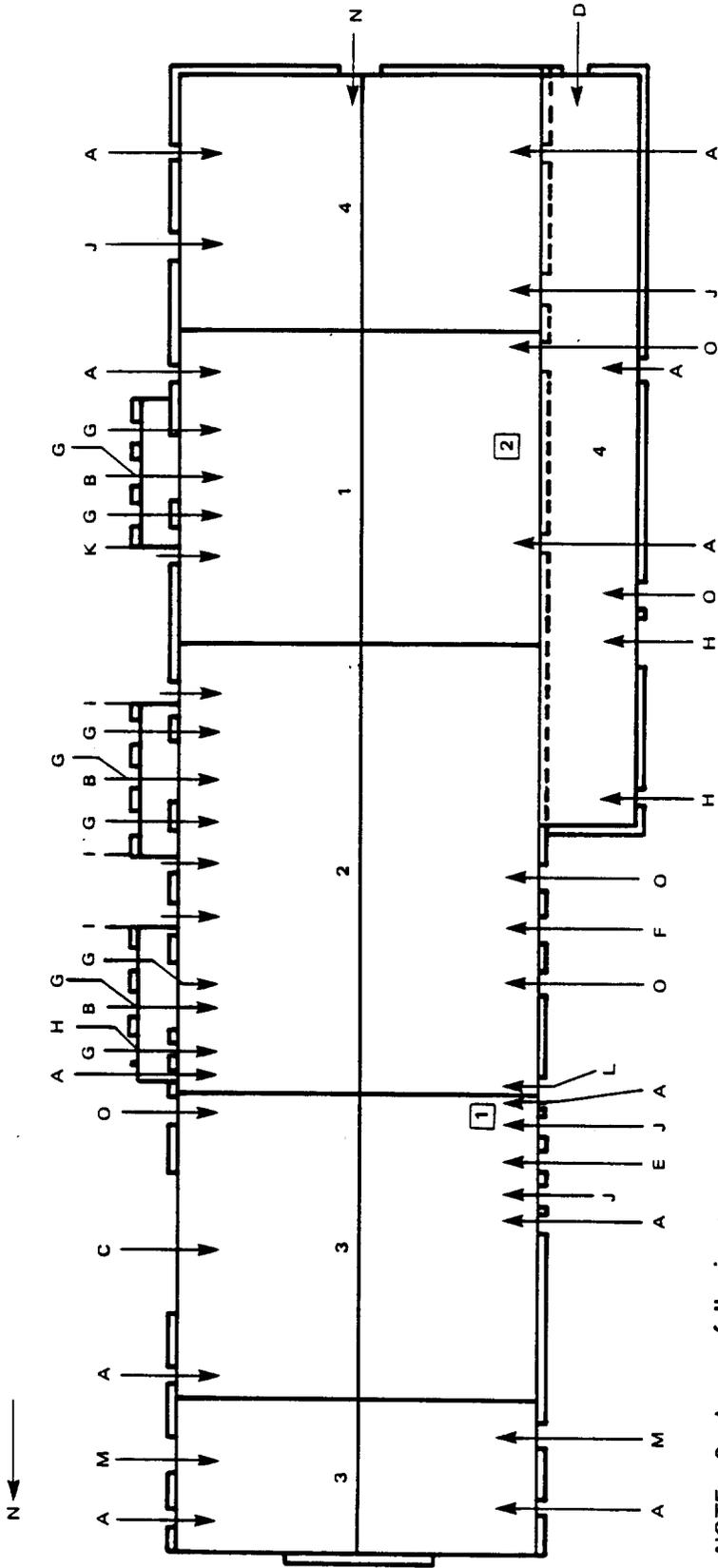


Figure 4-31. Uncontrolled airflow from a heated source.⁵²



NOTE: See key on following page.

Figure 4-32. Inlet-outlet openings in converter building at ASARCO—El Paso. 52

INLET (AIR INTAKE) SCHEDULE (NEW BAGHOUSE SYSTEM)					
KEY NO.	TYPE	SIZE	NO. REQD.	EACH (scfm)	TOTAL (scfm)
PERMANENT OPENINGS					
A	Egress Openings in Walls	7'-6" H x 3'-8" W	7	13,500	94,500
B	Converter Wall Openings	5'-0" H x 16'-0" W	3	40,000	120,000
C	Anode Casting Wheel Opening	12'-0" H x 37'-0" W (20 ft ² Net Opening)	1	60,000	60,000
D	Hi-Line Track Entrance	12'-0" H x 8'-0" W	1	45,000	48,000
E	Zinc Fuming Wall Opening	3'-2" H x 4'-6" W	1	7,000	7,000
F	Skull Breaker Wall Opening	5'-8" H x 5'-8" W	1	16,000	16,000
LOUVERED OPENINGS					
G	Tuyere Puncher Housing	1'-8" H x 1'-0" W	9	1,300	11,700
H	Hi-Line Track Enclosure, #3 Conv.	3'-2" H x 2'-3" W	3	3,000	9,000
O	Skull Breaker Wall Openings	5'-3" H x 6'-3" W	3	16,000	48,000
I	#2 & 3 Converters	4'-5" H x 5'-6" W	3	16,000	48,000
J	Zinc Fuming Wall	3'-2" H x 5'-0" W	2	6,500	13,800
K	#1 Converter	4'-5" H x 6'-3" W	1	12,000	12,000
TOTAL					485,000
AUXILIARY LOUVERS					
C	Matte Tap Hood Makeup Air	5'-8" H x 6'-3" W	2	15,000	30,000
L	Slag Tap Hood Makeup Air	6'-11" H x 8'-3" W	1	25,000	25,000
TOTAL					55,000
AUXILIARY LOUVERS					
A	Egress Openings in Walls	7'-6" H x 3'-8" W	4	13,500	54,000
H	Lead Slag Track Entrance	12'-0" H x 10'-0" W	1	60,000	60,000
J	Louvered Openings	3'-2" H x 5'-6" W	2	7,000	14,000
M	Louvered Openings	5'-8" H x 8'-0" W	2	21,000	42,000
TOTAL					170,000
OUTLET (EXHAUST) SCHEDULE					
KEY	Existing Hood Systems	Proposed Roof Evacuation (New Baghouse System)		Gravity Draft at Extremes of Building (Variable)	
	scfm	KEY	scfm	KEY	scfm
1	25,000	▽	130,000	▽	68,000
2	30,000	▽	200,000	▽	102,000
		▽	136,000		
		▽	16,000		
TOTAL	55,000		488,000		170,000

Figure 4-32 (continued).

ventilation through the building will have the effect of raising the column of hot air. Increased ventilation can be obtained by increasing the area of supply openings and roof openings or by using mechanical means such as exhaust fans.

Building evacuation by means of natural air changes or by a combination of natural and mechanical air changes is used at most domestic copper smelters. The captured fugitive emissions are usually vented to the atmosphere either through roof monitors or through roof stacks.

At the ASARCO-El Paso smelter, the concept of controlled ventilation is being used to capture and collect the emissions from the converter aisle. Controlled ventilation is accomplished by controlling the airflow patterns within the building and determining the flow of air to be handled. Control of airflow in the ventilated area is obtained by isolating it from other areas and by the proper design and placement of inlet and outlet openings. A well-contained and isolated area results in the handling of a minimum volume of air. Proper location and sizing of inlet and outlet openings provide effective airflow patterns so that the fugitive emissions cannot escape to adjacent areas or recirculate within the area. The configuration of the converter building inlet and outlet openings at the ASARCO-El Paso smelter is shown in Figure 4-32.

Isolation of the ventilated area at the ASARCO-El Paso smelter was accomplished by installing additional sheeting in the roof truss area along the converter building column lines to enclose the flow from the smelting furnace area. The tuyere punching platforms east of the three converters were enclosed. The larry car rail line at the west side of the converter building was enclosed to contain the dust and SO_2 released when the larry cars were emptied. The location and sizes of these enclosures were selected to provide maximum feasible containment without interference with metallurgical operations. Partitions within the roof of the converter building were provided to prevent lateral migration of fume into adjacent areas.

The air velocity through the inlet openings was controlled to provide directional flow control and supply an adequate volume of air into locations where needed. This was achieved by using adjustable louvers on air inlet openings through building walls. Ventilating outlets are located at the

ridge line of the converter building roof in the center of each partitioned area.

Inlet air is admitted to the converter aisle through louvers and permanent openings in the east and west walls of the building. Makeup air for the zinc holding and reverberatory furnaces matte tap exhaust systems, which operate periodically, enters through adjustable louvers along the west wall. Inlet air for the reverberatory furnace charge area enters through a permanent opening in the south wall for the high-line railroad train and through adjustable louvers along the west wall. Inlet air for the extremes of the converter building is admitted through egress openings and louvers along the east and west walls and through a permanent opening in the south wall. The latter opening is permanent to accommodate the fairly frequent lead matte car railroad traffic.

During winter operation, a majority of the gravity roof ventilators in the extremes of the converter building are closed to keep heat in the building. This requires partial closing of inlet air louvers. The gravity roof ventilators over the portion of the building that is vented to the building evacuation system are normally closed; however, they automatically open in the event of power failure to provide emergency ventilation. The ventilators over the extreme ends of the converter building are normally open; they remove heated air from areas where emissions are slight.

Railroad doors are kept closed when cars and slag haulers are not entering or leaving the building. Allowing these doors to remain open causes harmful effects depending on wind conditions; e.g., (1) airflow is reduced through the normal inlets, resulting in poor inlet air distribution; (2) the air moving through the shop forms eddies that pick up fume from the furnaces, entrain it, and spread the fume throughout the converter building; and (3) a strong wind through the railway car door entering the building results in air volume exceeding the total ventilating capacity of the building. A positive pressure within the building could occur, and fume could be forced out of the building through the normal inlet openings.

The present volume evacuation rate of this system at the ASARCO-El Paso smelter is 16,800 Nm³/min (600,000 scfm)--equivalent to 18 air changes per hour.⁵² Supplementary air is provided when the zinc slag holding furnace

or reverberatory furnace matte launder local exhaust systems are in use. The average exhaust gas temperature from the converter building after the exhaust gases from the four building exhaust ducts mix is 55° C (130° F). Nominal duct design gas velocities are 1,500 m/min (5,000 ft/min) from the converter building to a baghouse and 900 m/min (3,000 ft/min) from the baghouse to the annulus of the main stack. The building exhaust gases contain negligible water vapor and sulfur trioxide. Observations made at the smelter indicated that, when operating properly, the building evacuation fugitive emissions capture system is very effective in capturing fugitive emissions being discharged in the converter aisle. A capture efficiency of 95 percent or better was estimated.⁵²

The baghouse receiving building ventilation gases at the ASARCO-El Paso smelter contains 4,800 bags, each 15 cm (6 in) in diameter by 9 m (30 ft) long. It is sized with a nominal air-to-cloth ratio of 3 to 1. Three backward curved air foil fans are used on the clean-air side of the baghouse and are sized on the basis of 110 percent of the estimated airflow. The results of tests that EPA performed on this baghouse are summarized in Section 4.7.7.

4.7.6.2 Secondary Mechanical Hoods as Means of Capturing Fugitive Emissions Generated by Converter Operations. In normal practice, primary converter hoods are used when the converters are in the blowing mode. However, fugitive emissions that occur as a result of primary hood leaks are uncontrolled unless some type of additional capture equipment is employed. Currently, there are several domestic primary copper smelters that utilize some form of secondary mechanical hooding to capture fugitive emissions that result from primary hood leaks. The types of hoods currently in use are:

1. Fixed type--Attached to the primary hood; currently in use at Phelps Dodge-Ajo, Phelps Dodge-Hidalgo, Phelps Dodge-Morenci, and Kennecott-Magna.
2. Wing-wall type--Supported by walls on either side of the converter; currently in use at ASARCO-Hayden.

The fixed-type hood, illustrated in Figure 4-33, is approximately 3 m (10 ft) long, 6.4 m (21 ft) wide, and 1.7 m (5.5 ft) high and is affixed to

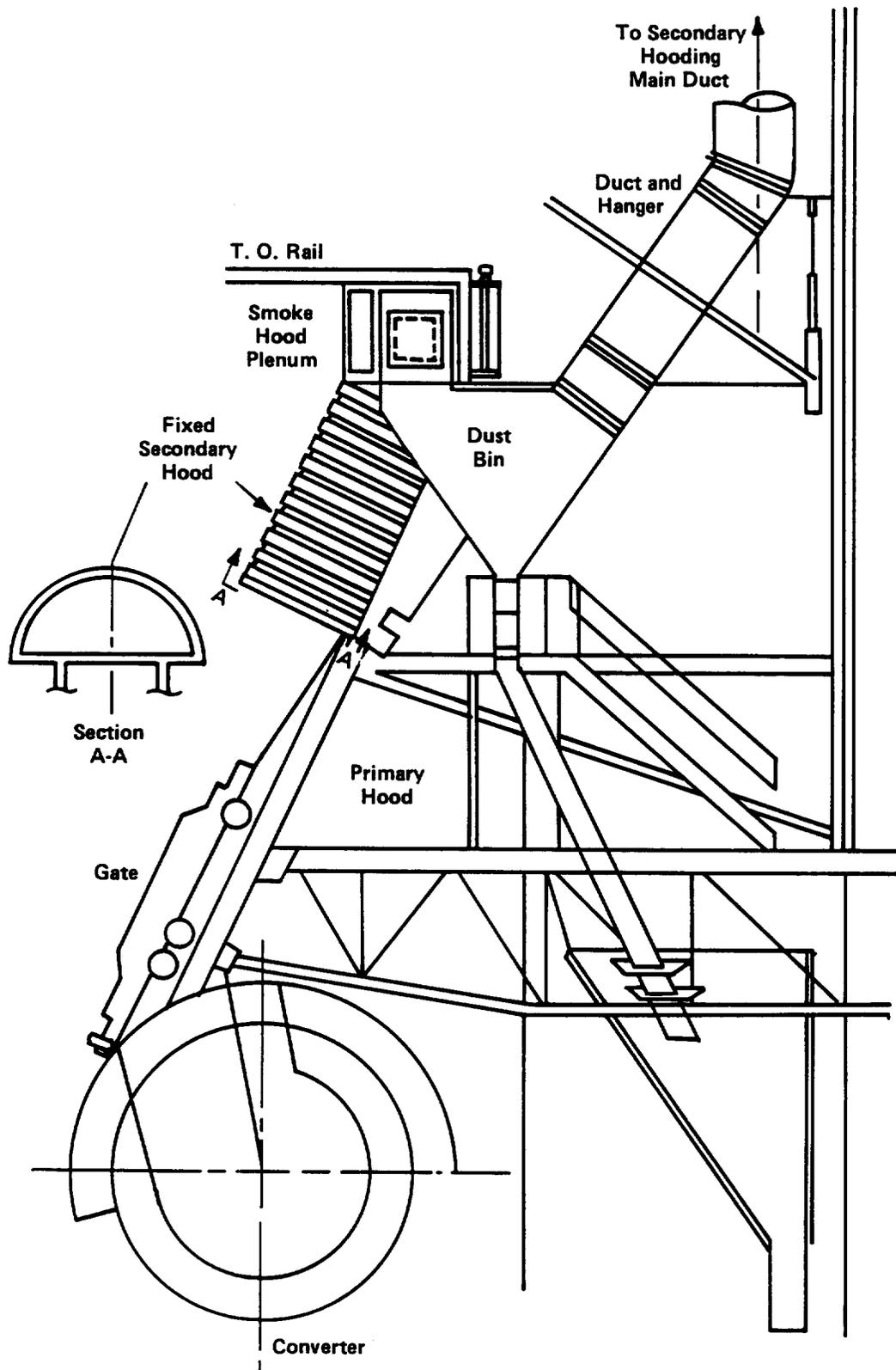


Figure 4-33. A typical fixed secondary converter hood.⁵²

the upper front side of the converter primary offtake hoods. Visual observations indicate that this type of hood is only marginally effective in capturing fugitive emissions that are generated during blowing.⁵² Therefore, this discussion will concentrate on the wing-wall-type hood (shown in Figure 4-34).

Visual observation of a wing-wall-type enclosure at the ASARCO-Hayden smelter yielded an estimated __ percent capture efficiency of fugitive emissions that escaped the primary hood during blowing operations. Thus, although the hood is not intended to capture emissions that occur while the converter is "rolled out," it is quite effective in capturing fugitive emissions that occur during blowing operations.

The secondary hood, as shown in Figure 4-34, is retracted during charging, pouring, and skimming operations so that the crane operator can have access to the converter mouth as well as the area directly in front of the converter. Then, as blowing begins, both the primary and secondary hoods are lowered into position over the mouth of the rolled-in converter. The most significant source of emissions that escape capture by this hooding system during blowing are slots in the top of the secondary hoods through which the cables for primary hood retraction are passed.

In summary, the ASARCO-Hayden hood is judged by EPA to be reasonably effective in capturing fugitive emissions that are generated by converters during the blowing mode. The primary shortcoming of this type of hood is its inability to capture fugitive emissions that occur during operations other than blowing. The following discussion dealing with fixed enclosure/air curtain systems will address the capture of fugitive emissions generated during all converter operating modes.

4.7.6.3 Air Curtains and Fixed Enclosure Hoods as Means of Capturing Fugitive Emissions Generated by Converter Operations. Another method of controlling fugitive emissions from copper smelter converting operations involves the use of an air curtain system along with a secondary converter hood system. Although air curtains for the control of fugitive emissions are not currently being used in the domestic primary copper smelting industry, they are being used abroad and in other U.S. industries.⁵²

An air curtain is a suitably shaped air jet with sufficient momentum to resist the forces of fugitive gas streams working against it and to

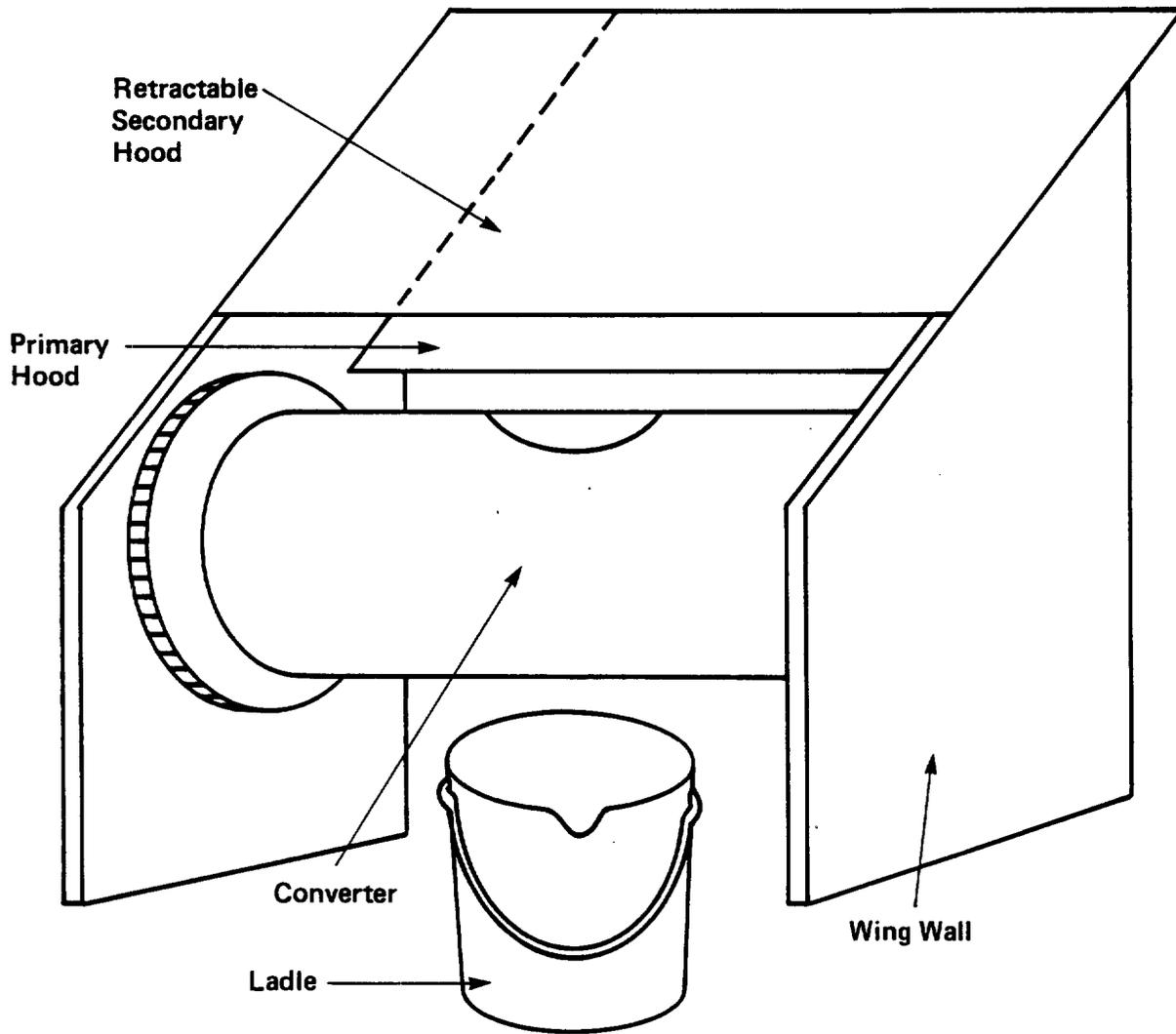


Figure 4-34. Wing-wall-type secondary hood as employed at ASARCO-Hayden.

maintain its continuity across the opening it protects. Consideration in air curtain design must also be given to secondary or entrained flows that start forming as the air curtain jet stream leaves its slot or nozzle. As the entrained flows become fully mixed with the air curtain jet stream some distance from the nozzle, the hot or cold secondary flows are carried from one side of the air curtain jet stream to the other where they are ducted for suitable discharge (see Figure 4-35). The greater the entrained flow, the greater the energy loss. To minimize energy loss, a thick, slow-moving jet stream with a large air volume is required. A basic rule in the design of air curtains is to project the thickest and lowest velocity air stream possible across the shortest dimension of the opening.

The design of air curtains is quite complex because of the curving pattern of the airflow from the air curtain jet nozzle or slot. Also, the presence of secondary flows further complicates the design. Air curtain design methods are discussed in references 56, 57, and 58.

The type of air curtain system being used at the Onahama and Naoshima primary copper smelters in Japan is shown in Figure 4-36. The capture/shielding device includes two steel plate partitions, one on each side of the converter. The air jet is blown from a slot at the top of one of the plates across the opening to provide a sheet or curtain of air that prevents fugitive emissions from escaping. The other plate is equipped with an exhaust hood. The opening allows the crane cables to move into position above the converter mouth.

A propeller fan is used to push the air through an elongated slot on one side and a backward inclined fan provides suction on the opposite side to pull in both the fugitive gases and the push air. Captured gas passes through steel duct work to a baghouse. The combined temperature of the converter fugitive gases with 100 percent of the push air entering the duct work on the pull side of the air curtain is approximately 80° C (100° F), which makes gas cooling unnecessary before gas entry into the control device.

The inlet air forming the air curtain above the converters at the Naoshima smelter has a flow rate of approximately 600 Nm³/min (21,000 scfm). The exhaust hood on the opposite side pulls in approximately

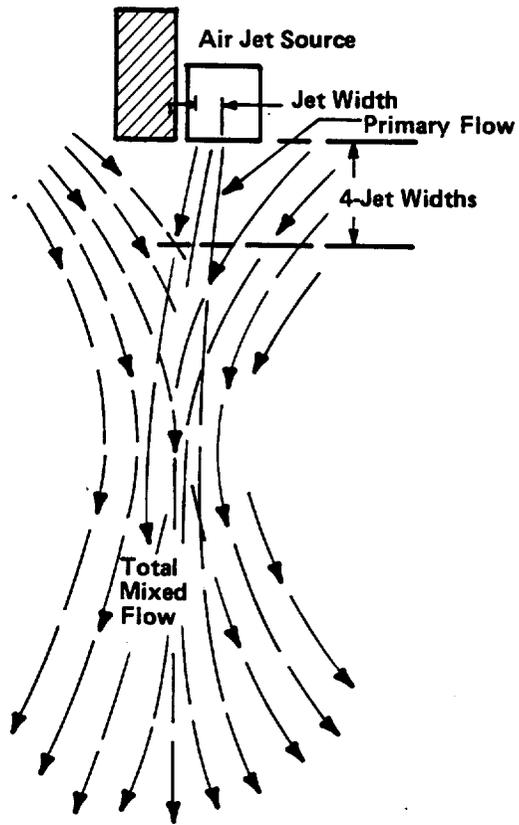


Figure 4-35. Entrained flow diagram.⁵²

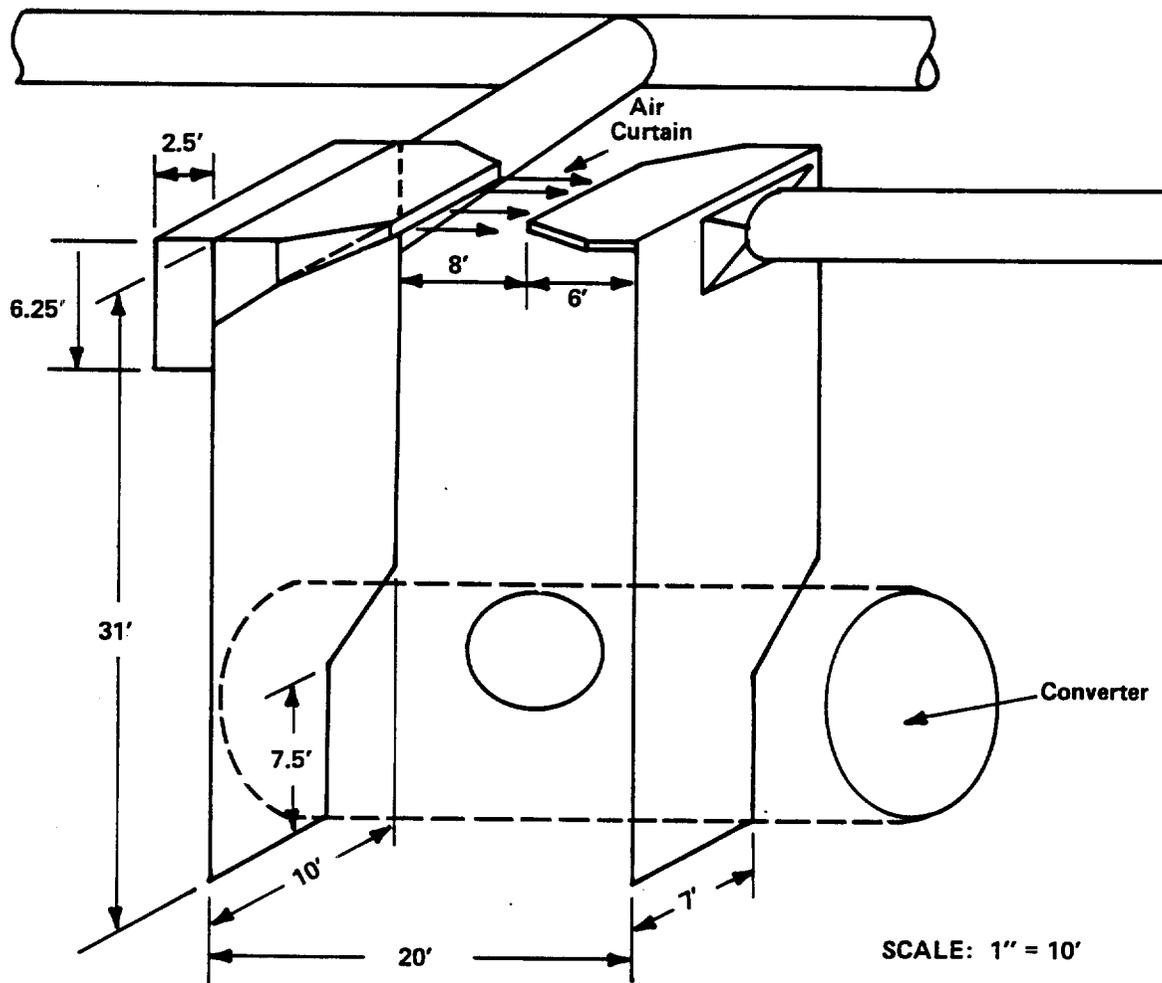


Figure 4-36. Converter air curtain/secondary hooding system as employed at the Onahama and Naoshima smelters.⁵²

1,000 Nm³/min (35,000 scfm) of gas to the main system. The capacity of the total pull system at this smelter is three times this value or 3,000 Nm³/min (105,000 scfm) to allow for the operation of three hoods at a time. According to the Naoshima authorities, the overall collection efficiency of these hoods for fugitive emissions is approximately 90 percent.⁵²

The Tamano copper smelter in Japan uses a differently designed air curtain system along with a fixed hood, which is essentially a total enclosure, for controlling fugitive emissions from each of its three converters. (Usually one converter is operated at a time.) A sketch of the air curtain system being used at the Tamano smelter is shown in Figure 4-37. The enclosure has two front doors and a movable roof that is slightly inclined toward the front. The air curtain ducts are located at the top of the enclosure level at a position to push air from one side of the converter to the other side. Ambient air is supplied by a ground fan rated at 70,000 Nm³/h (41,000 scfm).

The typical functions of the air curtain system and secondary hood system during each mode of a converter cycle at the Tamano smelter are summarized in Table 4-16 and are described in the following paragraphs.

For charging matte and other material to the converter, the secondary hood doors and the movable roof are opened and the air curtain system is turned on. When opened, the movable roof slides toward the side away from the air curtain ducts. The air curtain system is turned on only during charging of the converters when the movable roof is kept open. The movable roof is closed during all other modes of converter operation. A ladle containing charge material is brought inside the secondary hood enclosure by an overhead crane. The converter is rolled down to an inclined position. The ladle is lifted up by the crane, and the material is charged into the converter. Usually three ladles of matte and one boat of cold material are charged to the converter within a 10- to 30-minute period. Actual charging of each ladle lasts 1 to 1.5 minutes. At the completion of material charging, the ladle is brought out from the enclosure. The converter is moved to its upright position and its mouth is contained in the primary hood. The secondary hood housing doors and roof are closed.

During charging of material as well as discharging of material, two fugitive gas streams are generated. A relatively high concentration gas up

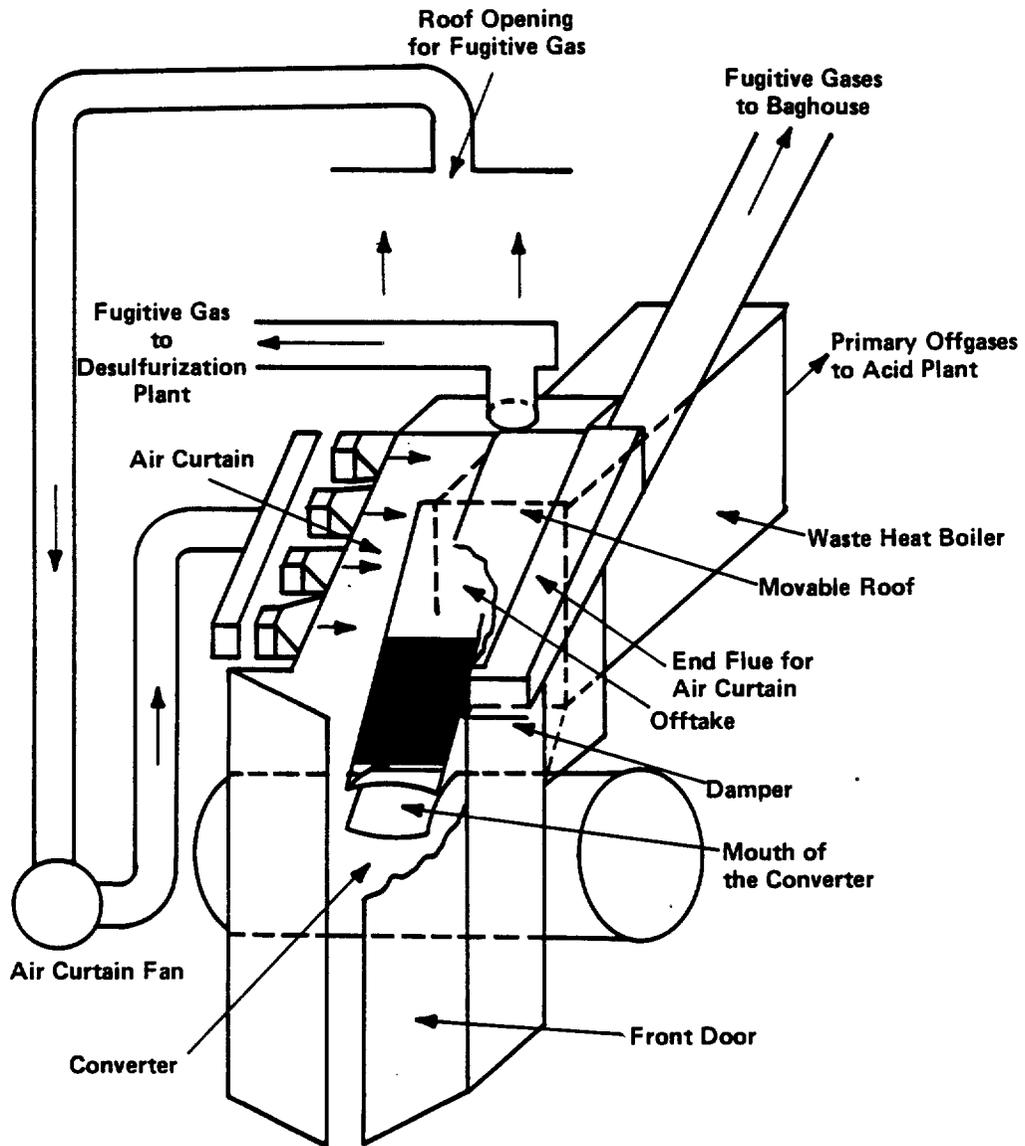


Figure 4-37. Schematic diagram of the converter housing/air curtain system at the Tamano smelter.⁵²

TABLE 4-16. FUNCTION OF AIR CURTAIN AND SECONDARY HOOD SYSTEM DURING VARIOUS MODES OF CONVERTER OPERATION AT TAMANO SMELTER⁵²

Mode of operation	Configuration of primary hood and secondary hood ^a
Material charging (matte, or cold dope)	A, C
Slag blow	B, D
Slag discharge	A, D
Copper blow	B, D
Blister discharge	A, D

^aPrimary hood position: damper closed, A; damper open, B. Secondary hood position: doors and roof open and air curtain on, C; doors and roof closed and air curtain off, D.

to 30,000 Nm³/h (18,000 scfm) in volume, generated in the vicinity of the converter mouth, is captured by the duct work located at the lower inside wall of the enclosure. The captured gas stream is continuously pulled into a lime desulfurization plant for treatment. The larger portion of fugitive gases is mixed with air generated by the air curtain system. The combined total gas flow of up to 190,000 m³/h is captured by a duct work located at the upper level of the enclosure. The captured gas is sent to a baghouse for particulate matter removal.

Any gases escaping from the air curtain system are recirculated through a building roof hood.

During the slag blow and copper blow, the converter mouth is housed under the primary duct, and the secondary housing doors and roof are closed. The primary offgases, which range between 65,000 and 75,000 Nm³/h (38,000 to 44,000 scfm) from each converter are treated along with offgases from the flash furnace smelter in a 156,000-Nm³/h (92,000-scfm) capacity acid plant for SO₂ removal. Any fugitive emissions generated from the converter due to primary hood leaks will pass to the baghouse and then to the stack.

During slag discharge at the end of each slag blow and during blister discharge at the end of copper blow, a ladle is brought into the secondary hood enclosure by the overhead crane and placed on the ground in front of converters. The secondary hood doors and roof are closed. The mouth of the converter is rolled down and the slag or blister is poured into the ladle. After the slag or blister discharge is completed, the converter mouth is moved up, the housing doors and roof are opened, and the ladle is moved out.

High SO₂ concentration gases and low SO₂ concentration gases are passed through the corresponding ducts to the lime desulfurization plant and the baghouse system, respectively.

Subjective evaluation of the air curtain and fixed enclosure system by visible observation at the Tamano smelter in Japan indicate the system to be at least 90 percent effective in controlling fugitive emissions.⁵² Tables 4-17 and 4-18 summarize visible emissions data that were obtained at the Tamano smelter during matte charging and blister pouring.

TABLE 4-17. VISIBLE EMISSION OBSERVATION DATA FOR CONVERTER
SECONDARY HOOD SYSTEM DURING MATTE CHARGING
AT THE TAMANO SMELTER⁵²

Sample run	Method 22		Method 9		
	Observation period, min	Percent of time emissions observed	Observation period, min	Average opacity for observation period, percent	Range of individual readings
1	1.5	44	1.5	5.0	0 to 25
2	1.25	56	1.25	4.0	0 to 10
3	1.75	77	1.75	3.0	0 to 10
4	--	--	1.5	0	--
Total	4.50	60	6.25	2.8	0 to 25

TABLE 4-18. VISIBLE EMISSION OBSERVATION DATA FOR BLISTER DISCHARGE AT THE TAMANO SMELTER⁵²

Sample run	Method 22		Method 9		
	Observation period, min	Percent of time emissions observed	Observation period, min	Average opacity for observation period, percent	Range of individual opacity readings
1	25 ^a	42	--	--	--
2	--	--	15.0	6.2	0 to 30
3	15 ^b	86	12.0	13.0	0 to 35
4	6 ^c	19	3.5	3.2	0 to 25
Total	15.3	49	30.5	8.5	0 to 35

^aObservations started when secondary hood doors opened 12 minutes prior to the blister discharge, during which time the converter body was hit by a vibrating ram.

^bObservations started with the blister discharge and continued for 3 minutes after completion of the blister discharge.

^cObservations started with the blister discharge and continued for 2½ minutes after completion of the blister discharge.

ASARCO's Tacoma facility is currently installing an air curtain system on one of their converters. The design volume for the system is the anticipated possible maximum, which would occur when two converters require 2,832 actual m³/min (100,000 acfm) each.⁶³ Thus, the total design volume is 5,663 actual m³/min (200,000 acfm) at 66° C (150° F). Design data for the ASARCO system are summarized in Table 4-19. ASARCO has estimated that the following overall capture efficiencies will be in evidence after the system is placed into operation:⁵⁹

- ~98 percent during blowing
- ~60 percent during roll-in and roll-out
- ~85 percent during skimming
- ~85 percent during charging
- ~90 percent during holding.

The gases that are captured by the air curtain system will be subjected to particulate removal before being passed to the atmosphere.

Based upon data supplied to EPA by ASARCO, EPA has tentatively concluded that the ASARCO air curtain system will be able to achieve the capture efficiencies outlined above. EPA does feel, however, that the addition of doors and a retractable roof may merit consideration as a means of enhancing capture efficiency.

4.7.7 Summary of Visible Emissions Data for Fugitive Emissions Sources.

4.7.7.1 Local Ventilation Techniques Applied to Calcine Discharge, Matte Tapping, and Slag Skimming. The performance of local ventilation techniques used at the ASARCO-Tacoma Smelter for the control of fugitive emissions from calcine discharge, matte tapping, and slag tapping operations was evaluated.⁵² These techniques were previously described in Sections 4.7.4 and 4.7.5. Visual observations were made using either EPA Method 22 or EPA Method 9, depending on whether the emissions observed were intermittent or continuous. Method 22 is used to determine the occurrence of visible emissions and Method 9 is used to determine the opacity of emissions. A summary of the visible emissions data obtained is presented in Table 4-20.

Thirteen calcine transfer operations, averaging about 2 minutes in duration each, were observed. The visual observations were made using EPA Method 22 at the opening of the tunnel-like structure used to house the

TABLE 4-19. SUMMARY OF DESIGN DATA FOR THE ASARCO-TACOMA CONVERTER SECONDARY HOODING/AIR CURTAIN SYSTEM⁶³

Mode of operation	Air curtain push rate, actual m ³ /min	Main offtake evacuation rate, actual m ³ /min
Matte charging	510 (18,000 acfm)	2,322 (82,000 acfm)
Blowing	- ^a	1,700 (60,000 acfm)
Slag skimming	510 (18,000 acfm)	2,322 (82,000 acfm)
Holding	510 (18,000 acfm)	850 (30,000 acfm)
Worst conditions ^b	1,020 (36,000 acfm)	4,644 (164,000 acfm)

^aAir curtain will not be used during the blowing mode.

^bWorst conditions would consist of either (1) two converters being charged simultaneously or (2) one converter being charged while another was being skimmed.

TABLE 4-20. SUMMARY OF VISIBLE EMISSION OBSERVATION DATA⁵² FOR CAPTURE SYSTEMS ON FUGITIVE EMISSION SOURCES AT ASARCO-TACOMA^a

Operation	EPA Method 22				EPA Method 9			
	Number of readings taken	Average observation time, min:sec	Average percent time emissions observed on all readings	Range of percent time emissions observed	Number of readings taken	Average observation time, min:sec	Average opacity, percent	Range of opacity observed
Calcine transfer system	13	1:55	0	0				
Matte tapping								
At matte tap port and launder	16	5:28	0.2	0-3				
At matte discharge into ladle	15	5:21	0	0				
Slag skimming								
At slag skim bay and launder	8	13:38	5.3	0-15	2	13:45	6	0-30
At slag discharge into pots	11	15:27	88	72-99	7	14:32	12	0-50

^aVisible emission observations made June 24 through 26, 1980.

calcine hoppers and larry cars during the calcine transfer (discharge) operations. As the data indicate, no visible emissions were observed at any time.

Visible emission observations during furnace matte tapping were also made using EPA Method 22. Simultaneous but separate observations were made both at the furnace tap port and at the launder-to-ladle transfer point. Sixteen taps, averaging approximately 5.5 minutes in duration, were observed. Out of the 16 observations made at the amtte tap port, no visible emissions were observed 100 percent of the time on 14, with only slight emissions ranging from 1 to 3 percent of the time for the remaining 2. No visible emissions were observed 100 percent of the time from the launder or launder-to-matte-ladle transfer point during all 16 observations.

Slag skimming emissions were observed using both EPA Methods 22 and 9. As with matte tapping, separate observations were made at the furnace skim bay location and at the slag-launder-to-slag-pot transfer point. Results obtained using EPA Method 22 for 8 observations at the slag tap port showed that visible emissions were observed about 5 percent of the time on the average, with the highest single observation showing the presence of visible emissions 15 percent of the time. Visual observations made at the slag-launder-to-pot transfer point indicated very poor performance, with visible emissions being observed 72 to 99 percent of the time over 11 slag taps. Additional data obtained using EPA Method 9 showed significant emissions, with opacities as high as 50 percent. Conversations with smelter personnel revealed that the ventilation hood at the slag launder discharge point has been damaged when hit by a truck. Although an inspection of the ventilation hood and ancillary duct work showed no apparent damage, ventilation at this location was concluded to be inadequate to handle the volume of emissions and fume generated.

4.7.7.2 Fugitive Emission Controls for the Converter Fixed Enclosure/Air Curtain Hood Capture System at the Tamano Smelter. All three converters at the Tamano smelter in Japan are equipped with a fixed enclosure and air curtain system for control of fugitive emissions generated during various modes of converter operation. The enclosure doors and roof are kept open and the air curtain system is turned on during the matte charging. During

all other modes of the converter operation the doors and roof are kept closed and the air curtain system is turned off. A detailed description of the system is presented in Section 4.7.6.3.

Visible emission observations were made for the fixed enclosure/air curtain system operated on the No. 3 converter during day shifts on March 12 and March 13, 1980. The converter is a conventional Pierce-Smith design, measuring about 9 meters in length and 4 meters in diameter. Observations were made using EPA Method 22 and EPA Method 9, depending on whether the emissions observed were intermittent or continuous, for the different modes of converter operation comprising a converter cycle. Discussions of the results obtained during each mode of converter operation are presented in the following sections.

4.7.7.2.1 Visible emissions from matte charging. Usually three ladles of matte are brought to the converter and charged in a 10- to 30-minute period. Actual matte charging from each ladle lasts for 1 to 1.5 minutes. The fixed enclosure doors and roof are opened, the air curtain system is turned on, and the ladle of matte is brought into the secondary hood by an overhead crane. The converter is rolled down to an inclined position, the matte ladle is lifted up by the crane, and matte is charged into the converter. At the completion of matte charge, the ladle is moved out of the enclosure and, if needed, another ladle of matte is brought in. After the matte additions are completed, the converter is rotated into the primary converter hood, the roof and doors are closed, and slag blowing commences.

Three separate matte charges were observed using both EPA Methods 9 and 22 simultaneously, and one matte charge was observed using EPA Method 9 only. Visual observations for each matte charge observed were made only during the period when the matte was actually flowing into the converter. Results of the visual observations obtained are summarized in Table 4-15.⁵²

As shown in Table 4-15, visible emissions were observed for three individual matte charges. The observations ranged from 44 to 77 percent of the time (EPA Method 22). Although somewhat continuous, the opacity results indicate that these emissions were generally slight, typically ranging from 0 to 10 percent opacity, with the highest average opacity recorded for a

single matte charge being 5 percent. When present, the emissions appeared as small puffs that penetrated the air curtain stream.

4.7.7.2.2 Visible emissions during slag blowing and copper blowing.

During slag blowing and copper blowing, the converter mouth is contained in the primary duct, and offgases are directed to the acid plant. The converter secondary hood doors and roof are closed, and the air curtain system is turned off. Fugitive emissions generated during blowing as a result of primary hood leaks are captured inside the converter housing and are vented to a baghouse for collection. The slag blow, which is divided into three segments, lasts for about 150 minutes per converter cycle and the copper blow for about 200 minutes per cycle.

Visible emissions observations were made using EPA Method 9 for the converter hood system for 30 minutes during the slag blow and for 27 minutes during the copper blow. No visible emissions (zero percent opacity) were observed at any time.

4.7.7.2.3 Visible emissions during converter slag discharge.

At the end of each of the three slag blow phases, slag is skimmed into a ladle and transported to a sand bed area for cooling. Because of the quantities involved, slag is discharged from the converter two times after the first slag blow and once after the second and third. Each slag skim lasts for about 10 minutes. During each skim, an empty ladle is brought into the enclosure by an overhead crane and placed on the ground in front of the converter. The crane is moved out, and the enclosure doors and roof are closed. The converter is rolled down and slag is poured into the ladle. After the slag skimming is completed, the converter is rotated upward slightly, the enclosure doors are opened, and the slag ladle is moved out.

Only two skims were observed. The first, which lasted 11 minutes, was observed using EPA Methods 22 and 9. The second slag skim, lasting 9 minutes, was observed using EPA Method 22 only. Each observation period began as the converter started rolling down to pour the slag into the ladle and lasted until the pouring was completed and the converter started rolling up. During the first slag skim observed, no visible emissions were observed at any time. In contrast, during the second slag skim, visible emissions were observed 100 percent of the time. The majority of time, however,

these emissions were slight, ranging from 5 to 10 percent opacity and consisting of small puffs that escaped from the enclosure through a narrow opening between the front doors and the enclosure roof.⁵²

4.7.7.2.4 Visible emissions during converter blister discharge. At the end of copper blow, blister copper is discharged into a ladle and transported to a refining furnace. Usually four ladles of blister are filled per converter cycle. Each of the first three blister pours lasts about 12 to 14 minutes, with one final blister pour lasting about 4 minutes. The time between each blister pour is about 8 to 15 minutes.

At the end of a copper blow, the secondary hood doors and roof are opened. An empty ladle is brought into the secondary hood by the overhead crane and placed in front of the converter. The crane is moved out, and the secondary hood doors and roof are closed. The converter is rolled out, and blister is poured into the ladle. After the blister pour is completed, the converter is rolled in slightly, the hood doors are opened, the blister ladle is taken to the refining furnace by the crane, and the hood doors and roof are closed.

Four blister discharges were observed. Both EPA Methods 22 and 9 were used. A summary of the results obtained are presented in Table 4-16.⁵² Although the observations periods used in obtaining the EPA Method 22 data were inconsistent (i.e., different start and end times), the results nonetheless indicate that visible emissions during blister discharge were generally continuous. The EPA Method 9 data, which were obtained only during periods when the blister copper was actually being poured, show that the visible emissions observed were somewhat more substantial than those observed during either matte charging or slag skimming. As shown in Table 4-16, the highest average opacity recorded for a single blister pour was 13 percent, with individual opacity readings ranging from 0 to 35 percent. Again, as with slag skimming, the emissions observed generally appeared above the narrow opening between the front doors of the enclosure and the enclosure roof.

4.7.8 Removal of Particulate Matter From Fugitive Gases

Currently, the building evacuation baghouse at ASARCO's El Paso facility is the only control device for which emission data exist that controls a

gas stream composed only of fugitive gases. Gases from the converter building evacuation system are routed to a fabric filter for particulate matter removal. The baghouse that receives the 16,800 Nm³/min (600,000 scfm) of building evacuation gases contains 4,800 bags, each 15 cm (6 in) in diameter by 9 m (30 ft) long. It is sized with a nominal air-to-cloth ratio of 3 to 1 (cfm/ft²). The baghouse consists of 12 compartments; however, only 10 are used at any given time. The total net cloth area is approximately 19,732 m² (212,400 ft²). The baghouse was designed to treat 15,280 m³/min (540,000 acfm) at 54° C (130° F). Mechanical shaking is used as the cleaning mechanism.

Emissions testing has been performed by EPA to determine the capture efficiency of this baghouse.⁶² The results of these tests are summarized in Table 4-21. As indicated, the test results showed that the baghouse had an average collection efficiency of 88 percent based upon the grain loadings that were in evidence during the three test runs that were made. Inlet and outlet grain loadings were 442.78 µg/m³ (0.20 g/ft³) and 198.83 µg/m³ (0.084 g/ft³), respectively. Because of the amount of dilution that occurs as the fugitive gases are being collected, no gas cooling is necessary prior to gas entry into the baghouse.

Due to the relatively small volume of SO₂ contained in fugitive gases, the removal of SO₂ from fugitive gases is not considered cost-effective by EPA, and, consequently, is not considered in this document.

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TABLE 4-21. SUMMARY OF EMISSIONS TESTING PERFORMED ON THE CONVERTER BUILDING EVACUATION BAGHOUSE AT ASARCO-EL PASO⁶²

Sampling location	Average grain loading, mg/m ³	Average particulate mass rate, kg/h	Average particulate matte collection efficiency, % ^a
Baghouse inlet	442.78	358.19	88
Baghouse outlet	198.83	167.50	

^aCalculated based upon the average inlet and outlet grain loadings.

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5. MODIFICATION AND RECONSTRUCTION

Under the authority of Section 111 of the Clean Air Act of 1970, the new source performance standards (NSPS) are applicable to newly constructed facilities and to existing facilities that have undergone modification or reconstruction. A facility to which the standards apply is termed an affected facility. An existing facility is one of the type for which standards have been promulgated and for which the construction or modification was begun prior to the proposal date of the applicable standards.

The criteria used to identify modifications and reconstructions are summarized in the Code of Federal Regulations (40 CFR 60), U.S. Environmental Protection Agency (EPA) Standards of Performance for New Stationary Sources, under Subpart A, "General Provisions," Sections 60.14 and 60.15.

5.1 SUMMARY OF 40 CFR 60 PROVISIONS FOR MODIFICATION AND RECONSTRUCTION

5.1.1 Modification

A modification is defined to be, with certain exceptions, "any physical or operational change to an existing facility which results in an increase in the emission rate to the atmosphere of any pollutants to which a standard applies." However, a facility that undergoes such a change is considered to be modified only if the cost of the change as a percentage of the original facility cost is greater than the annual guideline repair allowance percentage specified in the latest edition of Internal Revenue Service Publication 534. Merely increasing production to a higher level when adequate capacity exists is not considered a modification. Other items that are not considered as modifications include (1) maintenance, repair, or replacement that is judged by the Administrator to be routine; (2) an increase in the

hours of operation; (3) use of an alternative fuel or raw material if, prior to the standard, the existing facility was designed to accommodate that alternative use; and (4) the addition or use of any system or control device whose primary function is the reduction of air pollutants, except when an emission control system is removed or replaced by a system considered to be less efficient.

5.1.2 Reconstruction

While a modification refers to relatively minor changes to an existing facility, major changes are deemed reconstructions. Upon reconstruction, an existing facility becomes a new source, irrespective of any change in emission rate. Generally, a reconstruction occurs when components of an existing facility are replaced to such an extent that the fixed capital cost of the new components exceeds 50 percent of the fixed capital cost that would be required to construct a comparable entirely new facility, and it is economically and technically feasible to comply with the applicable standards.

The Administrator provides the final judgment that indicates whether a replacement constitutes a reconstruction and if it is technologically and economically feasible to comply with the applicable standards. The Administrator's final determination will be based upon (1) a comparison of the fixed capital costs of the replacement components with the costs of a comparable new source; (2) the estimated life of the source after the replacements compared to the life of a comparable entirely new source; (3) the extent to which the components being replaced cause or contribute to the emissions from the source; and (4) any economic or technical limitations on compliance with applicable performance standards which are inherent in the proposed replacements.

The purpose of the reconstruction provision is to ensure that an owner or operator does not perpetuate an existing source by replacing all but vestigial components, support structures, frames, and housing rather than totally replacing the source in order to avoid being subject to applicable new source standards.

5.2 APPLICABILITY TO PRIMARY COPPER SMELTERS

5.2.1 General

Most of the changes to existing primary copper smelting facilities that could be considered as possible modifications relate to increasing production capacity. These changes are discussed under modifications.

Changes that would qualify as reconstructions rather than modifications are expected to be relatively few. Major activities that might be considered include rebuilding/relining of affected facilities such as roasters, smelting furnaces, and converters. Rebuilding is an inherent consequence of extracting copper by existing methods and is practiced on a routine, though relatively infrequent, basis. Major reverberatory furnace rebuilds, for example, have been reported as occurring every 5 to 8 years¹ and every 20 years.² Converter relining, either partial or complete, typically occurs one to three times per year.³ Other activities that might be considered reconstructions include physical expansions of existing process equipment. These changes are discussed in succeeding paragraphs.

5.2.2 Modifications

Various options that have been employed by the industry to increase or expand production capacity are discussed here and are described in greater detail in Section 3.4. Most of these options cause an increase in particulate and SO₂ emissions proportional to the increased production. A notable exception is the conversion from green- to calcine-charged furnace operation. In this case SO₂ emissions will not necessarily increase because some sulfur removal occurs in the newly installed roaster.

5.2.2.1 Multihearth Roasters. As discussed in Section 3.4.1, increasing the shaft rotation speed has been used as a means of increasing the throughput rate of multihearth roasters by over 100 percent.⁴ However, most domestic smelters use the shaft rotation speed as a means of altering residence time in order to control the degree of sulfur elimination.⁵ Because these units are designed for such operation, increasing shaft rotation speed to gain increased throughput would not be considered a modification.

Physical expansion of multihearth roasters is not considered feasible because of the geometry of these units.

5.2.2.2 Fluid-Bed Roasters. Fluid-bed roasters can potentially expand capacity by increasing blower capacity or by oxygen enrichment of the fluidizing air. Increasing the blower capacity may be unfeasible because of constraints associated with existing calcine recovery systems (see Section 3.4.2). As a result, this potential modification is considered unlikely. Oxygen enrichment of the fluidizing air could possibly be used to increase roaster throughput by 20 to 25 percent. However, some melting of the feed may result, which would lead to operational problems (see Section 3.4.2). Therefore, this expansion option is also considered unlikely. Furthermore, oxygen enrichment is not foreseen as a modification because oxygen can be introduced into the blowing air with essentially no hardware changes. Hence, costs should be minimal. The cost of an oxygen plant, if constructed, would not be included in the determination because it is not a part of the affected facility.

5.2.2.3 Reverberatory Furnaces. Four different methods of increasing reverberatory furnace production capacity are described in Section 3.4.3. These methods are (1) conversion from green to calcine charging, (2) physical expansion of the furnace, (3) elimination of converter slag return, and (4) oxygen enrichment.

5.2.2.3.1 Conversion from green to calcine charging. Reverberatory furnace capacity has been increased by up to 50 percent with the conversion from green- to calcine-charged operation.⁷ Alterations to the furnace would likely include the installation of water-cooled panels around the furnace perimeter and changes to the feed system. Emissions of SO₂ from the altered furnace would not necessarily increase, depending upon the extent of sulfur removal in the new roaster. Particulate emissions from the expanded furnace should increase at least in proportion to the increase in throughput achieved.

5.2.2.3.2 Physical expansion of the furnace. Furnace capacity has been increased by 20 percent in the past by physical expansion.⁸ Emissions of SO₂ and particulates should increase in proportion to the

expansion obtained. Costs associated with physical expansion may be sufficiently great to qualify it as a reconstruction. Other problems, such as a substantial down-time requirement and possible physical space limitations, may preclude the use of this option at some smelters. Hence, physical expansion of reverberatory furnaces is considered an unlikely expansion option.

5.2.2.3.3 Elimination of converter slag return. Processing converter slag in separate facilities (e.g., flotation plants) rather than returning it to the reverberatory furnace has been reported to increase furnace capacity by up to 25 percent.⁹ Emissions of SO₂ and particulates should increase in proportion to the increase in capacity achieved. Changes to the furnace proper, if any, would be expected to be minimal. Hence, this expansion option is not foreseen as a modification.

5.2.2.3.4 Oxygen enrichment. Reverberatory furnace expansion options involving the use of oxygen are as follows: (1) the enrichment with oxygen of the combustion air fed to existing burners, (2) the injection of oxygen or oxygen-enriched air into the furnace through lances positioned beneath the existing burners, (3) the addition of roof-mounted oxy-fuel burners, (4) oxygen lancing through the roof, or (5) the addition of roof-mounted oxy-sprinkle burners. These options are discussed in detail in Section 3.4.3.4.2.

The technique of oxygen enrichment of the combustion air has produced increases of up to 56 percent in furnace production capacity.¹⁰ Particulate and SO₂ emissions should increase approximately in proportion to the increase in production. Because of its simplicity, this scheme should require essentially no hardware changes to the furnace. Hence, there would be minimal costs. As a result, this expansion option would not likely be considered a modification. It should be noted that, if an oxygen plant were required, its construction cost would not be included for the determination because it is not part of the affected facility. This statement is also true for the other oxygen enrichment schemes described below.

The injection of oxygen into the furnace through separate ports beneath the existing burners--undershooting--has produced a 36-percent

increase in throughput with a calcine-charged furnace¹¹ and a 45-percent increase in throughput for a green-charged operation.¹⁰ Particulate and SO₂ emissions should increase approximately in proportion to the increase in furnace production.

Large increases in capacity have been reported with oxy-fuel burners installed in the furnace roof. In the case of green-charged furnaces, production increases of more than 100 percent have been reported,¹² and a 45-percent increase in furnace capacity has been reported for a calcine-charged furnace.¹³ The costs associated with this scheme are expected to be those associated with the burners themselves. Particulate and SO₂ emissions should increase approximately in proportion to increases in production.

Production increases of 20 percent have been reported with the use of roof-mounted oxygen lances.¹² The costs inherent with this scheme would be those associated with the lances themselves. Particulate and SO₂ emissions should increase approximately in proportion to increases in production.

The oxy-sprinkle process is an option that could be adopted by the industry, although it is still in the development stage. Testing of oxy-sprinkle burners on a reverberatory furnace is currently being performed, and production increases of 100 percent have been reported.¹⁴ This scheme differs from the other techniques in that it is based on the principle of flash furnace operation. Because some sulfur in the feed is combusted, SO₂ emissions would be expected to increase somewhat more than linearly with the increase in production achieved. Particulate emissions would be expected to increase at least in proportion to the increase in capacity. Costs associated with this scheme would include, in addition to burner costs, the costs of additional feed handling equipment.

5.2.2.4 Electric Furnaces. Electric furnaces can increase capacity by converting from green to calcine charging and by eliminating converter slag return. Other conceivable expansion options include installing a larger transformer and physically expanding the furnace. Additional discussion on each of these options is provided in Section 3.4.4.

As in the case of reverberatory furnaces, green-charged electric furnaces may also expand capacity through the conversion to calcine charging, because less time is required to smelt hot, roasted calcine than dried concentrates. Production increases of 40 percent are believed to be achievable. Costs associated with making the conversion on electric furnaces are believed to be lower than those for reverberatory furnaces because side-wall cooling and extensive feed system changes would probably not be required. SO₂ emissions from the expanded furnace would not necessarily increase, depending upon the extent of sulfur removal in the roaster. Particulate emissions should increase in proportion to the increase in capacity.

Based on experience achieved with reverberatory furnaces, production increases of 25 percent are believed to be achievable when converter slag is processed in other facilities rather than returned to the electric furnace. Emissions of SO₂ and particulates should increase in proportion to the increased capacity achieved. Changes required at the furnace proper appear to be minimal; hence, this expansion option is not foreseen as a modification.

Electric furnaces can conceivably increase capacity by installing a larger transformer. Emissions of SO₂ and particulates should increase in proportion to the increase in capacity achieved. However, this potential modification would cause increased refractory wear¹⁵ and is considered unlikely.

Physical expansion of an electric furnace is a conceivable option but would require extensive changes to the furnace proper. In addition to enlarging the furnace, a larger transformer and electrodes would be required.¹⁵ Costs may be sufficiently great to qualify as a reconstruction. Emissions of SO₂ and particulates should increase in proportion to the increase in capacity. Because substantial changes would be required, this expansion option is considered unlikely.

5.2.2.5 Outokumpu Flash Furnaces. As discussed in Section 3.4.5, the primary expansion mode for Outokumpu flash furnaces is via oxygen enrichment of the combustion air. Increases of 60 to 70 percent have been reported.¹⁶ Emissions of SO₂ should increase in proportion

to the increased capacity achieved. Particulate emissions should increase somewhat less than proportionately with the expansion because of the lower offgas volume per unit of charge afforded by oxygen enrichment. Oxygen enrichment is not foreseen to be a modification on Outokumpu flash furnaces because oxygen can be introduced through the existing burners with essentially no hardware changes. Hence, costs should be minimal. As discussed previously, oxygen plant costs would not be included in the determination.

Physical expansion is not considered to be a feasible expansion option because of furnace geometry.¹⁷ The elimination of converter slag return is not an available option for increasing capacity because converter slag is processed in other facilities by design.

5.2.2.6. Noranda Reactors. As discussed in Section 3.4.6, the primary expansion mode for Noranda reactors is via oxygen enrichment of the blowing air.¹⁸ Emissions of SO₂ and particulates should increase approximately in proportion with the increase in capacity. Oxygen enrichment is not foreseen as a modification, however, because oxygen can be introduced into the blowing air with essentially no hardware changes.

Other conceivable expansion modes for Noranda reactors include increasing the blowing rate via the installation of a larger blower, and physically expanding the vessel coupled with increasing the number of tuyeres. Emissions of SO₂ and particulates should increase approximately in proportion to increases in capacity achieved using either of these schemes. However, because of offgas handling constraints (with respect to physical expansion only), physical space limitations, and downtime requirements, both of these schemes are considered unlikely.

5.2.2.7 Converters. Converter capacity can be increased by physical changes to the vessel. Other conceivable expansion modes include increasing blower capacity and oxygen enrichment. All of these options are discussed in further detail in Section 3.4.7.

Increases in converter capacity by approximately 13 percent have been attained by physical expansion coupled with increasing the number

of tuyeres.¹⁹ Emissions of SO₂ and particulates should increase in proportion to the increase in capacity achieved.

Converter throughput can potentially be increased by increasing the size of the blower. Emissions of SO₂ and particulates should increase in proportion to the increase in blowing rate. However, excessive ejection of molten material from the vessel may occur, and this expansion option is considered unlikely.

Oxygen enrichment of converter blowing air may increase converter capacity, although any increase may be offset by interruptions in the cycle arising from the need of additional "cold dope" materials. Oxygen enrichment is not foreseen to be a modification because oxygen can be introduced into the blowing air with essentially no hardware changes.

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6. MODEL PLANTS AND ALTERNATE CONTROL TECHNOLOGIES

6.1 INTRODUCTION

This study focuses on three principal issues:

- The possible deletion of the existing exemption of new or modified reverberatory furnaces from the new source performance standard (NSPS) when the smelter processes a high impurity charge.
- The possible establishment of emission standards for fugitive emission sources at primary copper smelters.
- The effect of the NSPS on future capacity additions or expansions at existing smelters.

In considering the deletion of the existing exemption, candidate demonstrated technologies for the control of weak SO₂ process gases from reverberatory furnaces will be evaluated for their environmental, cost, economic, and energy effects. A model plant representative of a new "greenfield" smelter capable of processing high impurity materials will be used for the purpose of analysis. Baseline conditions will be the current NSPS. The candidate technologies and the model plant are discussed in Section 6.2.

Candidate demonstrated technologies for the control of fugitive emissions from selected sources will be analyzed for their environmental, cost, economic, and energy effects on new greenfield smelters and modified or reconstructed existing facilities. Baseline conditions for process facilities will be the current NSPS, while baseline conditions for fugitive sources will be those identified in Chapter 3. Fugitive emission sources selected for control are described in Section 6.3, along with candidate technologies and model plants.

Expansion options available for each existing smelting configuration will be identified and alternative control technologies capable

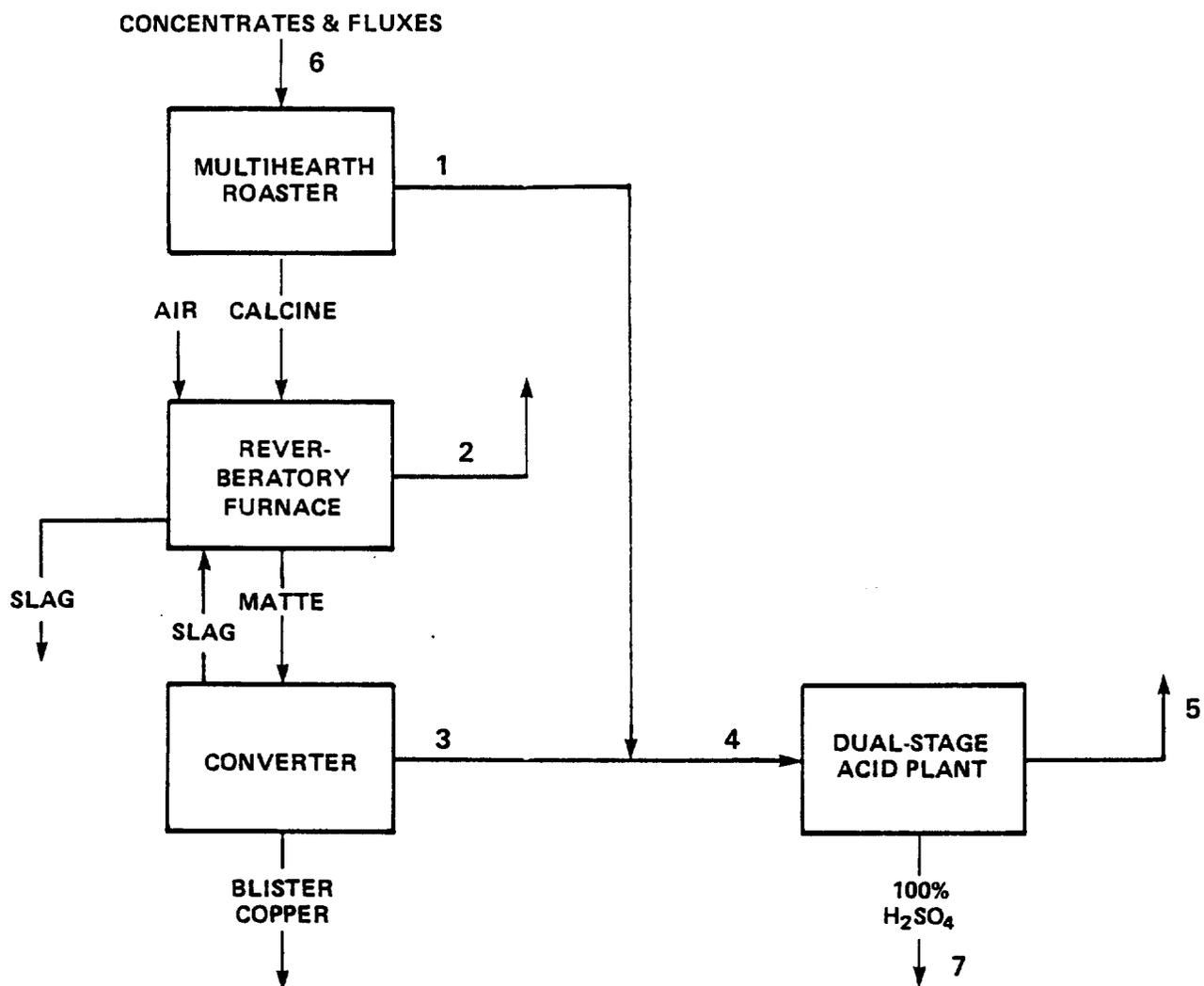
of reducing emissions from expanded facilities to preexpansion levels applied. Cumulative costs for the expansion, including the cost associated with the physical or operational process change(s) resulting in the capacity addition and the cost of added control to achieve preexpansion emission levels, will be estimated and a determination made in this study on whether the total cost for a particular expansion scenario is prohibitive. Model plants representative of existing U.S. smelters will be developed, sized identically so that comparisons between expansion scenarios can be made on a uniform basis. Baseline conditions for these models will reflect existing control levels. Expansion options and alternative control technologies are discussed in Section 6.4, along with the model plants selected as representative of existing smelters.

6.2 REVERBERATORY FURNACE EXEMPTION

Under the existing NSPS,¹ new, modified, or reconstructed reverberatory smelting furnaces are exempt from SO₂ control when the total smelter charge contains more than 0.2 weight percent arsenic, 0.1 weight percent antimony, 4.5 weight percent lead, or 5.5 weight percent zinc. Smelter charges containing higher percentages of these four impurities are high impurity (HI) charges, and they may be processed in reverberatory furnaces without controlling the emitted SO₂ or particulates. When this standard was promulgated, a commitment was made to examine further the use of oxygen enrichment and the blending of gases from reverberatory furnaces with those from multihearth roasters and converters as a means of controlling SO₂ emissions from reverberatory smelting furnaces.

An additional issue requiring examination is the need for particulate control on reverberatory furnaces in the event that the SO₂ control exemption for smelters which process HI feeds continues.

The model smelter representative of a new "greenfield" smelter capable of processing HI materials is shown in Figure 6-1. This model is rated at a capacity of 1,500 tons/day of feed material, equivalent to 380 tons/day of blister copper.



	scfm	Percent SO ₂	Percent O ₂	Tons/day
1	19,800	4.5	16.5	
2	93,900	1.3	10.9	
3	50,000	7.8	13.2	
4	69,880	6.9	14.1	
5	65,100	0.065	—	
6				1,500
7				933

Figure 6-1. Model plant for new "greenfield" smelter processing high-impurity materials.

The feed composition to the model plant is shown in Table 6-1. Components of the feed are based on an analysis of the average feed reported by ASARCO for its Tacoma smelter during March 1979.³ Also shown are sulfur eliminations projected for roasting, smelting, and converting the feed. These are based upon a matte grade of 43, a value selected to represent about the mid-range of the 40 to 45 reported by ASARCO for its Tacoma smelter.³

This model conservatively sets the roaster exit gas SO₂ concentration at 4.5 volume percent, which is slightly below the 5.0-percent level indicated in Chapter 3 as achievable for new roasters (see Section 3.2.1.2). The reverberatory furnace gas concentration, 1.3 percent, is based on operation of the furnace to maintain an uptake oxygen concentration of 1 percent and subsequent dilution of the gases at the waste heat boiler and at the electrostatic precipitator.³ This concentration is conservative when compared to the 1.6 percent SO₂ from the waste heat boiler achieved at ASARCO-Tacoma. The ASARCO value derives from a high level of pyrite sulfur in the calcines fed to the furnace, which may not always be available. Roaster and furnace gases have been treated as steady flows at average SO₂ concentrations.

Converter exit gases after gas cleaning, as shown in Figure 6-1, are assigned an average concentration of 7.8 percent SO₂ and an average flow rate of 50,000 scfm based on the removal of 250.5 tons of sulfur per day in the converter and 130 percent dilution with air (through the primary hood and gas cleaning system) before the offgases reach the SO₂ control device.

The SO₂ concentration in the offgases varies during the converter cycle. Normal converter operations consist of a series of intermittent slag blows, each following a matte charge, and a final finishing blow. During an average converter cycle of 10 to 11 hours, slag blowing occurs about 6 hours and finishing blowing about 3 hours. This characteristic cyclic operation results in periods during which no offgas flows occur from an individual converter. Scheduling of multiple converters, by which downtimes of individual converters are

TABLE 6-1. MODEL PLANT--REPRESENTATIVE FEED AND SULFUR
ELIMINATION FOR GREENFIELD HI SMELTER

<u>Component</u>	<u>Amount contained in raw feed, t/d</u>
Copper	387
Iron	259.5
Sulfur	387
Arsenic	47.7
Antimony	13.1
Lead	1.05
Zinc	15.2
<u>Processing step</u>	<u>Sulfur eliminated, t/d</u>
Roasting	57.3 (14.8%)
Smelting	79.2 (20.5%)
Converting	250.5 (64.7%)

staggered, can be used to minimize fluctuations in the aggregate flow and SO₂ concentration of offgases, thereby facilitating operation of the SO₂ control system.

A computerized simulation of converter scheduling at the Ilo Smelter⁵ involving three converters resulted in a converter offgas profile with aggregate converter offgas flows that varied from 47 percent to 142 percent of the average flow. The SO₂ concentrations varied from 89 percent to 147 percent of the average SO₂ concentrations. Using this profile, six sets of converter offgas parameters were developed and applied to the model smelter shown in Figure 6-1. Table 6-2 shows these six sets of converter offgas parameters and the corresponding cumulative hours per day for which they are applicable to the model greenfield smelter.

The average flows shown in Figure 6-1 are used for material balance purposes. The varying flows shown in Table 6-2 are used for acid plant operation and costing.

The model smelter has four converters--three in operation plus one spare. In considering converter scheduling, no specific allowance was made for upsets such as power failure, equipment failure, or elective downtime. These factors are determined largely by the maintenance practices and equipment redundancies at any plant. Acid plants for this model are equipped with burners to heat the gases at startup and during operation if necessary. This is in accordance with current practice.

The model plant controls the SO₂ from roasters and converters using a double contact/double absorption (DC/DA) acid plant, consistent with the existing NSPS, which is the baseline for new "greenfield" smelters. As indicated in Figure 6-1, the acid plant yields 936 tons/day of sulfuric acid.

Candidate SO₂ control technologies for control of the weak SO₂ exit gas from the reverberatory furnace are as follows:

1. Blending the furnace gas with the roaster and converter gases and processing the blended gases in a DC/DA acid plant designed for 3.5 percent SO₂, with supplementary fuel if needed.

TABLE 6-2. MODEL PLANT--GREENFIELD HI SMELTER REPRESENTATIVE
CONVERTER EXIT GASES

Cumulative hours	Total gas flow from converters (scfm)	Vol. % SO ₂	Vol. % O ₂
4.8	70,100	6.94	14.8
8.0	46,500	6.94	14.8
4.0	23,500	6.94	14.0
0.5	24,500	11.5	8.9
4.0	48,000	9.9	10.4
2.7	71,100	9.4	11.0

2. Partial blending of the furnace gases with the roaster and converter gases and processing in a DC/DA acid plant designed to operate autothermally at 3.5 percent SO_2 .
3. Oxygen enrichment with Wagstaff gun charging of calcine, blending the furnace gas with the roaster and converter gas, and treatment in a DC/DA acid plant designed for 3.5 percent SO_2 .
4. Use of oxy-fuel burners with sidewall charge or Wagstaff gun charging of calcine with water cooled furnace sidewalls, blending the furnace gas with the roaster and converter gas, and treatment in a DC/DA acid plant designed for 4.5 percent SO_2 .
5. Treatment of the reverberatory furnace exit gases using the lime/limestone process (see Section 4.3.2) or the regenerative Cominco Ammonia process (see Section 4.3.3), or the MAGOX Process (see Section 4.3.4), followed by a DC/DA acid plant designed for 4.5 percent SO_2 .

Table 6-3 shows the Model Plant process parameters estimated for SO_2 Control Alternatives 1 through 4. Roaster and furnace gases are blended at the steady rates shown for each alternative. Converter gases are blended according to the six sets of conditions given in Table 6-2. For example, the flow rate of 182,400 scfm to the acid plant shown for the 4.8 cumulative hours period of Alternative 1 consists of the sum of 19,800 scfm from the roaster, 92,500 scfm from the reverberatory furnace, and 70,100 scfm from the converters.

There are two critical concentrations for Alternative 1. Both the 2.7- and 3.4-percent SO_2 levels shown are moderately below the 3.5-percent level considered necessary for a DC/DA acid plant (see Section 4.2.3). When these conditions arise and continue for more than 45 minutes, supplemental heat will be required.

Control Alternative 2 shows no conditions that would prevent application of a DC/DA acid plant designed to operate autothermally at 3.5 percent SO_2 . However, only 45 percent of the SO_2 by the reverberatory furnace is controlled.

Control Alternative 3, oxygen enrichment, requires 116 tons/day of oxygen to process the 1,443 tons/day feed to the reverberatory furnace. Fuel combustion is attained using air enriched to 25 percent

TABLE 6-3. MODEL PLANT, NEW GREENFIELD HIGH IMPURITY SMELTER CONTROL ALTERNATIVES

Stream	Control alternative											
	(1)			(2)			(3)			(4)		
	100% blending of reverberatory stream		45% blending of reverberatory stream		Oxygen enrichment and 100% blending of reverberatory stream		Oxy-fuel and 100% blending of reverberatory stream					
	scfm	% SO ₂	% O ₂	scfm	% SO ₂	% O ₂	scfm	% SO ₂	% O ₂	scfm	% SO ₂	% O ₂
Roaster gas	19,800	4.5	16.5	19,800	4.5	16.5	19,800	4.5	16.5	19,800	4.5	16.5
Reverberatory gas	92,500	1.3	10.9	41,900	1.3	10.9	65,800	1.8	11.3	35,400	3.3	11.7
Converter gas ^a	50,000	7.8	13.2	50,000	7.8	13.2	50,000	7.8	13.2	50,000	7.8	13.2
Stream to acid plant (hour/day)												
4.8	182,300	3.8	13.0	131,700	4.8	13.8	155,600	4.5	13.5	125,200	5.5	14.2
8.0	158,800	3.4	12.7	108,200	4.3	13.6	132,100	4.0	13.3	101,700	5.2	14.1
4.0	135,800	2.7	12.4	85,200	3.6	13.3	109,100	3.4	13.0	78,700	4.7	13.8
0.5	136,800	3.6	11.4	86,200	4.9	11.6	110,100	4.4	11.7	79,700	6.1	12.1
4.0	160,300	4.3	11.4	109,700	5.6	11.7	133,600	5.1	11.7	103,200	6.6	12.0
2.7	183,300	4.8	11.5	132,700	6.1	11.8	156,600	5.6	11.8	126,200	6.9	12.1
Acid plant effluent	156,400	0.065	-	106,400	0.065	-	142,900	0.065	-	127,700	0.065	-
SO ₂ controlled (tons/day) (%)	750.8	97		621.5	80		750.8	97		750.8	97	
SO ₂ emissions (tons/day) (%)	23.2	3		152.5	20		23.2	3		23.2	3	
100% acid (tons) ^b	1,150			951			1,150			1,150		

^aAverage value.

^bDouble contact/double adsorption.

oxygen. Fuel usage is accordingly reduced to 82 percent of the 4.5×10^6 Btu/ton of feed estimated by ASARCO to be required for the conventional reverberatory furnace.³ This alternative results in a 3.4-percent SO_2 concentration for a cumulative period of 4 hours per day. Supplementary heat estimated at 135,000 Btu/ton of feed would be required at the DC/DA acid plant during this period.

Control Alternative 4, oxy-fuel burners, uses 219 tons of oxygen per day to enrich the air to 35 percent oxygen. Since the combined roaster and smelter gases contain 3.9 percent SO_2 and may be controlled in a DC/DA acid plant without blending with converter gases, this alternative does not have to depend on any scheduling of converter operations.

Control Alternative 5, the use of any one of the three flue gas desulfurization (FGD) systems, is technically feasible. The gas stream fed to the FGD is identified in Table 6-3 (92,500 scfm; 1.3 percent SO_2 , 10.9 percent O_2). Ninety percent of the SO_2 fed will be controlled by the FGD system (see Section 4.3.6). This level plus the 97-percent control of roaster and converter gases gives a total control of 95.6 percent (741 tons/day SO_2) for the nonregenerative lime/limestone process and 95.2 percent (737 tons/day) for the Cominco Ammonia and MAGOX processes. The lower control using the regenerative processes is due to the additional loss through the acid plant (10 percent loss from the FGD plus 3 percent loss from the acid plant).

Control Alternatives 1 through 5 will be analyzed to determine their environmental, cost, economic, and energy impacts.

In the event that the exemption of the reverberatory furnace continues, a separate standard for particulate control will be needed. Candidate particulate control alternatives for reverberatory smelting furnaces are identified and evaluated in Section 4.4.4.2. They include the following:

1. A hot ESP to recover copper-containing dusts, with the treated gases vented to the atmosphere.
2. Gas cooling (by evaporative water cooling) to approximately 121°C (250°F), followed by a cold ESP or fabric filter to collect all particulates, and venting the gases to the atmosphere.

3. A hot ESP (for copper-rich dusts), followed by a cold ESP or fabric filter to collect condensable volatile impurities (e.g., arsenic), followed by venting to the atmosphere.

The hot ESP alone (Alternative 1) will allow an estimated fifty percent of volatilized fumes to escape. Alternatives 2 and 3 will capture essentially all of the particulates. If, for metallurgical reasons, the copper-containing dusts to be recycled cannot tolerate substantial quantities of metallic oxides (e.g., As, Sb, etc.), hot and cold ESP's in series would be preferable. However, if the metallurgy involving the dust is not sensitive to impurities, Alternative 2 would be preferred, especially since it appears to be less expensive than Alternative 3.

6.3 FUGITIVE EMISSION CONTROL

Fugitive emissions include those that escape from material transfer operations, leakage from process vessels, and leakage from primary offgas flues. Their control includes capture and collection. Capture is accomplished by hoods or air curtains into which the emissions are drawn by induced or natural draft. Collection may be accomplished by fabric filters, ESP's, or scrubbers.

This study is limited to particulate control. Although the fugitive emissions contain SO₂, their capture results in dilution to very low concentrations considered impractical to control. The capture and collection of particulate emissions will, however, result in the capture of the fugitive SO₂ emissions and their dispersal through a tall stack with the result being a reduction in the ambient SO₂ levels near the smelter.

Sources selected for possible regulation and their particulate emission rates in kg per Mg of blister copper are as follows:

- Multihearth roasters: Calcine discharge, 5.20
- Smelting furnaces: Matte tapping, 0.34; Slag skimming, 0.31.
- Converters: Blowing, 6.60, Charging, skimming, and pouring, 3.34.

The ranking of these sources is detailed in Section 3.3.4.

Table 6-4 shows the capture and collection alternatives to be evaluated for these sources. Calcine discharge is best captured by an interlocked larry car connection to the roaster, plus ventilation using an enclosure (e.g., ASARCO-Tacoma, Section 4.7.4).

Furnace matte and slag tapping emissions may be controlled by hoods with induced draft at the tap ports and ladles. When hoods are used in these positions, close fitting launder covers direct emissions into the hood. Collection of captured emissions is accomplished using a fabric filter or an ESP.

Converter fugitive particulate emissions from blowing, charging, skimming, and pouring can be captured by either building evacuation or an air curtain and fixed enclosure hoods. The captured emissions are then controlled by fabric filtration or an ESP. Building evacuation has an overall 95-percent capture efficiency; an air curtain and fixed enclosure hood capture system has an estimated overall capture efficiency of 90 percent.

6.4 EXPANSION OPTIONS AND ALTERNATIVE CONTROL TECHNOLOGIES

For the purpose of analyzing smelter expansions, it is assumed that (1) owners/operators will opt for expanding existing facilities rather than building a new greenfield smelter, (2) owners/operators will consider reducing emissions to levels at or below preexpansion levels so that the expanded facility does not become subject to the provisions of 40 CFR 60 for modifications, and (3) the fixed capital cost of the expansion of an existing facility would be kept below 50 percent of that required for an entirely new comparable facility so that the expanded facility does not become classified as a reconstruction. Thus the objective of the analysis, insofar as expansion options are concerned, is to determine if it is economically feasible to increase production at existing smelters by increasing the capacity of existing facilities and reducing emissions from the expanded facilities to preexpansion levels by treatment of part of the effluent stream. Generally, emissions from an expanded piece of process equipment will increase proportionately to the increase in capacity achieved as a result of the expansion.

TABLE 6-4. FUGITIVE PARTICULATE EMISSIONS

Source	Capture system	Capture efficiency	Particulate matter collection system	Collection system efficiency
Roasters Calcine discharge	Larry car interlock with ventilated enclosure	90 ^b	Fabric filter or ESP	-- ^d
Smelting Furnaces Matte tapping and slag skimming	Tap port and skin bay hoods, ladle hoods, and close-fitting launder covers	90 ^b	Fabric filter or ESP	-- ^d
Converters Blowing, charging, skimming and pouring	1. Building evacuation 2. Air curtain and fixed enclosure	95 ^c 90 ^e	Fabric filter or ESP Fabric filter or ESP	88 ^a -- ^d

^aBased upon actual emissions test data obtained on the building evacuation baghouse at the ASARCO-E1 Paso smelter.

^bBased upon visible emissions data obtained at the ASARCO-Tacoma smelter.

^cBased upon visible emissions data obtained at the ASARCO-E1 Paso smelter.

^dNo test data available. Particulate matter removal capabilities of fabric filters and ESPs as reported in Section 4.4 as high as 95 percent depending upon the particulate matter size distribution.

^eEstimate based upon preliminary data supplied by ASARCO.

As discussed in Section 3.4, the production-rate limiting process at most existing U.S. smelters is the smelting furnace. Capacity expansion options for existing reverberatory furnaces include the following:

1. Moderate expansion of 20 percent using oxygen enrichment of air fed to existing burners, or oxygen blown between the burners and the melt.
2. Forty to 50 percent expansion depending on whether the furnace is fed calcine or green charge by conversion to oxy-fuel burners, using sidewall charge or water-cooled sidewalls.
3. Forty percent expansion by conversion of a green-charged furnace to a calcine charged furnace.

These levels of expansion are based on reported experience with the technologies (see Section 3.4.3.4.4). Additional options not considered for further analysis include physical expansion of the existing furnace and elimination of converter slag return. Physical expansion is currently regarded by the U.S. industry as options unlikely to be exercised. Physical expansion will increase emissions of weak SO₂ gases. Elimination of converter slag return will require the addition of slag treatment facilities, with necessary pollutant controls. The extra investment, plus the additional operating costs of another processing unit, would tend to exclude this alternative.

Conversion to calcine charge will require an additional roaster and an additional converter since the same matte grade is to be attained. These would be subject to the DC/DA acid plant level of control under the established NSPS. In projecting expansion of furnace capacity, the additional roaster and converter capacity must be considered. While converters have been expanded physically, the increase in capacity has not been great enough to make this a viable option (see Section 3.4.1). Up to 20 percent excess roaster and converter capacity is considered to be available for each of the model plants to accommodate throughput increases up to that amount. A new roaster and/or converter are required for expansion options resulting in more than 20 percent capacity increase.

No viable expansion options for fluid-bed roasters are considered to be available (see Section 3.4.2).

Model plants for analysis of expansion options are defined using the terms of SO₂ control systems representative of existing conditions and may or may not reflect the SO₂ control systems yet to be installed to satisfy State implementation plans (SIP's), which are yet to be put in place (see Chapter 3). The present uncertainties about timing of SIP's precludes their use as a baseline case for model plants at this time.

Each of the five model plants for existing smelters represents those using a given smelting technology, as shown below:

<u>Existing smelter model</u>	<u>Smelters represented</u>
I	ASARCO-Tacoma ASARCO-Hayden ASARCO-El Paso Phelps Dodge-Douglas
II	Kennecott-Hunley Kennecott-McGill Phelps Dodge-Morenci Phelps Dodge-Ajo Magma
III	Kennecott-Hayden Phelps Dodge-Morenci
IV	Inspiration
V	Phelps Dodge-Hidalgo

The Kennecott Garfield smelter, which uses Noranda reactors, is not represented in the models because (1) the only viable expansion option indicated by the company is the addition of a new Noranda reactor controllable using a DC/DA acid plant, and (2) the industry indicated that no new smelters of this type will be built in the United States.

The Cities Service smelter, which uses a fluid-bed roaster, electric furnace, and converter, is not represented because the only

practical expansion option indicated is addition of new units. The White Pine smelter also is not represented because of the nature of the concentrates processed.

The smelting configurations for the models, including the number of each type of processing unit employed, are shown in Figures 6-2 through 6-6. A spare multihearth roaster is available for Model I. All models have a spare converter to allow for frequent maintenance of these units.

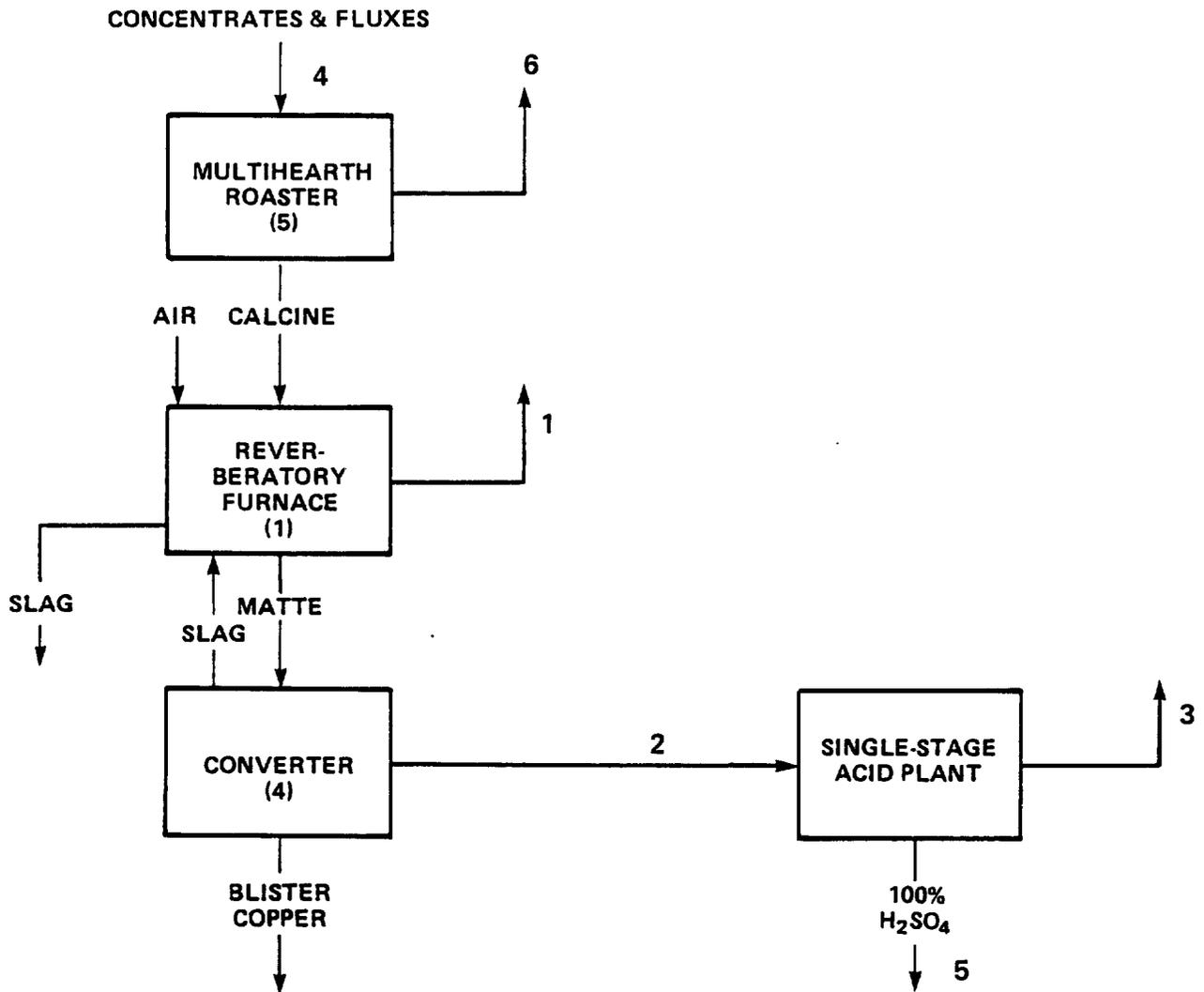
It should be noted that the SO₂ control system for Models I, II, and III is a SC/SA sulfuric acid plant. Although DC/DA acid plants are in use in some of the smelters represented, the SC/SA acid plant was selected for the models as the more costly case for expansion because conversion to a DC/DA plant would be involved.

Each model plant processes a feed of average composition for the smelters represented. These compositions are shown in Table 6-5. Model V, representing flash smelting, processes two distinctly different feeds. Both the range and average feed composition are shown for this model to indicate the experience gained with this smelting technology.

Matte grades selected for the models are within the range of grades reported by the smelters represented. Sulfur eliminations were derived based upon the matte grade and then checked to ensure that the values lay within the range of sulfur elimination practiced at the smelters. Table 6-6 summarizes the ranges of sulfur elimination and matte grade for the smelters represented by each model plant.

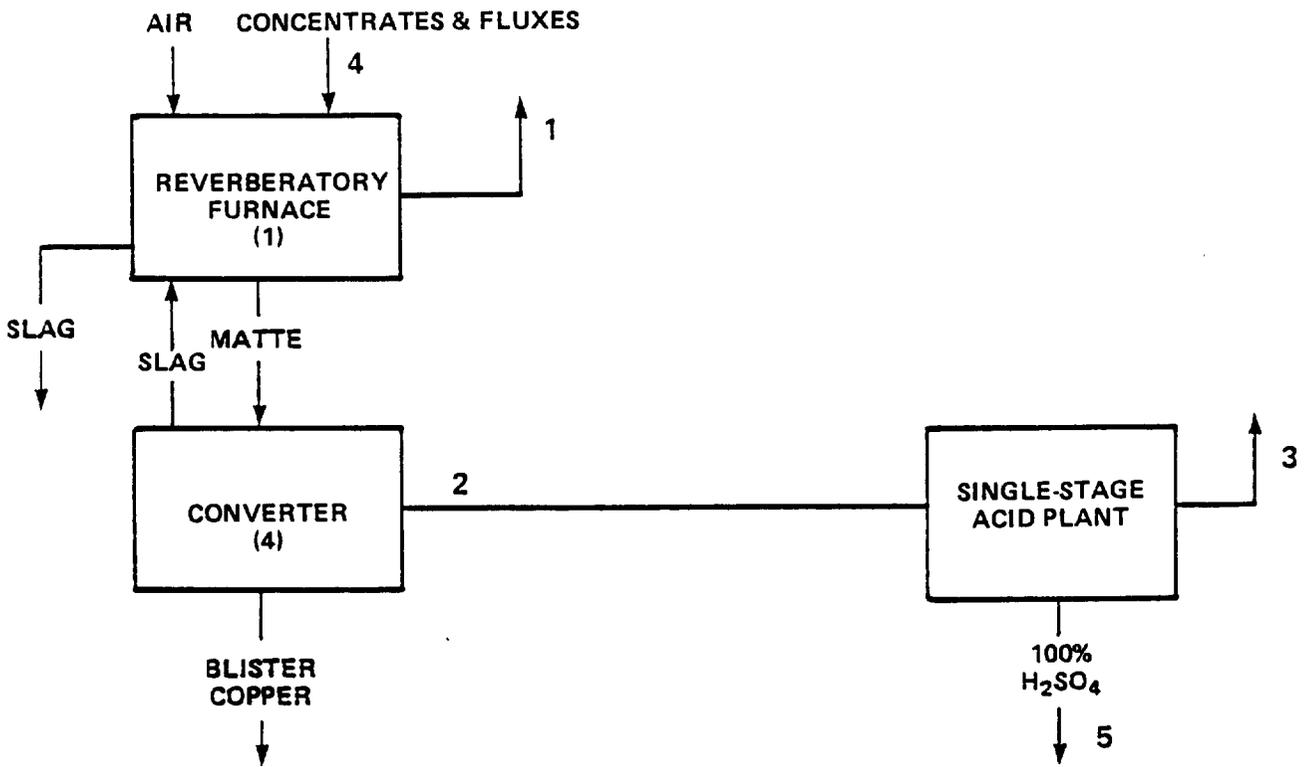
Expansion scenarios--that is, expansion options plus alternative controls--presented for further analysis are shown in Table 6-7. Models are indicated by primary equipment. Thus, MHR-RV-CV designates Model I, the multihearth roaster (MHR)-reverberatory furnace (RV)-converter (CV) model. Oxygen enrichment is to be used for a 20-percent increase in capacity. Control of SO₂ is by partial blending (PB) and an SC/SA acid plant.

In all expansion scenarios the designated SO₂ control options are considered as a means of (and for the purpose of) reducing emissions



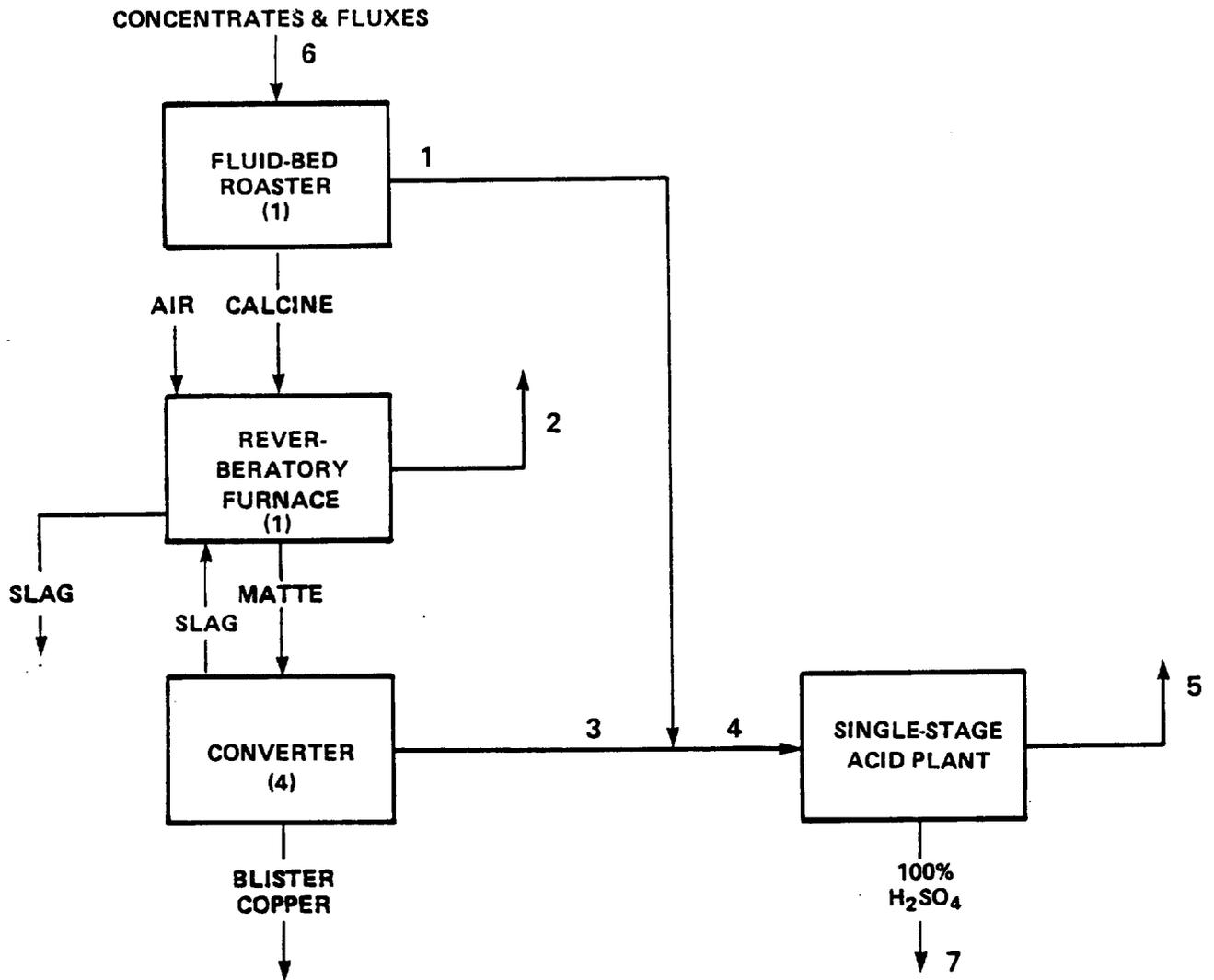
	scfm	Percent SO ₂	Percent O ₂	Tons/day
1	122,700	0.8	11.4	
2	75,500	4.3	15.4	
3	72,400	0.2	-	
4				1,500
5				610
6	104,600	1.5	18.7	

Figure 6-2. Model Plant I for expansion of existing smelters.



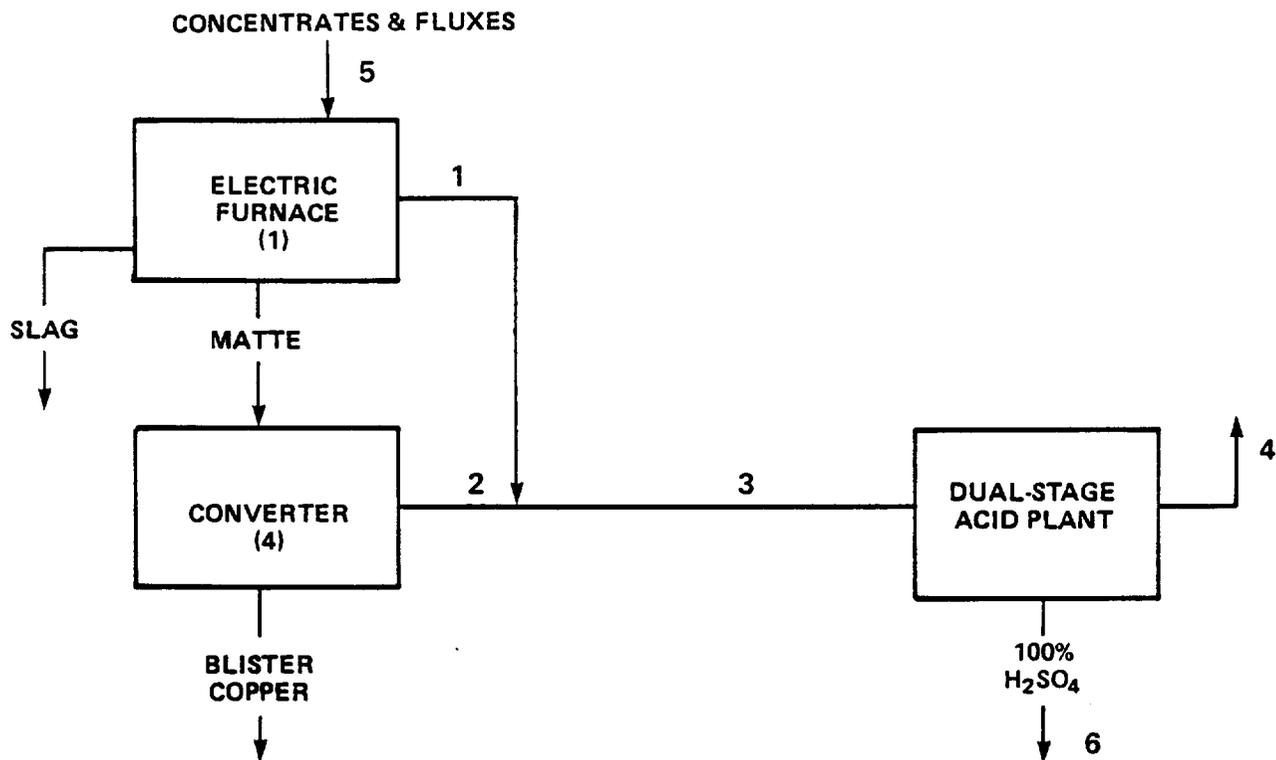
	scfm	Percent SO ₂	Percent O ₂	Tons/day
1	194,800	1.4	11.0	
2	90,900	4.3	15.4	
3	87,200	0.2	—	
4				1,500
5				734

Figure 6-3. Model Plant II for expansion of existing smelters.



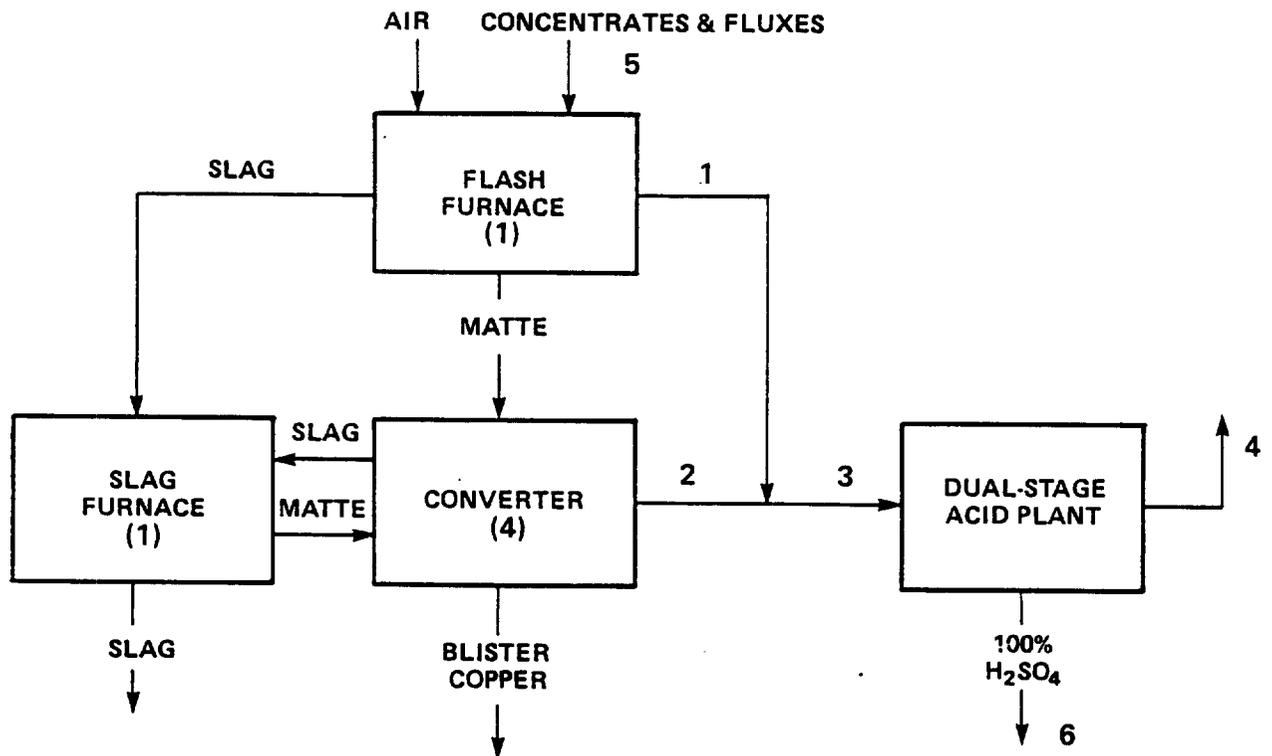
	scfm	Percent SO ₂	Percent O ₂	Tons/day
1	34,100	9.6	11.4	
2	164,200	0.4	13.2	
3	43,500	6.5	13.0	
4	77,600	7.9	12.3	
5	71,600	0.2	—	
6				1,500
7				1,176

Figure 6-4. Model Plant III for expansion of existing smelters.



	scfm	Percent SO ₂	Percent O ₂	Tons/day
1	37,900	6.0	19.7	
2	69,600	4.3	15.4	
3	107,500	4.9	16.9	
4	102,200	0.065	-	
5				1,500
6				1,021

Figure 6-5. Model Plant IV for expansion of existing smelters.



	scfm	Percent SO ₂	Percent O ₂	Tons/day
1	48,500	10.3	5.0	
2	72,000	4.3	10.1	
3	120,400	6.7	8.0	
4	112,500	0.065	-	
5				1,500
6				1,576

Figure 6-6. Model Plant V for expansion of existing smelters.

TABLE 6-5. MODEL PLANTS FOR EXPANSION OPTIONS: REPRESENTATIVE FEEDS AND SULFUR ELIMINATION

	Model						
	I	II	III	IV	V		
<u>Component, wt. %</u>							
Copper	21.9	22.4	1.96	28.7	17.6 ^a	24.8 ^b	21.2 ^c
Iron	20.4	24.8	23	25.3	26.5	22.1	24.3
Sulfur	24.8	28.4	28.9	29.8	35.4	26.5	31
Cu/S	0.88	0.79	0.68	0.96	0.49	0.94	0.68
Matte grade	43	39	44	40			55
<u>Sulfur eliminated, tons/100 tons feed</u>							
Roaster	6.7		14				
Smelter	4.2	11.7	2.8	9.7			21.4
Converter	13.9	16.7	12.1	20.1			9.6

^aTyrone ores.

^bBagdad ores.

^cAverage, Tyrone and Bagdad ores.

TABLE 6-6. MODEL PLANT EXPANSION OPTIONS: SULFUR ELIMINATION
PRACTICED BY REPRESENTED SMELTERS, WEIGHT PERCENT

	Model				
	I	II	III	IV	V
Processing unit					
Roaster	18-55		50		
Smelting furnaces	14-27	26-41	10-50	37	78 ^a
Converters	31-55	59-74	40-50	63	22
Matte grade	40-96	33-45	38-45	36-44	55-60
					43 ^b

^aTyrone ores.

^bBagdad ores.

TABLE 6-7. MODEL PLANT EXPANSION SCENARIOS

Scenario	Model	Unit expanded	Percent capacity increase	Expansion option	Control option, expanded smelting furnace
1	MHR-RV-CV	RV	20	Oxygen enrichment	PB-SC/SA
2	MHR-RV-CV	RV	20	Oxygen enrichment	LL
3	MHR-RV-CV	RV	20	Oxygen enrichment	MgO-SC/SA
4	MHR-RV-CV	RV	20	Oxygen enrichment	NH ₃ -SC/SA
5	MHR-RV-CV	RV+new MHR+CV	40	Oxy-fuel burners	PB-DC/DA
6	MHR-RV-CV	RV+new MHR+CV	40	Oxy-fuel burners	LL
7	MHR-RV-CV	RV+new MHR+CV	40	Oxy-fuel burners	MgO-DC/DA
8	MHR-RV-CV	RV+new MHR+CV	40	Oxy-fuel burners	NH ₃ -DC/DA
9	RV-CV	RV	20	Oxygen enrichment	PB-SC/SA
10	RV-CV	RV	20	Oxygen enrichment	LL
11	RV-CV	RV	20	Oxygen enrichment	MgO-SC/SA
12	RV-CV	RV	20	Oxygen enrichment	NH ₃ -SC/SA
13	RV-CV	RV+New CV	50	Oxy-fuel burners	PB-DS/DA
14	RV-CV	RV+New CV	50	Oxy-fuel burners	LL
15	RV-CV	RV+New CV	50	Oxy-fuel burners	MgO-DS/DA
16	RV-CV	RV+New CV	50	Oxy-fuel burners	NH ₃ -DS/DA
17	RV-CV	RV+Roaster+CV	40	Conversion to calcine charge	Not required ^b
18	FBR-RV-CV	RV	20	Oxygen enrichment	PB-SC/SA
19	FBR-RV-CV	RV	20	Oxygen enrichment	LL
20	FBR-RV-CV	RV	20	Oxygen enrichment	MgO-SC/SA
21	FBR-RV-CV	RV	20	Oxygen enrichment	NH ₃ -SC/SA
22	FBR-RV-CV	RV+Roaster+CV	40	Oxy-fuel burners	PB-DC/DA
23	FBR-RV-CV	RV+Roaster+CV	40	Oxy-fuel burners	LL
24	FBR-RV-CV	RV+Roaster+CV	40	Oxy-fuel burners	MgO-DC/DA
25	FBR-RV-CV	RV+Roaster+CV	40	Oxy-fuel burners	NH ₃ -DC/DA
26	EF-CV	EF+New FBR+CV	40	Conversion to calcine charge	DC/DA
27	FF-CV	FF	20	Oxygen enrichment	DC/DA

^aControl option covers only smelting furnace stream. Existing roasters and converters constructed by SC/SA acid plant under scenarios 1 through 37. Existing roasters, smelting furnaces, and converters controlled by DC/DA acid plant under scenarios 38 through 40. New roasters and converters controlled by DC/DA acid plant under all scenarios.

^bNo control required; existing plant postexpansion emissions < preexpansion. New converter and roaster controlled by DC/DA.

MHR = Multiearth roaster.

RV = Reverberatory furnace.

CV = Converter.

FBR = Fluid-bed roaster.

SC/SA = Single contact/single absorption acid plant.

DC/DA = Double contact/double absorption acid plant.

LL = Lime/limestone FGD on partial converter stream.

MgO = Magnesium oxide FGD on partial converter stream.

NH₃ = Cominco NH₃ FGD on partial converter stream.

PB = Partial blending.

EF = Electric furnace.

FF = Flash furnace.

to preexpansion levels. Four control options are considered for each expansion scenario, all of them involving treatment of a sufficient percentage of the expanded reverberatory streams to reduce emissions to preexpansion levels. The control options considered are:

1. Blending with strong streams and treatment in a sulfuric acid plant.
2. Treatment in a nonregenerative FGD, i.e., lime/limestone.
3. Treatment in a regenerative FGD, i.e., MAGOX or Cominco NH_3 , blending the FGD gas with other strong streams, and treatment in a sulfuric acid plant.

For scenarios resulting in a 20-percent capacity expansion, blended streams are treated in an expanded existing acid plant; for over 20 percent capacity expansion blended streams are treated in a new or expanded DC/DA acid plant. The existing acid plant for Models I, II, and III is a SC/SA; for Models IV and V, a DC/DA.

Table 6-8 provides the exit gas parameters to be considered in further analysis of expansion scenarios. The five model plants are shown together with their expansion scenarios. Exit gas flows for the models shown are based on SO_2 and oxygen concentrations reported by the smelters represented, using matte grades and sulfur eliminations shown in Table 6-5. Flows and concentrations for the expansions are based on reported experience with the expansion and control technologies described in Chapters 3 and 4. For oxygen enrichment and oxy-fuel scenarios, the furnaces gas flows are based upon fuel combustion with 10 percent excess oxygen, using sufficient oxygen to provide an air-oxygen mixture in the furnace containing 25 percent oxygen (oxygen enrichment) and 35 percent oxygen (oxy-fuel), respectively. The gases generated under these conditions, containing the SO_2 equivalent to the sulfur eliminated, are diluted with air before entering the SO_2 control system just as they were before expansion.

Table 6-8 shown average converter gas flows. Since converter gases vary in flow rate and in concentration, analysis of the options must be based upon the further breakdown of the concentrations to show

TABLE 6-9. MODEL PLANT EXPANSION OPTIONS: MINIMUM ESTIMATED
SO₂ CONCENTRATIONS TO ACID PLANT

Expansion option	Type of acid plant	Minimum SO ₂ content (%)
1	SC/SA	3.0 ^a
2	SC/SA	3.8
3	SC/SA	3.9
4	SC/SA	4.0
5	DC/DA	3.3 ^b
6	DC/DA	4.4
7	DC/DA	4.9
8	DC/DA	5.2
9	SC/SA	3.2 ^c
10	SC/SA	4.4
11	SC/SA	4.9
12	SC/SA	5.2
13	DC/DA	3.7
14	DC/DA	4.5
15	DC/DA	4.7
16	DC/DA	4.8
17	DC/DA	6.3
18	SC/SA	6.1
19	SC/SA	7.2
20	SC/SA	7.2
21	SC/SA	7.3
22	DC/DA	4.0
23	DC/DA	7.7
24	DC/DA	7.9
25	DC/DA	8.3
26	DC/DA	4.4
27	DC/DA	6.5

the minimum expected value. These minimum concentrations, estimated using the converter operating schedule described in Section 6.2, are shown in Table 6-9.

When an expansion scenario requires new equipment, the exit gas parameters are shown separately for these. Where regenerative FGD systems are used, the "pregnant gas" from these to the acid plant is also shown.

The 27 expansion scenarios will be analyzed to determine their cost and economic impact, and their status relative to modification and reconstruction aspects of emissions control regulations.

6.5 REFERENCES

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4. Background Information Document for New Source Performance Standards. Primary Copper, Lead, and Zinc Smelters. Vol. I. Proposed Standards. EPA-450/2-74-002a. October 1974.
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APPENDIX

THEORETICAL MODEL FOR THE GAS BLENDING TECHNICAL
FEASIBILITY ASSESSMENT

The following development illustrates the rationale used in assessing the feasibility of partial weak stream blending as a means by which to maintain total postexpansion SO₂ emissions to the atmosphere at preexpansion levels.

Consider the theoretical sulfur dioxide material balance presented in Figure -1. A postexpansion scenario with partial weak stream blending is illustrated. In addition to the terms defined in Figure -1, the following terms must be defined in order to proceed with the development:

B_a = the total reverberatory furnace SO₂ emissions to the atmosphere after expansion

B_b = the total reverberatory furnace SO₂ emissions to the atmosphere prior to expansion

Z = the SO₂ concentration required in the blended stream for autothermal acid plant operation.

The basis for the entire analysis is the fact that SO₂ emissions to the atmosphere after expansion must be equal to or less than SO₂ emissions to the atmosphere prior to the expansion. This constraint can be stated mathematically in the following manner:

$$B_a \leq B_b \quad (-1)$$

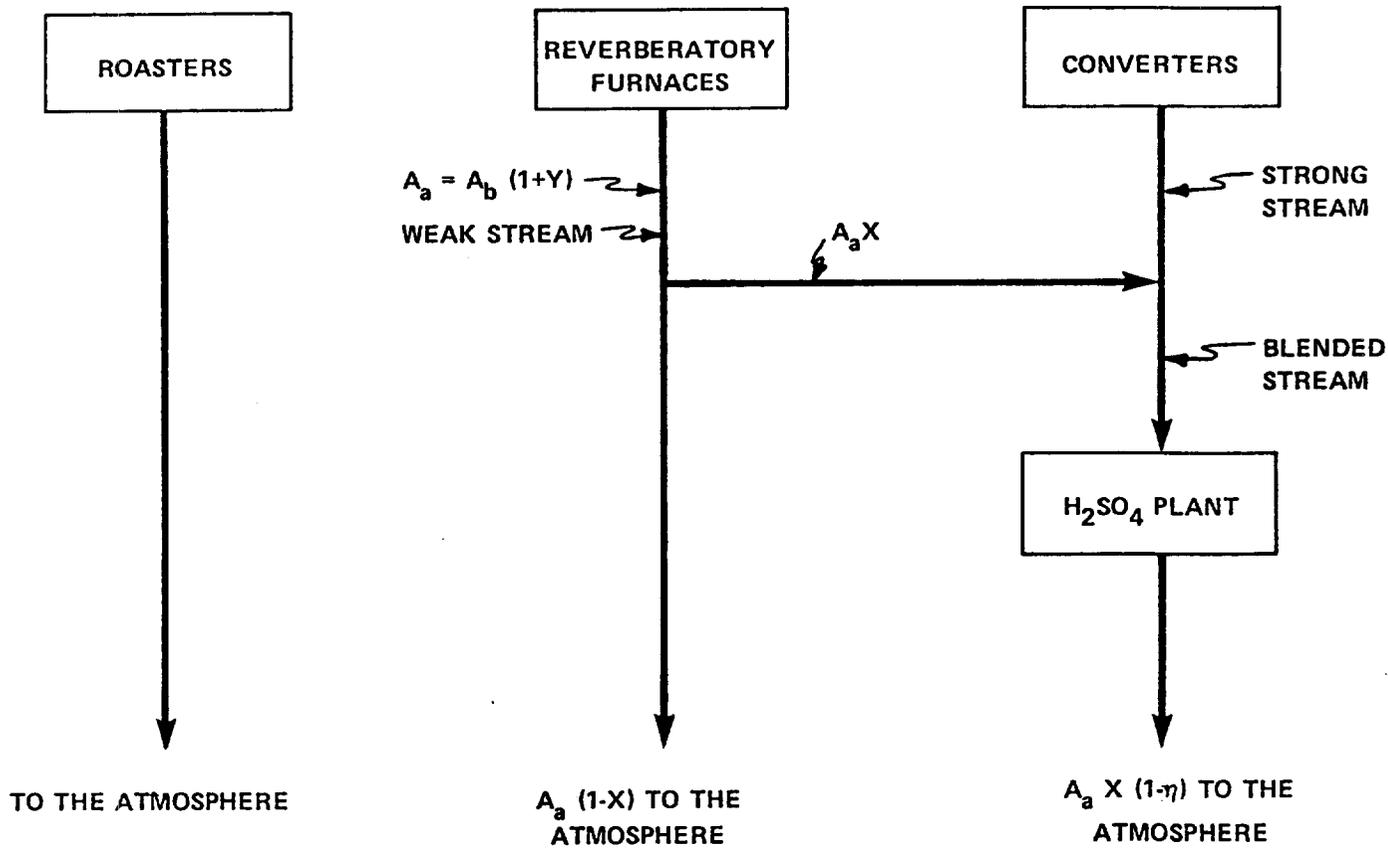
At present, SO₂ emissions from reverberatory furnaces are uncontrolled. Consideration of this point, along with the fact that facilities opting to use this expansion mode would reduce postexpansion SO₂ emissions only to preexpansion levels and no lower, yields the following expression:

$$B_a = B_b = A_b \quad (-2)$$

Therefore, by the material balance presented in Figure -1,

$$\begin{aligned} B_a &= A_a (1 - X) + A_a X (1 - \eta) \\ &= A_a [(1 - X) + X (1 - \eta)] \\ &= A_a (1 - X\eta) \end{aligned} \quad (-3)$$

By assuming that the mass of SO₂ generated in the reverberatory furnace(s) increases in direct proportion to the furnace capacity,



where

- A_a = the total mass of SO₂ generated in the reverberatory furnace(s) after expansion
- A_b = the total mass of SO₂ generated in the reverberatory furnace(s) prior to expansion
- X = the fraction of the weak stream that is blended
- Y = the fractional increase in production capacity associated with a given expansion
- η = the control system (acid plant) SO₂ removal efficiency

Figure __-1. Postexpansion sulfur dioxide material balance for a conventional primary copper smelting facility.

i.e., that $A_a = A_b (1 + Y)$, a relationship between X --the portion of the weak stream that must be blended to ensure that postexpansion SO_2 emissions are equal to preexpansion emissions--and Y --the fractional increase in production capacity--may be derived as follows:

By material balance,

$$B_a = A_a (1 - X\eta) = A_b (1 + Y)(1 - X\eta) .$$

Noting that $A_b = B_a$ from Equation _-2,

$$1 = (1 + Y)(1 - X\eta) = 1 + Y - X\eta - YX\eta$$

$$0 - Y = -X (\eta + Y\eta) .$$

Thus,

$$X = \frac{Y}{\eta(1+Y)} . \quad (_ -4)$$

Equation _-4 defines the relationship that must exist between X and Y in order to ensure that SO_2 emissions to the atmosphere after expansion are equal to the SO_2 emissions to the atmosphere prior to expansion.

There is an additional constraint on X that must exist to ensure that the blended stream has the SO_2 concentration required to maintain autothermal acid plant operation. The limiting value of X can be determined by a material balance at the point where the weak and strong streams are blended. To ensure that the blended stream will exhibit the SO_2 concentration required for autothermal acid plant operation, the following relationship must exist:

$$\frac{V_{s_a} C_{s_a} + XV_{w_a} C_{w_a}}{V_{s_a} + XV_{w_a}} \geq Z , \quad (_ -5)$$

where

V_{s_a} = the strong stream volumetric flow rate after expansion

C_{s_a} = the strong stream SO_2 concentration after expansion

V_{w_a} = the weak stream volumetric flow rate after expansion

C_{w_a} = the weak stream SO_2 concentration after expansion

Z = the SO_2 concentration that must exist in the blended stream to ensure autothermal acid plant operation.

By algebraic manipulation of Equation _-5, the limiting value of X , X_{max} , can be derived as follows:

From Equation _-5,

$$V_{s_a} C_{s_a} + XV_{w_a} C_{w_a} \geq (V_{s_a} + XV_{w_a}) Z$$

↓

(_-6)

$$XV_{w_a} C_{w_a} - ZXV_{w_a} \geq ZV_{s_a} - V_{s_a} C_{s_a}$$

Multiplying Equation _-6 by a negative 1 yields

$$-XV_{w_a} C_{w_a} + ZXV_{w_a} \leq -ZV_{s_a} + V_{s_a} C_{s_a}$$

Solving for X yields

$$X \leq \frac{V_{s_a} (C_{s_a} - Z)}{V_{w_a} (Z - C_{w_a})}$$

or equivalently

$$X_{max} = \frac{V_{s_a} (C_{s_a} - Z)}{V_{w_a} (Z - C_{w_a})}$$

(_-7)

Equation _-7 defines the maximum value of X that can exist while maintaining the SO_2 concentration required for autothermal acid plant operation.

Thus, based upon the preceding development, the criterion for feasibility becomes:

- The fraction of the weak stream that must be blended to maintain the preexpansion SO₂ emission level must be less than or equal to the maximum fraction of the weak stream that can be blended while maintaining the blended stream SO₂ concentration required for autothermal acid plant operation.

The limiting criterion can be expressed mathematically as follows:

$$X - X_{\max} \leq 0 \quad (_8)$$

or equivalently

$$X_{\max} - X \geq 0 \quad (_9)$$

where

X = the fraction of the weak stream that must be blended (as predicted by Equation _4) to ensure that the postexpansion SO₂ emissions are equal to the SO₂ emissions that were in evidence prior to expansion.

X_{\max} = the maximum fraction of the weak stream (as predicted by Equation _7) that can be blended while maintaining the blended stream SO₂ concentration required for autothermal acid plant operation.

A plot of $X_{\max} - X$, the partial blending feasibility criterion, as a function of Z , the required blended stream SO₂ concentration, would have the general form illustrated in Figure _2. Since $X_{\max} - X$ must be positive for partial gas blending to be feasible, the point at which the feasibility curve crosses the horizontal axis is indicative of the required blended stream SO₂ concentration above which partial blending becomes infeasible. Implicit in this technical feasibility assessment is the assumption that adequate acid plant capacity either already exists or could be created to handle the increase in the volume of gas processed due to the partial blending of the reverberatory furnace offgases. Under this assumption, the limiting criterion expressed in Equation _8 holds true for any type of reverberatory furnace expansion accompanied by partial blending of the weak stream. By estimation of the postexpansion parameters required to perform the analysis, the feasibility of partial gas blending has been assessed

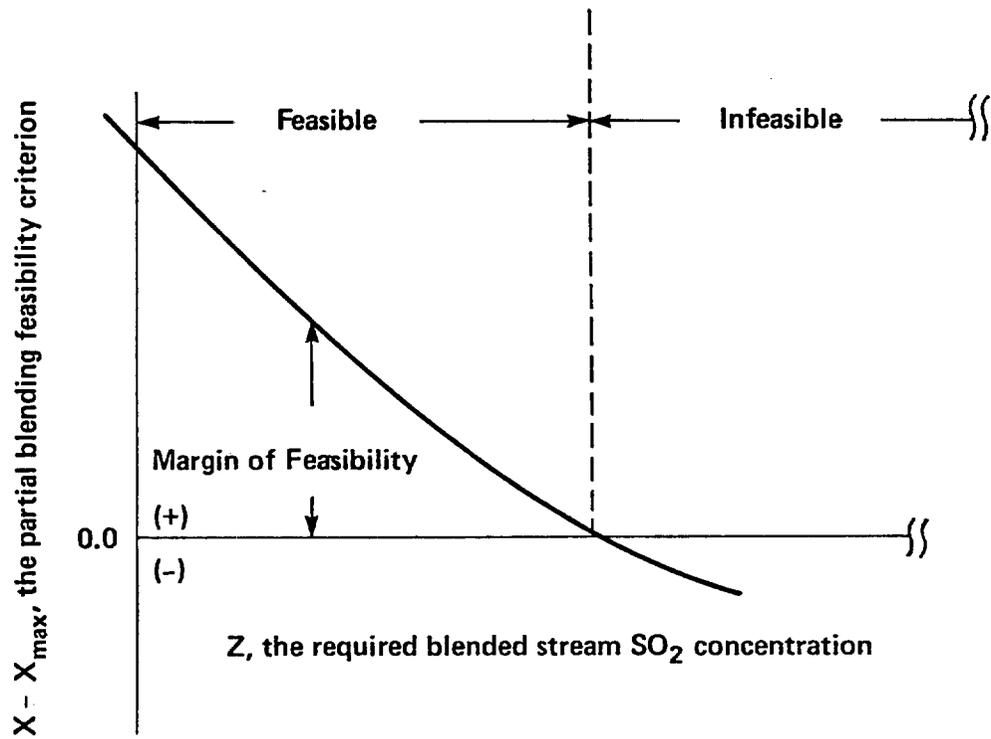


Figure __-2. General form of the partial blending feasibility criterion as a function of the required blended stream SO_2 concentration.

for two types of reverberatory furnace expansions: (1) oxygen enrichment of the combustion air and (2) expansion via the use of oxy-fuel burners. The results of the technical feasibility assessment are presented in Section 4.6.

APPENDIX

MATHEMATICAL MODEL FOR ESTIMATING POSTEXPANSION REVERBERATORY GAS
FLOW AND SO₂ CONCENTRATION FOR OXYGEN ENRICHMENT
AND OXY-FUEL EXPANSION OPTIONS

MATHEMATICAL MODEL FOR ESTIMATING POSTEXPANSION REVERBERATORY GAS
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AND OXY-FUEL EXPANSION OPTIONS

Assumptions:

1. Ten percent excess O₂.
2. Fifty percent of base case off-gases is dilution air. Amount of dilution air does not vary with expansion.
3. Fuel is equivalent to CH₄ for determining volume of combustion products.

Notation:

V = volume rate of off-gas

S = volume fraction of SO₂

C = volume of combustion products, excluding nitrogen,
at theoretical O₂

O = volume rate of excess O₂

N = volume rate of nitrogen

P = volume fraction of oxygen in combustion air

E = Ratio of expansion capacity to base case capacity

H = ratio of expansion fuel to base case fuel

subscript b = base case

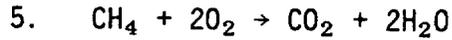
subscript e = expansion

Procedure:

1. $V_b = \text{dilution air} + SO_2 + C_b + O_b + N_b$
2. Dilution air = $\frac{V_b}{2}$
3. SO₂ rate = $V_b S_b$

$$4. \quad C_b + O_b + N_b = \frac{V_b}{2} - V_b S_b \quad (\text{from 1, 2, \& 3})$$

$$= \frac{V_b(1-2S_b)}{2}$$



Three volumes of combustion products require, at 10 percent excess O_2 , 2.2 volumes of O_2 and $2.2 \times \frac{79}{21}$ or 8.3 volumes of nitrogen. This represents 0.2 volumes of excess O_2 .

6. Using ratios of C_b , O_b , N_b determined in 4, the following relationships with $V_b + S_b$ are determined:

$$O_b = \frac{V_b(1-2S_b)}{2} \times \frac{0.2}{0.2 + 3 + 8.3} = 0.0087 V_b(1-2S_b)$$

$$N_b = \frac{V_b(1-2S_b)}{2} \times \frac{8.3}{11.5} = 0.3609 V_b(1-2S_b)$$

$$C_b = \frac{V_b(1-2S_b)}{2} \times \frac{3}{11.5} = 0.1304 V_b(1-2S_b)$$

$$7. \quad V_e = \frac{V_b}{2} + S\text{O}_2 + C_e + O_e + N_e$$

$$8. \quad S\text{O}_2 = E V_b S_b$$

$$9. \quad C_e = H C_b$$

$$= 0.1304 H V_b(1-2S_b) \quad (\text{from 6})$$

$$10. \quad O_e = H O_b$$

$$= 0.0087 H V_b(1-2S_b) \quad (\text{from 6})$$

11. From 5, 3 volumes of combustion products require, at 10 percent excess O_2 (0.2 volumes), 2.2 volumes of oxygen and $2.2 \frac{(1-P)}{P}$ volumes of nitrogen.

Each volume of combustion products is therefore associated with $2.2 \frac{(1-P)}{3P}$ volumes of N_2 .

$$N_2 = 0.1304 HV_b (1-2S_b) 2.2 \frac{(1-P)}{3P} \quad (\text{from 9})$$

$$= 0.0956 HV_b (1-2S_b) \frac{(1-P)}{P}$$

12. Combining 7, 8, 9, 10, 11

$$V_e = \frac{V_b}{2} + EV_b S_b + 0.1304 H V_b (1-2S_b) + 0.0087 HV_b (1-2S_b)$$

$$+ 0.0956 HV_b (1-2S_b) \frac{(1-P)}{P}$$

$$V_e = V_b \left[0.5 + ES_b + H(1-2S_b) 0.1391 + 0.0956 \frac{(1-P)}{P} \right]$$

$$= V_b \left[0.5 + ES_b + H(1-2S_b) 0.1391 + 0.0956 \frac{(1-P)}{P} \right]$$

13.

$$S_e = \frac{EV_b S_b}{V_e}$$