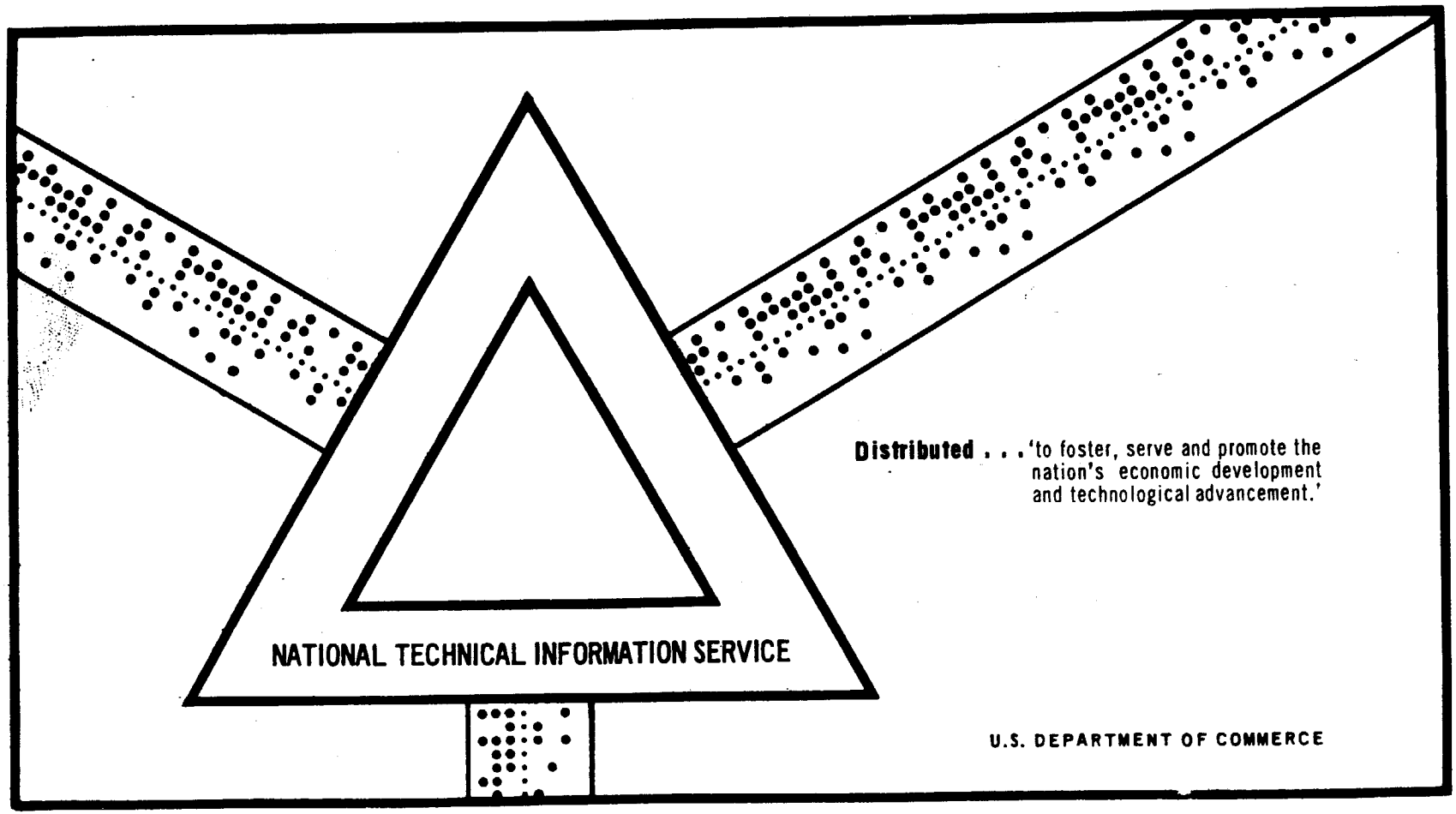
AP-42 Section 7.14
1° Ref.

PB 184 884

SYSTEMS STUDY FOR CONTROL OF EMISSIONS PRIMARY NONFERROURS SMELTING INDUSTRY - VOLUME I

Arthur G. McKee and Company
San Francisco, California

June 1969



SYSTEMS STUDY FOR CONTROL OF EMISSIONS PRIMARY NONFERROUS SMELTING INDUSTRY

VOLUME I of III

FINAL REPORT UNDER CONTRACT PH 86-65-85

FOR
DIVISION OF PROCESS CONTROL ENGINEERING
NATIONAL AIR POLLUTION CONTROL ADMINISTRATION
PUBLIC HEALTH SERVICE
U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

JUNE 1969

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WESTERN KNAPP ENGINEERING DIVISION
SAN FRANCISCO, CALIFORNIA

McKEE

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I ABSTRACT

Process gases emitted to the atmosphere from primary copper, zinc, and lead smelters in the U.S. contain 1,920,000 short tons of sulfur per year. Copper smelters are the source of 76.5 percent of this. Their problems of emission control are the most difficult in the nonferrous smelting industry. Over 97 percent of all emissions are from smelters west of the Mississippi river.

Neither now nor in the period up to at least 1975 can all of the potentially recoverable sulfur in the west be sold as sulfuric acid. All of it can be sold if a portion can be converted from sulfur oxides to elemental sulfur at a cost that is low enough to be competitive. The area of Arizona - New Mexico - West Texas has the largest potential production of sulfur byproducts but a relatively small market for sulfuric acid.

Production of sulfuric acid from the more concentrated gases can be profitable where a market for the acid exists. The production cost for converting sulfur oxides in the gases to elemental sulfur by modern processes is not yet defined. Production of sulfur for sale at competitive prices will probably be possible only by recovery from gases containing high concentrations of sulfur oxides.

The major technical and economic problem is the control of offgases containing low concentrations of sulfur oxides. Present technology is not adequate to economically recover and concentrate sulfur oxides from these weak offgases. Economical control may best be attained through process or practice changes that have the effect of curtailing generation of weak offgases and delivering other offgases to sulfur oxide conversion units at the highest feasible concentrations.

II. INTRODUCTION

The National Air Pollution Control Administration (NAPCA) and other cognizant government offices have a qualitative appreciation of the competitive and economic pressures on the smelting industry and a limited awareness of the technological obstacles to effective control of sulfur dioxide emissions by the industry. In order to enhance this appreciation and awareness to a sound basis for research and development programs that hopefully can be sponsored jointly by government and industry, NAPCA funded this study. The nature of the study was defined in a Contract for Technical Services entered into by NAPCA and Arthur G. McKee & Company (McKee) and dated December 15, 1967.

A subcontract was negotiated between Stanford Research Institute (SRI) and McKee and approved by NAPCA which defined work to be done by SRI on certain phases of the systems study. Collaboration between McKee and SRI was required in the evaluation of the results of all phases of the study.

Objectives of the Study

This study of the primary copper, zinc, and lead smelting industries is intended to make clear the technological and economic factors that bear on the problem of control of sulfur oxide emissions. It also examines the scope of capital and operating costs of several processes that control emissions by converting sulfur oxides to marketable byproducts or disposable waste material. In conjunction with this, a marketing study determines the economic factors relating to the sale of sulfur-bearing byproducts. To increase the usefulness of the study, a survey projects into the

future the present trends in metal requirements and attempts to forecast industry changes that may affect the amount of sulfur oxide emissions. Note that this is all generalized economics and application to specific individual plants is not intended.

The results of the above work and of a survey of emission sources at smelter locations have led to conclusions and recommendations as to fields of investigation that appear most promising for future research and development work. Consideration has been given to those areas that show promise of giving the greatest reduction of sulfur oxide emissions while simultaneously yielding economic benefit to the smelting industry.

Limitations of the Report

The report and its conclusions are based on information that was available from the smelters, or on facts already known to the contractors and not restricted as confidential. It should not be viewed as absolute documentation, for in some areas the data available were incomplete and may have been inaccurate.

Plan of the Report

The report is presented in three volumes. In Volume I, (this volume,) sections I, III, and IV present the essence of the conclusions reached and the resulting recommendations. Section II, (this section,) gives the purpose of the study and the plan of the report.

Sections V through VII are less detailed and technical than the sections that follow. The smelter air pollution problem, methods of control, and the statistics of emission and control are discussed. These sections contain references to the more detailed material in the appendices in volumes II and III.

Sections VIII through X discuss the economics of control, the research objectives, and research recommendations. In section VIII, which also gives results of the market study, control methods are matched with smelter models to obtain costs that are illustrative of the effects of some possible courses of action in the industry.

Volume II contains appendices A and B and volume III contains appendices C through G. The appendices have the tabulated data, drawings, and extended technical discussions that support the summaries and briefer discussions of volume I.

Acknowledgements

The assistance and cooperation of the smelter industry in the work of gathering the material for this study is acknowledged. The critical review and suggestions of the Industry Liaison Committee were very helpful and the counsel of Mr. Louis V. Olson, who has acted as consultant to McKee on this project, has been greatly appreciated.

Important sections of the report were prepared by Stanford Research Institute (sections V b, VIII a and b, and appendices D through G), and SRI worked with McKee in the preparation of other sections and in the evaluation of the results of the study.

III SUMMARY

Some 2,800,000 short tons of sulfur are contained in the sulfur oxide gases generated annually at U.S. smelters. Of this, 850,000 tons or 31 percent are recovered, almost all as sulfuric acid, and the remaining 1,920,000 tons are emitted to the atmosphere. Smelters east of the Mississippi generate 350,000 tons and recover 86 percent of it, while western smelters recover 23 percent of the 2,420,000 tons that they generate. Western smelters are the source of over 97 percent of emissions to atmosphere from smelters in this country.

Some 76 percent of smelter emissions to the atmosphere come from copper smelters, 17 percent from zinc smelters, and seven percent from lead smelters. Zinc smelters recover 59 percent of their emitted sulfur oxides, and lead smelters recover 27 percent.

Five of the 16 copper smelters studied control sulfur oxide emissions to some degree. Altogether, the copper smelter industry recovers 19 percent of the sulfur oxides generated, and this is expected to rise several percent in 1970. The control of emissions at copper smelters is hampered by conditions that are inherent in existing processing methods; namely, weak reverb offgases and varying flow of converter offgases. Most of the smelters are also poorly located with respect to sulfuric acid markets.

Nature of the Smelter Air Pollution Problem

Present smelting practice in primary copper and lead smelters of the U.S. is fairly uniform from smelter to smelter for each metal. In zinc smelters, there are greater differences in processing methods and in equipment used.

Usually some 93 to 97 percent of the sulfur in the feed to a zinc smelter is eliminated as sulfur oxides in the offgas from the roasting operation. Offgases from the newer fluidized or suspension roasters have from seven to 12 percent sulfur dioxide. Older types of roasters emit weaker gases. Sintering of roasted zinc ore in pyroreduction plants produces offgases containing from 0.1 to 2.4 percent sulfur dioxide, depending upon the amount of residual sulfur left in the roaster calcine.

The sintering operation in lead smelting eliminates about 85 percent of the total sulfur from the feed as sulfur oxides. Offgases from a smelter that uses updraft sintering machines may contain from four to six percent sulfur dioxide. Offgases from the first stages of two-stage downdraft machines can be of this strength, but the second stage gases contain only 0.8 to 1.8 percent sulfur dioxide. One percent of the feed sulfur is in the very weak blast furnace and dross furnace offgases, and the remaining 14 percent is retained in the slag and other solid byproducts.

In a copper smelter, the reverberatory furnace emits a steady flow of dilute gas, whereas converter offgas has a higher sulfur oxide concentration but an irregular and cyclical flow. If a roaster is used, the offgas flow is steady and the concentration can be about eight percent sulfur dioxide, after dust removal, depending on the volume of air drawn into the flue system.

Control of Sulfur Oxides

One control method, conversion of sulfur dioxide to sulfuric acid, is now being used by nearly half the smelters in this country. It is an efficient, low-cost method for controlling offgas having over four or five percent sulfur dioxide. The flow rate and concentration of the feed gas to an acid plant needs to be fairly uniform.

The Cominco process is the only absorption process in use by a smelter in the U.S. or Canada for removing and concentrating sulfur oxides from offgases with less than three percent sulfur dioxide. Its disadvantage is that it has high costs, consumes ammonia and sulfuric acid, and necessarily produces ammonium sulfate as a secondary byproduct.

The DMA absorption process delivers a pure sulfur dioxide gas and is used at two plants for recovering sulfur dioxide from offgases that contain over four percent of this oxide. Cost data were not available for this study.

No process is known to be available to extract and concentrate sulfur oxides from weak smelter gases at low cost. A satisfactory process should efficiently remove sulfur oxides from gases containing 0.3 to four percent sulfur oxides. It should be cyclic and should not consume large amounts of reagents or produce secondary byproducts in quantity. Neither the DMA or Cominco processes meet these requirements.

Offgases can be wet-scrubbed with lime or sometimes with limestone slurries. Sulfur oxide removal is more efficient with lime than with limestone. The products are waste materials that must be conveyed to disposal areas. The cost of the lime or limestone is a substantial part of total costs. Costs would limit application of these processes to small volumes of weak offgases or of stronger offgases that cannot be used to make sulfuric acid or sulfur.

Elemental sulfur, from reduction of sulfur dioxide, can be stored or shipped at much lower cost than sulfuric acid. In this study, costs for the old Asarco reduction process were estimated for offgases containing from four to eight percent of sulfur dioxide. The process has high capital and operating costs and has never been used on a full commercial scale. Reduction processes that use catalysts and are more conserving of heat have been developed more recently, but data for cost calculations were not available for this study.

The control processes that convert sulfur dioxide to useful byproducts all operate at unit costs that decrease as the sulfur oxide concentration of the feed gas increases. Therefore, any change in metallurgical practice that results in more concentrated offgases should reduce the cost of control. Copper smelters need process changes that do away with the cyclic pattern of offgas flows from the converters. Improved metallurgical processes have been adopted by some smelters, and others are being developed or are in use abroad. The improved processes may reduce the costs of metal production and improve offgas flows and concentrations.

Improvements are needed in process enclosures, specifically in connections between equipment such as copper converters and their offgas duct systems. Tighter connections and reliance on waste heat boilers and cooling coils or jackets instead of on air dilution for cooling the offgases will be needed for realizing the full benefit of some process changes in the form of smaller gas volumes and higher concentrations of sulfur oxides.

Markets for Sulfur Byproducts

The market study considered four primary sulfur byproducts: elemental sulfur, sulfuric acid, sulfur dioxide, and ammonium sulfate. Of these, liquid sulfur dioxide is used in such small quantities that its production offers no further significant potential outlet for recovered smelter effluents. Ammonium sulfate was considered as a primary product because it is the unavoidable byproduct of the Cominco absorption process, which may be used for concentrating sulfur dioxide from lean gas streams.

The average price for sulfur between now and 1975 will probably be about $30 per long ton fob the Gulf Coast. This conclusion resulted from an examination of possible future trends in supply and demand. The price of sulfur fob the Gulf Coast is frequently quoted as the reference basis for the world price. Prices obtainable for byproduct sulfur derivatives at smelters will be related to the world price of sulfur because elemental sulfur is an item of international commerce whose price is affected by world supply and demand. The $30 price was used as the basis for estimates of prices that smelter operators might obtain for their byproduct sulfur and sulfur derivatives.

The principal findings from the market study follow:

1. Smelters west of the Mississippi River can potentially produce more sulfuric acid than could currently be disposed of even if part were given away. The maximum quantity of acid that could be sold at prices ranging down to $0 per short ton fob smelters would be about 3.1 million short tons per year or 43 percent of potential production. At prices ranging down to a minimum of $4, 2.8 million tons or 38 percent of potential production of acid could be sold. Potential markets for acid from smelters might grow to as much as 5.3 million tons by 1975, but this would still constitute only 73 percent of current potential acid production. However, if sulfur oxides from western smelters not already being recovered were converted to elemental sulfur, all the sulfur (1.6 million long tons per year) could be sold at prices ranging from a maximum of $35 per long ton to a minimum of $25.50 fob the smelters. These prices represent the maximum production costs of the sulfur that are allowable if the smelter operators are to break even on the recovery operation.

2. Smelters in the Arizona - New Mexico - West Texas area have the greatest potential sulfuric acid production of any group, but a relatively small potential market. Currently, there is a potential market for only 571,000 short tons per year of acid (15 percent of potential production) at prices of $4 or more per ton fob smelters. The market for acid from this smelter group can grow rapidly between now and 1975. However, the potential 1975 acid market is still estimated to be only 1.86 million tons, or 49 percent of the current potential production. In contrast, these smelters should be able to sell all the elemental sulfur they can produce if they can match or better the price of sulfur from the present suppliers.

3. Current potential markets for sulfuric acid from smelters in Idaho and Montana (minimum price $4 per ton fob smelters) are now equivalent to only 16 percent of potential production. However, a large growth in demand for acid can be expected by 1975, mostly for phosphate fertilizer production. By 1975, demand may reach about 1.26 million tons per year, or 90 percent of potential production in 1969.

4. Current potential demand for acid from smelters in the Pacific Coast states appears to be equivalent to about 70 percent of potential production. It was not possible to estimate the possible growth of future demand.

5. Operators of the remaining smelters in the western region should currently be able to sell nearly all their potential production of sulfuric acid for $4 or more per ton fob the smelters.

6. Markets exist for any additional sulfuric acid that smelters east of the Mississippi might produce from sulfur oxide emissions not already recovered.

7. The growth rate of consumption of sulfuric acid is higher than that of production of nonferrous metals. Hence, it is expected that future markets for acid should remain adequate in those marketing regions where they are already so. The largest growth in acid consumption will be in phosphate fertilizer production (supplied mainly from the Idaho-Montana region), along with some growth in leaching of copper ores (supplied mainly from the Arizona-New Mexico-West Texas region). Uranium ore processing should be another important and growing source of demand.

8. An estimate was made of the probable upper limit of ammonium sulfate production in the western region (924,000 short tons per year) by assuming that the Cominco absorption process might be used to concentrate sulfur dioxide from lean offgases of zinc sintering machines and copper reverberatory furnaces. Of the total, 573,000 tons would be produced in the Arizona-New Mexico-West Texas area, and 219,000 tons in Utah-Nevada. In neither area would it be possible to dispose of all the ammonium sulfate at prices high enough to pay for the ammonia used in its manufacture. In the other western smelter areas, it would be possible to dispose of the remaining ammonium sulfate at prices of $25 or more per ton fob the smelters.

It was estimated that it would be necessary to sell ammonium sulfate at prices ranging from $19 to $36.50 per ton fob the smelters in order to compete with alternative sources. The production cost of ammonium sulfate from the Cominco process is not easily definable because it is dependent on arbitrary apportionment of costs between ammonium sulfate and coproduct sulfur dioxide.

The market study was based on evaluating the extreme cases, ie, determining markets where only one major product (sulfuric acid or elemental sulfur) was assumed to be produced. However, in the realistic case, production of an appropriate mixture of the two major products, orderly penetration of available markets should be easier.

Control Method Evaluation with Plant Models

Evaluation of the general economics of the control process and of some combinations of processes was simplified by setting up hypothetical models of smelters using feed materials with specified ratios of sulfur to metal. Various systems of control processes were then applied to these models and costs were determined from the process cost graphs. Most of the models are of three sizes, covering a metal capacity range of three or four to one.

Copper Smelter Models

Two copper models were set up. Model B plant has a roaster and Model A does not. In the case of the small size Model A plant (230 tons of copper per day), gas flow is too irregular to be used in a sulfuric acid plant. A scheme that uses the stronger offgases from the medium and large model A plant, and all sizes of the model B plant, in making sulfuric acid produces the acid at costs that permit breakeven by at least some of the operators in each of the areas defined in the market study. Credits from sale of the acid cover the cost of scrubbing the weak gases with limestone slurry. With this added step, 88 to 91 percent control efficiency is attained. Without it, control efficiency is only 50 to 60 percent for model A and 83 percent for model B. Breakeven prices for the acid are lower with model B, which has a roaster, than with model A, which does not.

None of the other process systems considered are able to operate at costs that make breakeven possible under present or projected market conditions.

Zinc Smelter Models

Four zinc smelter models were created: model A, representative of modern plants with fluid-bed or suspension roasters; models B and C, representative of plants with Ropp and multiple-hearth roasters, respectively; and model D, representative of a plant using a sintering machine for simultaneous sintering and roasting. It is profitable to use the roaster gases from even the smallest model A plant to make sulfuric acid. The breakeven price for production of the acid is only $5.90 per ton for the smallest plant, and $4.80 per ton for the largest. Sulfur oxide recovery is 93 percent efficient. For model D (one size only), the breakeven price for the acid is $15 per ton. The breakeven prices of acid from models B and C are above any levels that can be realized in available markets.

None of the other schemes for recovery, such as reduction of the sulfur dioxide by the old Asarco process, can yield a product at a competitive breakeven price for any of the models.

Lead Smelter Model

Only one lead plant model was prepared, representing the three largest of the six smelters considered. These smelters use updraft sintering machines. Again, only the scheme that sends the strong sintering machine offgas to a sulfuric acid plant makes a byproduct with a competitive breakeven price. Acid production costs are $10.60 per ton for a small plant and drop to $7.30 for a large plant. One or more smelters in each marketing area can sell acid in this price range. Control is 93 percent efficient.

IV RECOMMENDATIONS

Although treatment of lean offgas streams constitutes the greatest current technical and economic problem in smelter emission control, it is believed that smelter technology will evolve toward lessening the importance of such offgas streams by adoption of newer smelting techniques that put out the bulk of the sulfur oxides in offgases of relatively high concentration. Even so, some weak offgases will continue to be produced, and since adequate technology for their control is not now available, it must be developed.

The size of the markets for sulfuric acid is so limited, particularly for smelters in the western United States, that it is necessary to emphasize research and development aimed at low-cost production of elemental sulfur, for which markets exceed potential production.

It is recommended that research and development projects be initiated in seven major areas of study:

1. Develop to the point of commercial feasibility more economic cyclic processes that can concentrate weak smelter offgas streams containing less than four percent sulfur dioxide. The goal should be a process with little or no production of secondary byproducts and minimum cost for renewal of reagents.

2. Develop to the point of commercial feasibility more economic cyclic gas absorption processes capable of concentrating sulfur dioxide from relatively rich gas streams (three to four percent sulfur dioxide, and higher) for subsequent reduction to elemental sulfur. To provide a

technical and economic baseline for these studies, an analysis should be made of the only currently operating commercial process in this category, the Asarco DMA process.

3. Develop to the point of commercial feasibility one or more conceptual processes and systems for reduction of sulfur dioxide to elemental sulfur, using natural gas, other hydrocarbon, or coke as the reductants. One objective should be to obtain realistic estimates of the probable attainable production costs for the elemental sulfur. Costs should be developed as functions of the sulfur dioxide concentrations in the feed gas, from 100 percent down to perhaps 10 percent.

4. Make an engineering study of process enclosures and process equipment designed to limit introduction or infiltration of air to a minimum. Estimated costs for a representative system, or systems, should be developed and compared with those for a typical conventional gas collecting and handling system. The economics achievable in the subsequent gas cleaning and sulfur recovery systems as the result of restricting air infiltration should be estimated.

5. Initiate a project to obtain quantitative information about smelter gases and their constituents. Measurements and analyses should be made at representative copper, zinc, and lead smelters. The objective is to define nature and magnitude of emission problems at typical plants and to define problems of catalyst poisoning, corrosion, and erosion to be considered in design of recovery systems.

6. Institute a program for development of efficient new metal recovery systems to produce metal at costs competitive with existing processes while producing offgases at high sulfur oxide concentrations.

7. Develop to the point of economical commercial application equipment capable of cleaning smelter offgases at temperatures above 600 F.

V. NATURE OF THE SMELTER AIR POLLUTION PROBLEM

a. Copper, zinc, and lead smelting practice

b. Potential air pollution problems in smelter areas

V a. COPPER, ZINC, AND LEAD SMELTING PRACTICE

Current copper and lead smelting practice in the United States is fairly uniform from smelter to smelter for each metal. There are necessary differences, since no two ores or concentrates are identical, but most of the major pieces of equipment are of similar design and are used in much the same way. In zinc smelting there are greater differences both in equipment and in processing methods.

Processes and equipment used for each metal are described in the following pages. Enough detail is given for a general understanding of each process, but the emphasis is on the sulfur contained in the materials and the variables that affect amounts and concentrations of sulfur oxides in gases released during processing.

A general idea of the process operations in the smelter plants can be obtained by referring to the flow diagrams in appendix A.

Most of the smelter plants in this country are relatively old; with few exceptions they were built more than twenty years ago. However, smelters are periodically modified, partly rebuilt, or enlarged. Several sulfuric acid units for recovery of sulfur dioxide have been added in recent years and more are planned or under construction.

Copper Smelting

Pyrometallurgical processes are used to extract the metal from copper-bearing feed materials delivered to the smelter plant. The feed materials may be prepared by drying or roasting, or they may be charged directly to a reverberatory furnace. This kind

of furnace is used in all copper smelters in this country, but in other countries blast furnaces, electric furnaces, flash furnaces, or direct-smelting converters blown with oxygen-enriched air are used in its place. Gases containing sulfur oxides are emitted from each pyrometallurgical operation except drying.

The charge is melted in the reverberatory furnace and the molten material allowed to separate into layers of matte and slag. The matte consists of copper and iron sulfides, plus minor quantities of other metals, sulfides, and oxides. One advantage of the pyrometallurgical process is that valuable metals such as gold and silver collect in the matte, another is that some volatile impurities are removed in the offgas.

The molten matte is transported to converters where flux is added and air is blown through the mass. First, iron sulfide is oxidized, the iron removed as a silicate slag and the sulfur evolved as sulfur dioxide gas, then the copper sulfide is converted to blister copper by oxidation of its sulfur to sulfur dioxide.

Blister copper is the principal product of the primary copper smelter. At some smelters, this product is fire-refined to make anode copper. For final purification, the copper is shipped to an electrolytic refining plant.

Raw Materials

By far the largest portion of copper-bearing feed material consists of concentrates containing copper and iron sulfides prepared from disseminated ore of low grade. Copper content of the sulfide concentrates usually ranges between 15 and 32 percent. Small quantities of direct-smelting sulfide and oxide ores containing four to six percent copper are added to the smelter feed where they are available, along with precipitate copper obtained from leaching mine wastes and oxidized ores. The precipitate usually contains between 70 and 85 percent copper.

A typical analysis of a high quality concentrate would show:

	percent (dry basis)
Copper, Cu	27.5
Iron, Fe	24.5
Sulfur, S	31.5
Silica, SiO_2	11.0
Other	5.5

Concentrates usually contain 10 to 12 percent free moisture as received at the smelter, precipitate contains 15 to 30 percent.

Drying the Raw Material

Since wet concentrate constitutes the major portion of the smelter feed, some degree of predrying may be economically advisable. Either rotary or multiple-hearth dryers may be used. It is normal practice to drive off only about half the moisture. Since the fuel used is natural gas in dryers at U.S. copper smelters, there is no significant amount of sulfur oxides from that source and there is none from the charge.

The flash smelting process for copper is not now used in the United States, but as practiced abroad it requires predrying the charge to a moisture content of 0.1 to 0.3 percent. Under these conditions as much as one percent of the sulfur content of the charge may be present in the dryer offgas as sulfur dioxide.

Roasting

Nearly half the copper smelters in the U.S. roast the charge of mixed concentrate and flux. The older multiple-hearth roasters have been abandoned in some plants in favor of more modern equipment. Multiple-hearth roasters usually have capacities of 150 to 200 tons of raw feed per day.

Recent installations are generally fluid bed roasters. These have been in use in copper smelters for about ten years. Capacities vary from 700 to 1500 tons (dry weight) of feed per day. The feed material may be sprayed into the top of the roaster as a water slurry or charged as a solid.

Roasting is indicated when the feed material is low in copper and high in iron and sulfur. The pyrite sulfur and iron is readily converted to sulfur dioxide and iron oxides in the roaster. Roasting generally reduces fuel consumption in the reverb to about half of that needed for greenfeed smelting, a result of the calcine being fed hot to the furnace.

Roasters can be the source of a relatively strong sulfur dioxide gas for the manufacture of sulfuric acid. Their primary advantage is that the sulfur evolved in the roaster gas and oxidized iron subsequently removed in the reverberatory furnace slag reduce the amount of matte formed and cause it to be richer in copper. This cuts the oxidizing load on the converters.

Multiple-hearth roasters usually operate at a temperature of about 1200 F. Sulfur dioxide concentration in the wet offgas is usually only five to ten percent because of low efficiencies in the furnace and dilution by air. The dust load in the offgas is around three to six percent of the weight of the feed. A large portion of the dust is recovered in the flues.

Fluid-bed roasters operate in the same temperature range as multiple-hearth roasters. However, about 85 percent of the feed is carried in the gas stream and most of it is immediately recovered in cyclone collectors. The wet offgases run 12 to 14 volume percent sulfur dioxide.

After preliminary solids collection, the gas from either type of roaster is cooled to 600 F by air dilution, water sprays, or heat exchangers before the final cleaning in electrostatic precipitators (Cottrells).

Handling of collected dust and hot calcine is the major problem in roasting. These are difficult materials. Much dust is generated and equipment maintenance costs are high.

Reverberatory Furnace Smelting

The reverberatory furnace melts the metal-bearing charge and forms the matte and slag. These furnaces range in size from 22 by 96 feet up to 38 by 125 feet and hold a molten bath 24 to 48 inches deep. Feed rates are on the order of 400 to 1100 tons of new charge per day. The charge is introduced through openings in the side wall or in the roof.

During the melting phase in the furnace about one-fifth to one-half of the sulfur in the charge is oxidized. When the feed is calcine from roasters, the sulfur dioxide evolution is lowest. The range of sulfur dioxide concentration in the wet offgas is 0.5 to 3.5 percent, depending on feed and operating conditions. Of the sulfur in the charge, 70 to 80 percent is removed in the matte, 18 to 30 percent in the flue gas, and one to two percent in the slag.

Typical operating conditions for natural gas or oil-fired furnaces are as follows:

Furnace bath temperature	2400 F
Excess air	1 - 4 percent
Furnace pressure	± 0.1 in. of water
Dust load in offgas	2 - 5 grains per scf
Sulfur dioxide in offgas	0.5 - 3.5 percent

The offgas composition at 2400 F for a typical furnace outlet of 45,000 to 60,000 scfm before air dilution is shown below in volume percent for both raw and calcined feed:

Component	Green Feed	Calcined Feed
Carbon dioxide	8.4	10.2
Nitrogen	69.3	71.0
Oxygen	0.25 - 1.0	0.25 - 1.0
Water	18.8	17.7
Sulfur dioxide	1.5 - 2.5	.6

The two molten products of the furnace generally have the following range of values (in percent):

Component	Matte	Slag
Copper	25 - 50	0.4 - 0.7
Iron	29 - 35	34 - 40
Silica	0.8 - 1.0	35 - 40
Sulfur	22 - 29	1.0 - 1.5

Reverberatory furnaces require substantial quantities of combustion air, about 12 volumes to one of natural gas. The ratio of air to gas is set so that it is just slightly on the oxidizing side of the theoretical ratio for complete combustion of the fuel. About a quarter of the heat generated is required to melt the charge and maintain the temperature. It is universal practice to install waste heat boilers at the gas outlet of the reverberatory furnaces. They serve to cool the gases and about half of the heat value is thus recovered for steam generation of electric power. Most of the power needs of the entire plant are supplied in this manner. The remainder of the furnace heat is lost in the offgases. Some smelters are recovering part of the waste heat by using it to preheat combustion air to obtain higher flame temperatures and reduce fuel requirements. This tends to reduce the volume of offgas and increase sulfur dioxide concentration.

Collection and recovery of dust from the furnace gas is a substantial problem. The heavier particles settle below the waste heat boilers, and into the hoppers of the balloon flues. Practically all copper smelters have a main collector system that includes drag or screw conveyors that remove the dust from the various places where it accumulates. The dust is then moved to locations where it can be worked back into the system for recovery of values it contains.

The main dust collector is an electrostatic precipitator. When properly designed and maintained, precipitators have a collection efficiency that ranges from 95 to 99 percent or higher. Sometimes dust recovery efficiency is improved by introduced conditioning agents. The gas is humidified and cooled to about 600 F before it enters the collector. Normal gas flows may be as high as 85,000 scfm per furnace, and dust loads are one to five grains per standard cubic foot at the precipitator inlet, depending on how much dust has dropped out in the flues and the boiler.

Conversion of Matte to Copper Metal

Molten matte produced in the reverberatory furnace is transferred in ladles to the converters using overhead cranes.

The converters now in use in nearly all copper smelters are of the cylindrical Peirce-Smith type. The most common size is 13 feet in diameter by 30 feet long, with a capacity of about 135 tons of copper per day from matte of average grade.

The function of the converters is to oxidize and separate the iron and sulfur from the matte. Air is blown into the liquid matte through openings called "tuyeres". The oxidation reactions supply enough heat to maintain the converter at a temperature of about 2250 F and no fuel is required. The sulfur dioxide is carried out with the other flue gases. Silica flux is added to combine with the iron oxide to form a fluid iron silicate slag. The slag is skimmed from the converter and returned to the reverberatory furnace for settling out some contained copper. Additional matte is added to the converter and the process repeated until a suitable charge of copper sulfide has been accumulated. Blowing is then continued without further matte additions until the remaining sulfur has been eliminated. The resulting blister copper is usually more than 99 percent pure. It is removed from the converter to be cast or further refined.

Generally two operating converters are required for each reverberatory furnace. A converter may make from one to three cycles in 24 hours, with actual blowing time totalling about 70 to 75 percent of the cycle. Converter air rates are 15,000 to 20,000 scfm. The finish (white metal) blow takes about 30 percent of the blowing time. The gas rate through each converter mouth averages 12,000 to 15,000 scfm over a 24-hour period, down-time included, and sulfur dioxide content is 14 to 21 percent. Maximum flow is about 18,500 scfm. However, air infiltration into the hoods and flues may be from one to over three

times the volume at the mouth, and the sulfur dioxide concentration in the flue system can range from 1.5 to 7.0 percent.

With hoods of special design and with vigilant draft control, it is practical to convey gas through the converter flue at a sulfur dioxide concentration of 3.5 to 7.0 percent, with an average of not more than 5.5 percent. To do that well requires careful planning of the cycles of two or more converters, although some smelters in Japan get less air dilution and higher sulfur dioxide concentration. Hoods of those smelters are designed to fit more tightly, are water-cooled, and waste heat boilers cool the gas without dilution.

The nearly air-tight Hoboken type of converter can deliver a richer and more uniform gas than the Peirce-Smith converter, but none have been installed in U.S. smelters.

The availability of efficient and low-cost air separation plants has made the use of oxygen-enriched air in the converters attractive for increasing metal production and improving the concentration of sulfur dioxide in gases fed to the acid plant. The process has less heat loss because the volume of nitrogen blown through is smaller, and this speeds up sulfur oxidation to the point where raw concentrates can be added to cool the reaction and produce matte in the converter. This in effect reduces sulfur emission from the reverberatory furnace and transfers it to the converter for more efficient recovery. Volume of material handled in the reverb is reduced. There are plans to use oxygen in all converters at one large U.S. smelter, and another is already doing so.

Dust loads in converter gases may amount to 10 to 20 tons per day per unit. About 75 to 85 percent of these solids settle in the flue system. The remaining 15 to 25 percent, composed of the smaller particles, is largely removed in the dust collectors, which are electrostatic precipitators or cyclone collectors.

Blister copper, the end product of the converter, requires further refining in order to meet most purity specifications for fabricated copper products. It usually contains about 0.04 percent sulfur. Of the 16 copper smelters in the U.S., five produce blister copper only. The others fire-refine part or all of the blister copper for anodes or other shapes.

Fire Refining

Fire refining is accomplished by blowing air through the molten metal to oxidize some impurities and skim them from the top as small amounts of slag. Those metals not oxidized, including the precious metals, remain in the copper to be removed at the electrolytic refineries. The cuprous oxide formed is subsequently reduced by immersing green logs in the molten copper, or by blowing reducing gases through it. Sulfur removed is only about 75 pounds per 100 tons of copper treated. The product of fire refining is a copper with excellent casting qualities for anodes and other shapes.

Sulfur Recovery

Recovery of sulfur in copper smelting has been limited to five of the 16 U.S. smelters. Sulfuric acid is the byproduct of recovery, except in one plant that produces small amounts of liquid sulfur dioxide. Sufficient concentration of sulfur dioxide for acid manufacture occurs only in converter gas and roaster gas. Converter gas is somewhat marginal in most smelters. Concentrated sulfur dioxide for liquefying is obtained by an absorption process from a side stream of the acid plant feed.

One large acid plant complex and a smaller one use only converter gas as feed. Two use a blend of roaster and converter gas, and one uses roaster gas only.

Zinc Smelting

Several different combinations of processes are used by zinc smelters to prepare the ore concentrates for extraction of zinc, as can be seen by referring to the zinc flow diagrams in appendix A. The choice of methods depends on physical and chemical properties of the raw material and on the extraction process that is to be used. Extraction of zinc requires that the raw material first be processed to convert the zinc content to a dense form of zinc oxide. Roasting, sintering, and calcining are three pre-extraction operations that are used to accomplish this.

Some plants both roast and sinter zinc sulfide concentrates before extraction. One plant uses only sinter machines, but in effect is both roasting and sintering in one operation. Calcining is performed only on oxide ores or on material that has previously been oxidized by roasting. Gases containing sulfur oxides are given off in large quantities in roasting and sintering, but very little in calcining.

The zinc metal is extracted from the preprocessed material either by pyroreduction with carbonaceous fuel, followed by distillation, or by dissolving the zinc oxide in an acid solution and then precipitating the metal electrolytically. Neither method generates significant amounts of sulfur oxide gases.

Zinc oxide and metallic zinc are the principal products of zinc smelting.

Development of the Industry

The zinc smelting industry was developed in the United States over a period of 70 years beginning in 1861. The latest zinc plant built is the one at Corpus Christi, Texas, which started operation in the fall of 1942. However, most of the older smelters have been modernized. Both methods and equipment for recovery have been altered to meet changing conditions and developments. Some older plants have been abandoned in recent years and another, the plant at Henryetta, Oklahoma, was scheduled to be closed early in 1969.

There are now 15 primary zinc smelters in the U.S. Five of these use electrolytic extraction and nine are distillation or retort plants. Two of the distillation plants process material that has been preroasted at other plants, and there is one smelter that produces only zinc chemicals, oxide, and calcine for shipment to other plants. Many of the smelters have zinc fuming units in which lead-rich material is fumed to recover the zinc.

Raw Materials

Zinc is found in nature most abundantly as a sulfide. The ore deposits usually contain an equal amount of lead, together with lesser quantities of iron and copper sulfides. The sulfides are

separated from the gangue and to a certain extent from each other by differential flotation. A typical zinc concentrate prepared for smelting may contain 52 to 60 percent zinc and 30 to 33 percent sulfur, with some 4 to 11 percent iron. There is also a small amount of lead and minor quantities of cadmium and copper.

Occasionally small quantities of oxide ores are available and are combined with a sulfide for processing. Franklinite ore is an exception. It contains nearly equal quantities of manganese, iron and zinc and is especially processed to recover zinc and a ferromanganese alloy in the one area in this country where it occurs.

Roasting

Zinc sulfide concentrates are usually converted to zinc oxide calcines by a roasting process that oxidizes 93 to 97 percent of the sulfur to sulfur dioxide. About one-sixth of the sulfur remaining in the calcine is present as sulfide and the rest is sulfate. Total sulfur in the completely roasted calcine from the roaster ranges from 2.0 to 3.5 percent, and in the calcine from a partial roast may be from eight to 20 percent. The several types of roasters are listed in Table V a - 1 along with some typical operating conditions.

There are 12 plants roasting sulfide concentrates. Two of these use the old Ropp roaster, which produces a roaster gas too low in sulfur dioxide for recovery by an acid plant. One plant uses multiple-hearth roasters that produce a much-diluted waste gas with less than 1.0 percent sulfur dioxide, also too low for recovery by an acid plant. Nine plants recover a large part of the sulfur with acid plants. One of these uses multiple-hearth furnaces only for the first stage of a two-stage roasting process. Roasting capacity in the remaining plants is about equally divided between fluid bed and suspension roasters.

Operating conditions for roasting zinc sulfide concentrates vary from plant to plant according to the composition of the raw material and the specific use of the roaster calcine. Higher roasting temperatures (1800 F and over) eliminate more cadmium, and

TABLE Va-1

TYPICAL ZINC ROASTING OPERATIONS (1)

Type of Roaster	Operating temp. F	Feed Capacity ton/day	Dust in Offgas % of feed	Offgas SO_2 %
Multihearth	1,200-1,350	50-120	5-15	4.5-6.5
Multihearth (2)	1,600-1,650	250	5-15	4.5-6.5
Ropp (3)	1,200	40-50	5	0.7-1.0
Fluid bed (4) (Dorr-Oliver)	1,640	140-225	70-80	7-8
Fluid bed (2) (Dorr-Oliver)	1,650	240-350	75-85	10-12
Fluid bed (Lurgi)	1,700	240	50	9-10
Suspension	1,800	120-350	50	8-12
Fluid column	1,900	225	17-18	11-12

(1) Dead roast except where noted otherwise.
(2) First stage is a partial roast in multihearth, second stage is a dry-feed dead roast in Dorr-Oliver fluid bed.
(3) Partial roast
(4) Slurry feed

increase the formation of ferrites. Excess oxidizing air results in lower temperatures and good sulfur elimination, but also lowers the sulfur dioxide concentration in the roaster gas.

Ropp Roasters

The few plants that still use the Ropp hearth roaster produce a calcine containing five to nine percent total sulfur.

The Ropp roaster is the oldest type still in use. It is a long, narrow, mechanically rabbled reverberatory furnace divided into two parallel hearths. Air dilution in the roaster is 50 to 80 percent of the theoretical offgas volume. Offgas volumes range from 20,000 to 35,000 scfm. Temperature of the offgas ranges from 730 to 900 F and sulfur dioxide content is 0.7 to 1.0 percent.

Multiple-Hearth Roasters

Multiple-hearth roasters are the next oldest type currently in use in the zinc industry. These units are usually 20 to 25 feet in diameter and have from seven to 16 hearths. When used for partial roasting, capacities are 100 to 250 tons of feed per day. Most of the calcine is completely roasted (dead-roasted), using the exothermic heat of reaction of the sulfur with the oxygen of the air. However, in order to attain a sulfide sulfur content as low as 0.5 to 1.0 percent in the calcine, some auxiliary fuel must be used on the lower hearth. This amounts to 3.5 to 4 million Btu per ton of feed. Waste heat recovery is not practical with multiple-hearth roasting because of the relatively low temperature and large volume of the offgas.

A typical multiple-hearth roaster operation produces 5000 to 6000 scfm of offgas containing about 5.7 percent sulfur dioxide. The gas is subsequently cooled by air dilution to 500 to 520 F and humidified before entering the Cottrell (electrostatic precipitator) for removal of dust. Volume and concentration at this point are 15,000 scfm and 3.3 percent sulfur dioxide, respectively. After the precipitator, the gas is diluted further to around 42,000 scfm and 0.75 percent before discharge through the stack.

Suspension Roasters

Suspension or flash roasting evolved concurrently with the increasing availability of finely-ground sulfide concentrates that resulted from development of ore concentration by flotation. The process resembles the burning of powdered coal in furnaces, in that the finely-ground concentrates are sprayed into the combustion chamber in a stream of combustion air. The sulfur content of the zinc concentrates becomes a fuel because of heat evolved by oxidation of the sulfides to sulfur dioxide.

A suspension roaster consists of a refractory-lined, cylindrical steel shell enclosing a large combustion chamber in its upper portion. The lower part contains two to four hearths similar to those of the multiple hearth furnace. Rabble arms on a rotating shaft move the material on the hearths. The lower one or two hearths dry the feed material before it is ground in an auxiliary ball mill and sprayed into the upper combustion chamber. Calcining is completed on the upper hearths.

The concentrate burns rapidly in suspension, eliminating from 90 to 98 percent of the sulfur while generating a temperature of 1800 to 1900 F. About half of the calcine particles are retained on the hearth and the rest leave in the offgas stream.

The combined offgases enter the waste heat boiler at 1600 to 1800 F and are cooled to 550 to 600 F. The gas is typically further conditioned by diluting it with air and humidifying it with water sprays before final cleaning by the electrostatic precipitator. Sulfur dioxide concentration of the gas leaving the roaster is usually 10 to 13 percent. The volume ranges from 10,000 to 15,000 scfm. After conditioning, water vapor has increased the gas volume to 17,000 to 25,000 scfm and the sulfur dioxide concentration has fallen to six to eight percent.

Dust particles are recovered from the gas in the waste heat boiler, cyclone collector, flues, and finally the precipitator. Recovered dust goes to the top calcine hearth for final roasting, except for the dust collected in the precipitator. Precipitator dust is recycled to the roaster.

The suspension roaster is operated to produce a calcine with less than 0.1 percent of sulfide when the calcine is to be further processed for recovery of zinc by electrolysis. The roasters are regulated to produce a calcine with up to two percent of sulfide sulfur when the calcine is to be nodulized or sintered.

Fluid-Bed Roasters

Fluid-bed roasters for zinc sulfide concentrates are a recent development. Several variations are now in use. The chief differences are in the methods used to charge the concentrates. Some Dorr-Oliver units are fed with a slurry, containing 70 to 80 percent solids, that is sprayed into the lower part of the reactor chamber. The rate of feeding provides some control of temperature, which ranges around 1625 to 1750 F. Some fluid-bed roasters are fed by means of feeders that convey a moist feed directly into the reactor chamber, others use a feeder that charges dry, solid feed.

The volume of gas from a single roaster is 6000 to 10,000 scfm and the sulfur dioxide concentration is 10 to 12 percent. As shown in Table V a - 1, from 50 to 85 percent of the feed to the roaster is carried as dust in the offgas stream. The gas usually passes through a waste heat boiler in which the gas is cooled and the first increment of dust is collected. More dust is recovered in a cyclone and the gas then flows to an electrostatic precipitator. In the process of cooling and cleaning the gas, it is diluted with air and water vapor and the volume is increased to between 11,000 and 18,000 scfm, with sulfur dioxide concentrations of six to seven percent.

Dust loads in the offgases may be reduced by enlarging the diameter of the combustion chamber above the bed. None of the collected dust returns to the roasters but is combined with the bed overflow that goes to the calcine cooler.

The use of solid feed and a larger combustion chamber usually results in a slightly increased operating temperature. The sulfide sulfur residue in the calcine may be as low as 0.1 percent, while a slurry-fed unit generally puts out a calcine with 0.7 to 3.0 percent.

Capacities of the slurry-fed units range from 140 to 225 tons per day. The solid-feed units have capacities from 240 to 350 tons per day. As now operated, fluid-bed roasters can furnish an acid plant with gases containing seven to nine percent sulfur dioxide.

Fluid-Column Roasters

A newer type of fluidization roaster was placed in operation during 1968. This unit is described as a fluid-column roaster and its operation approaches true fluidization, accomplished primarily by pelletizing and closely sizing the feed. The product does not require sintering.

The horizontal cross section of the fluid-bed area of the roaster is a long rectangle and above it is a large chamber. The charge is supported on a perforated false bottom through which some of the air enters. There are additional air inlets on each side of the bed. Gas from the upper chamber goes directly to a waste heat boiler. The unit has a capacity of 225 tons of feed per day and only 17 to 18 percent of the feed is carried off as dust. Operating temperature is 1900 F and the offgas contains 11 to 12 percent sulfur dioxide. Total sulfur in the calcine is 1.0 to 1.5 percent with the sulfide sulfur estimated at 0.3 percent.

Sintering

Sintering in the zinc industry is used mainly to agglomerate a roaster calcine for subsequent processing. Since the bulk of the sulfur has been removed in the roaster, only minor amounts of sulfur oxides are in the sinter machine offgas. However, the process is sometimes used with only raw sulfide concentrates or a mixture of calcine and raw concentrates as feed, and large amounts of sulfur oxides are then present in the offgas. Table V a - 2 shows three typical sintering operations, varying in size, capacity, and feed. Operating temperature is 1900 F in each case.

TABLE V a-2

TYPICAL ZINC SINTERING OPERATIONS

Case:	1	2	3
New feed material	calcine	calcine	concentrate
Total charge capacity tons per day	240-300	400-450	550-600
Machine size, ft	3.5 x 45	6 x 97	12 x 168
Fuel added to feed, %	6 - 7	10-11	0 - 2
Total sulfur in new feed, %	8	2	31
Recycle, % of new feed	35-75	40-70	80
Dust in offgas, % of feed	5	5 - 7	5 - 10
Offgas SO_2 content, %	1.5-2.0	0.1	1.7-2.4

Sintering machines have continuous conveyors made of grate-bar pallets, upon which the feed material is placed and processed. These conveyors range in size from 3.5 ft wide by 45 ft long up to 12 ft wide by 168 ft long. Downdraft machines are universally used in the zinc industry. The downdraft is produced by sectionalized wind boxes installed beneath the line of travel of the pallets. This construction permits draft regulation in separate areas of the grate. The gases may be recirculated from one end of the machine to the other.

Sintering machine sizes range from around 100 to 2000 square feet of bed area. In most of the calcine sintering plants the net capacity variation is from 0.75 to 1.75 tons per day of feed per square foot of bed area. Extreme values for capacity appear to be 0.25 tons per square foot for concentrate feed, and 2.5 tons for a specialized sinter of low-sulfide calcine.

Gas and air rates also range widely. With a calcined feed, exit gas rates are from 140 to 240 scfm per square foot of grate. In contrast, with a concentrate feed the gas rate is only 18 to 20 scfm per square foot.

With air at three to five times the theoretical amount to burn the coke and residual sulfur, the temperature of the combined exit gas ranges from 500 to 700 F. Sinter exit gas is further cooled by air dilution and water sprays to condition it for cleaning in dust collectors.

Feed for the sintering machine is a mixture consisting of calcine or concentrates, recycled ground sinter, recovered dust in some plants, and the required amount of carbonaceous fuel of proper particle size and moisture content for pelletizing. After the mixture is pelletized, it is sized in the range of 20 mesh to one-half inch.

A swinging feed spout distributes a continuous layer of pellets on the moving pallets. As the pallets come under a small oil- or gas-fired muffle, the bed is ignited. In the presence of the forced air stream flowing down through the porous bed, the ignited material burns rapidly, reaching temperatures high enough to form a porous and relatively hard clinker. The sintered product is discharged from the pallets as they turn over at the end of the

machine for return to the feed end. Combustion gas and dust are moved from the wind boxes by draft fans to dust collection equipment. Discharged sinter is usually recycled to the feed in amounts varying between 30 and 80 percent of the total machine feed. This recycle is obtained by first crushing and sizing the total discharge, then grinding the amount required for recycle. The balance of the discharge is a coarsely crushed material that is the product used for zinc extraction.

Sintering is also performed as a two-stage operation. In this case, extraction product and recycle come from the second stage discharge. Discharge from the first stage is crushed, mixed with fuel and recycle, and pelletized before being fed to the second stage. Other materials such as silica, dust, and concentrates may also be fed to the second stage. Two-stage sintering is done to get a finished sinter with specific physical properties.

Usually five to 10 percent of the total feed is carried out in the offgas as dust. Dust recovered from the offgas may be either recycled or treated for lead and cadmium recovery. Sulfur dioxide concentrations in the gas are rather low, ranging from 0.1 to 2.0 percent for calcine up to 2.4 percent for concentrates. However, it is possible to enrich the gas when sulfide concentrate rather than calcine is the major raw feed. This is done by recirculating the gases from the latter half of the machine to the feed end. Sulfur dioxide contents of 6.0 to 6.5 percent can be obtained in this way.

Calcining

Calcining is a heat treating process that is used for oxidized materials such as oxide ore concentrates or material from roasting of sulfide ore concentrates. It may be called nodulizing, since hard nodules of random sizes are produced when the calcining is done in a rotary kiln. The nodulized kiln product is subsequently treated for zinc extraction. Sulfur oxides are evolved only when processing roaster calcine that contains small amounts of sulfur, and in such cases the waste gas from the kiln may have from 0.1 to 0.2 percent sulfur dioxide. This represents 0.2 to 0.3 percent of the total sulfur in the concentrate fed to the roaster. The waste gas also contains some fume, which is removed in bag filters and treated for recovery of lead and cadmium.

Extraction

Roasting, sintering, and calcining are preliminary steps to one of the extraction methods: pyroreduction or leaching and electrolysis. Any sulfur entering the pyroreduction process is mostly in the sulfate form and tends to remain as such. Small amounts of sulfide sulfur are present in both the calcine and the carbonaceous reducing material, however, and the odor of sulfur dioxide is noticeable around some pyroreduction and zinc fuming plants.

Pyroreduction distillation or retorting of the sinter or calcine is performed in horizontal or vertical retorts, electrothermal open or submerged arc furnaces, or blast furnaces. Horizontal retorts are small ceramic cylinders that are mounted horizontally in racks that hold several rows of retorts mounted one over the other. They are fed with coal and sinter and produce liquid zinc metal, as do the larger and more modern vertical retorts. Vertical retorts make a byproduct carbon monoxide gas that is used as fuel in other parts of the plant.

A new blast furnace process was developed in the 1930's and is in use in several parts of the world but not in this country. This is the Imperial smelting process. One of its reported advantages is that it can be used to treat material containing both lead and zinc and produce each metal as a separate, molten product.

Zinc fuming can be either an extraction or a pre-extraction operation. In this step, zinc is reduced to metal by carbon or carbon monoxide, vaporized, and reoxidized to form a zinc oxide fume which is collected in bag filters. The zinc oxide collected may be fairly pure, in which case it is a final product. If it contains appreciable quantities of lead and cadmium it is usually treated further.

When calcine is extracted by leaching, the small amounts of sulfides dissolved are removed in the purification of the leach solution.

Sulfur Recovery

Nine of the fifteen zinc smelters in this country recover sulfur oxides from offgas. Two more are smelting material that contains very little sulfur. Four smelters handling sulfur-bearing raw materials do not have recovery units. The smelters with recovery units recover sulfur oxides as sulfuric acid, and only from roaster gas. No sulfur is recovered from the sintering process, primarily because more than 80 percent of sinter feed is dead-roasted calcine.

Lead Smelting

All primary lead smelters in this country use essentially the same processing steps, although there are differences in the equipment used and the details of operation. The principal process steps are sintering, reduction in a blast furnace, and refining. Refining includes operation of the dross reverberatory furnace. Smelter operations usually include cadmium recovery and slag fuming for zinc recovery.

Lead sulfides are converted to oxides of lead and sulfur in the sintering step at a relatively low temperature. The oxidized solid material is then reduced with coke in the blast furnace at a high temperature to form impure metal and slag. A preliminary refining operation is performed on the impure lead from the blast furnace. Lead bullion, 95 to 99 percent pure, is the principal product of lead smelting operations.

There are a number of secondary products. Some, such as zinc oxide products and cadmium dusts, may be ready for marketing as they leave the plant, and some, such as slag, matte, or dusts, may be shipped to other plants for extraction of values, primarily zinc, cadmium, silver, and copper. These other products vary from plant to plant, as one plant may put out several finished products, while another may ship only lead and unrefined materials.

This country had only six complete primary lead smelting plants in operation until toward the end of 1968. At that time construction of another lead smelter was completed in Missouri, the first new one in many years. Another was under construction in the same state and began operating in 1969. All of the older smelters have been expanded and modernized several times.

Sulfur Oxide Emissions and Control

Production of sulfur oxides from lead smelters, in proportion to the metal produced, is low as compared with copper and zinc smelters. This is because the lead mineral, galena, has only 0.155 pounds of sulfur per pound of metal, where zinc sulfide has 0.49 pounds and the principal copper sulfide minerals have from 0.25 to 1.01 pounds.

Only two of the older plants now have a plant unit to recover the sulfur oxides as sulfuric acid or are in the process of installing one, but another plans to install a sulfuric acid unit in 1969. One of the plants that now makes sulfuric acid also produces liquid sulfur dioxide with the help of a special scrubbing process developed over 20 years ago. At least one of the new Missouri smelters will make a sulfuric acid byproduct.

Raw Materials

The primary raw material is a lead sulfide concentrate containing minor amounts of zinc, iron, and copper. Some high-silica lead ores are added to provide some of the large proportion of silica needed for slag formation. Small quantities of electrolytic zinc plant residues are added when they are available. Some flux is necessary.

The concentrate generally has from 55 to 70 percent lead, up to 6.5 percent zinc, 0.5 to 4.0 percent copper, 13 to 18.5 percent sulfur, up to 5.0 percent iron, and minor amounts of silica, lime, cadmium, silver, gold, and arsenic depending on the source.

The flux materials used are high grade limestone, silica, and small quantities of scrap steel or iron. These are added in the proportions required to produce a free-running slag that contains the bulk of the zinc and iron from the furnace feed. Flux materials and ores are crushed, sized, and mixed with the concentrates, residues, and recycled sinter to form the feed to the sintering operation. Some flux materials may be added at the blast furnace.

Sintering Machine

Sintering is universal practice in the lead smelting industry. Its purpose is to roast to remove sulfur and at the same time sinter to produce a calcine that is consolidated in a strong and porous mass suitable for reduction in a blast furnace. Generally, about 85 percent of the total sulfur in the feed to the smelter is emitted in the sintering operation and 14 percent enters the slag and other solid byproducts. The remaining one percent is distributed between the blast furnace and dross furnace offgases.

The main chemical reactions taking place on the sintering machine are the oxidation of lead and other metal sulfides with oxygen of the air. Lead oxide and the oxides of other metals are formed, along with sulfur dioxide gas. Heat is generated by these reactions. The temperature should be kept below 1400 F as much as possible to prevent excessive loss of metals by volatilization, fusion of the clinker, and damage to the grating of the pallets.

Temperatures are controlled to some extent by limiting the sulfur in the charge to between six and 12 percent. The higher concentrations are only for two-stage sintering. Mixing the concentrates with sulfide-free fluxes such as silica and limestone, and with recycled sinter and blast furnace or fume furnace slag, dilutes the sulfur of the concentrates so that the percentage in the whole charge falls to the desired level. Substantial volumes of excess air, regulated as described farther on, complete the control.

Sintering machines are continuous conveyors made of grate-bar pallets joined together. They are known as Dwight-Lloyd machines, and are similar to the machines already described in this section for use in zinc smelting. Sizes range from 3.5 by 22 feet to 10 by 103 feet, and capacities are 1.5 to 2.75 tons of charged material per square foot of bed area per day.

Most of the older and smaller machines are of the downdraft type. A sectionalized windbox installed beneath the pallet line is used to regulate the burning rates in the machine. Newer installations usually have a single large updraft machine with the windbox located above the pallets. If gas is recycled from end to end, a second box is placed under the feed end to direct the recycle.

Feed for the sinter machine is mixed, then usually pelletized. A single feeder loads each pallet of the downdraft machines, and the pallets are ignited by a gas flame as they travel under a muffle. Updraft units have two feeders in series. The first puts down a thin layer that is ignited before the pallet reaches the second feeder. The second layer is usually 12 to 18 inches deep. The regulated updraft causes the burning zone to progress from bottom to top. Gases are drawn through the upper wind box into ducts leading to dust collection equipment.

As pallets turn over at the end of the machine, the clinker cakes drop to a coarse breaker and screen. Enough of the oversize material is ground and added to the fines to supply the required recycle to the front end of the machine.

Updraft Machines and Acid Units

Updraft machines have the advantage of better sulfur elimination with single-stage operation, higher concentration of sulfur dioxide in the offgas because of less air infiltration, ability to control the burning rate by a regulated recycling of a portion of the offgas from discharge end to feed end, and better cadmium recovery because of a lower ratio of dust to fume in the offgas. The higher sulfur dioxide concentration is needed for low-cost recovery of sulfur as sulfuric acid.

One of the older plants plans to replace its downdraft machines with a large updraft machine in 1969 and is installing a sulfuric acid recovery unit. About 67 percent of U.S. lead plant sinter machine capacity, excluding the two new plants in Missouri, will then be of the large updraft type. Both the new Missouri plants have updraft machines and one has an acid plant. Two other large plants already have updraft machines but do not have acid plants. One of these will have an acid plant operating in 1969.

Sintering in One or Two Stages

Sintering may be done in one or two stages. With either method, some 40 to 60 percent of the crushed final clinker is recycled and mixed with the feed. The final calcines or clinker are similar in single- and two-stage sintering and contain from 1.0 to 3.5 percent of sulfur values. Figure Va-1 shows a typical example of the distribution of major materials in single-stage sintering.

In two-stage sintering, from 30 to 40 percent of the sulfur is removed in the first stage. Clinker from the first stage is crushed, mixed with one to two percent of coke for fuel, and fed to the second stage.

Sinter Machine Gases

Sulfur dioxide concentration in the sinter machine offgas may be 0.8 to 1.8 percent by volume. Gas volumes run 100 to 220 scfm per square foot of bed area. When the offgas is to be fed to a sulfuric acid unit, the machine is operated to produce a smaller volume of gas with four to six percent or more of sulfur dioxide. These richer gases are obtained from updraft machines, as noted, by recycling gas or by drawing the gas for the acid plant mostly from the feed end of a downdraft machine.

Offgas temperatures depend on the amount of air entrained, but are usually between 250 and 600 F. The dust and fume load carried by the gas is usually from five to 20 percent of the feed to the machine. Either bag filters or electrostatic precipitators are used to recover this material, after the gas has been cooled and conditioned by water sprays. Collected material is recycled to the feed for the sintering machine. Fume is condensed and collected with the dust. The recovered dust contains portions of all the metals present in the concentrate, even gold, silver, and copper, and is relatively rich in the more volatile metals and oxides.

A small part of the lead and cadmium is vaporized during sintering. This condenses and is collected with the dust and recycled. Such vaporization and collection of the fume provides an opportunity for concentrating and recovering cadmium if enough is present. A portion of the dust containing 12 percent or more of cadmium may be diverted to a cadmium furnace and the balance recycled to the sinter machine.

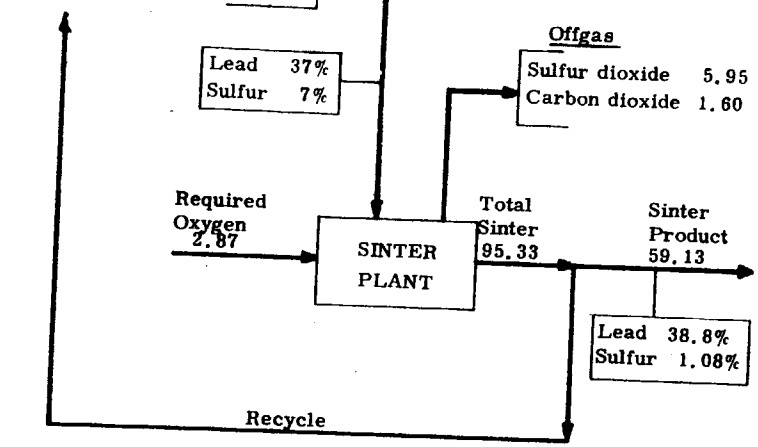

FIGURE V a-1

Typical Distribution of Major Materials in Single-Stage Lead Smelting

Quantities of dust, fume, air, etc. are not shown

In addition to the sulfur oxides, sinter machine offgases contain air, water vapor and carbon dioxide, and sometimes hydrogen fluoride, silicon tetrafluoride, and traces of other gases. Organic vapors from flotation reagents in the concentrates are present in the offgases. The flotation reagents are distilled and pass into the offgas stream without meeting temperatures high enough to completely oxidize them. Fumes contained in the offgas include oxides of arsenic, cadmium, lead, zinc, selenium, tellurium, and traces of other substances. Elemental sulfur is present and may be more than one percent if the percentage of pyrites in the sinter charge is relatively high. There is a real danger of fire in flues and bag filters because of this.

Sulfuric acid recovered from lead smelter offgases is often quite dark in color because of the organic vapors from flotation reagents. These get into the sulfuric acid in the gas-drying tower, where the strong acid chars them. The acid may be any color from yellow to black as a result. The concentrate from each mill is different. Even the coke used as supplementary fuel contains enough organic matter to discolor the acid. Because of the color, sulfuric acid from a lead smelter has usually sold at a lower price than acid from brimstone. The dark acid can be bleached by adding hydrogen peroxide, although this step may be expensive. From 0.5 to 4.0 kilos of 30-percent peroxide costing upwards of $0.38 per kilo may be needed per metric ton of acid.

Blast Furnace

The purpose of the blast furnace is to reduce the lead oxide in the sinter to metallic lead. The reducing agent is carbon monoxide derived from coke fed into the furnace. The heat needed for this main reaction and the various other reactions is supplied by complete combustion of some of the coke to carbon dioxide. Carbon monoxide for the reduction is formed in a reaction between the remaining coke and some of the carbon dioxide. The important reactions are

1) $PbO + CO + heat = Pb + CO_2$
2) $C + O_2 = CO_2 + heat$
3) $C + CO_2 + heat = 2\,CO$

Numerous other reactions take place, the more important being reduction of some of the iron and zinc oxides.

Furnace reactions 1) and 3) use heat generated by reaction 2) and proceed rapidly at the relatively low temperature of 1000 to 1200 F. The reduction of iron and zinc oxides to the metals requires higher temperatures and tends to be suppressed by the high concentration of carbon dioxide and oxygen. As a result these oxides react with silica to form slag. Blast furnace slag is fluid at the temperature of the lower part of the furnace and protects the liquid lead against reoxidation. In operating the blast furnace, temperatures in portions of the furnace are higher than the gas temperatures given here, and there is consequently some distillation and removal of lead oxide and zinc oxide fumes in the flue gas, along with the entrained dust. Cadmium oxide and oxides of other metals that can be vaporized in either reduced or oxidized form are also present in the fume.

Most of the sulfur contained in the sinter (1.0 to 3.5 percent) and the coke (about one percent) leaves the furnace in the liquids discharged from the furnace bottom. Only small amounts of sulfur dioxide have been reported in the furnace flue gas, ranging from 0.01 to 0.25 percent after dilution. Theoretical flue gas rates vary with the size of the furnace from 6000 to 14,000 scfm, but several times this volume of air leaks into the top of the furnace. By the time the gas leaves the bag house dust collector, additional dilution with air and water vapor has increased the flue gas volume to nine to 12 times the theoretical flow.

Dilution of the flue gas at the top of the furnace is necessary, since without it the gas would have a temperature near 1100 to 1300 F and contain 25 to 50 percent carbon monoxide. The dilution air burns the carbon monoxide to carbon dioxide but the volume is large enough to also cool the gas. Final gas temperature at the baghouse is usually 150 to 250 F.

Blast Furnace Design

Blast furnaces used in lead smelting have a horizontal cross section that is rectangular, with length at the hearth from 3.5 to five times the width. There are tuyeres in each side, and above these the two long sides slope outwards for a third of the shaft height. In the upper two-thirds of the shaft, the outward slope is less. Shaft sides and ends are made of steel, water-cooled panels.

The flue gas duct and charge openings are at the top of the furnace shaft. Below the hearth is a crucible or, in newer furnaces, a trough sloped to one end. Liquids from the furnace flow continuously down into the trough, then out from the end of the trough to an external settler-separator.

Hearth widths range from 4.5 to 6.0 feet and lengths from 15 to 28 feet. Shafts are 18 to 28 feet high. Furnace capacities are roughly proportional to hearth area. Furnace charge is 600 to 1200 tons per day for hearth areas from 80 to 150 square feet. Lead bullion production is eight or nine tons per day for each square foot of hearth.

Blast Furnace Charge and Products

The blast furnace is charged with a mixture of coarse sinter and coke. Some flux may be added. Coke is nine to twelve percent of the charge. The air blast is at low pressure and ambient temperature. Volume of air used is related to furnace capacity and is about 5000 to 9000 scfm.

Furnace products consist normally of four liquids that are discharged from the bottom, and flue gas that vents from the top. The four liquid products, from heaviest to lightest, are lead metal, matte, speiss, and slag. The first three, at one plant, are sent directly to lead refining without being separated from each other. At other plants the lead is separated and sent to refining and the matte and speiss go to the dross furnace. Slag is removed separately, and is conveyed hot to a fuming furnace for recovery of lead and zinc. Some slag may be granulated and recycled to sintering as part of the flux.

The slag contains 10 to 20 percent zinc, with up to about two percent lead and three percent sulfur. It is mainly siliceous and contains iron and calcium. Matte is mainly copper and lead sulfides. The copper may run from 44 to 62 percent, lead 10 to 20 percent,

and the sulfur up to 13 percent, with up to two percent zinc and small amounts of iron and silica. Speiss also is rich in copper, 55 to 64 percent, and may have eight to 18 percent lead. It also contains sulfur and arsenic, up to one percent zinc, and 0.5 percent or less each of iron and silica.

Lead Refining

The lead refining process in a primary smelter consists of the dross reverberatory furnace and lead refining kettles. The product is lead bullion. The dross reverb produces also matte and speiss, which are shipped to a copper smelter for recovery of the large percentage of copper they contain.

The dross furnace usually operates only 50 to 70 percent of the time the refinery operates. A very small amount of sulfur oxide is emitted. Matte and speiss both contain sulfur, but most of this remains in the material that is shipped from the lead plant. There is a layer of dross on the hot material in the furnace that permits oxidation of only a small portion of the sulfur. Depending on the capacity of the plant, the offgas volume from the dross reverb ranges from 1100 to 3000 scfm. The sulfur dioxide content of this offgas usually averages less than 0.05 percent. Gas temperature is 1400 to 1800 F. However, brimstone is sometimes added to both the refining kettles and the dross reverb to make matte. Following this, sulfur oxide concentration in the offgases from dross reverb and refining may be as high as 0.2 percent for a few minutes.

Other than as just mentioned, the lead refining process does not generate significant amounts of sulfur oxides.

Other Smelter Operations

Some lead smelters operate such other equipment as cadmium roasters, slag fuming furnaces, and deleading kilns. The slag furnace recovers zinc oxide from blast furnace slag. The volume of gas from the slag fuming furnace at one plant is over 200,000 scfm at the stack and there is an average 0.02 percent of sulfur dioxide. Data are not available for the other two operations, but the emission of sulfur oxides is probably negligible.

Minor Constituents in Nonferrous Smelting

Ores and concentrates of copper, zinc, and lead have varying amounts of minor constituents that sometimes require the use of special processing methods to recover them or to overcome or avoid the problems they could cause. There is not only considerable variation in the constituents from one smelter to another, but also from time to time in any particular smelter. These constituents include chlorine compounds in lead smelters, fluorine in copper, zinc, and lead smelters, and arsenic in most ores of the western United States. Cadmium is commonly associated with zinc. and the quantities are large enough so that most plants recover it. Mercury is found in some zinc ores and has been recovered in some instances. Bismuth, selenium and tellurium are often present in ores of most nonferrous metals.

Volatile constituents such as arsenic get into the gases and usually deposit in the flue system. One copper smelter has recovered and purified arsenic for sale as a byproduct.

Vb. POTENTIAL AIR POLLUTION PROBLEMS IN SMELTER AREAS

For at least the past 150 years, air pollution damage, particularly to vegetation, has been observed to result from the release of sulfur oxides from nonferrous smelters (see appendix G). A large body of literature has been published on the subject during this same period. It was already well known in Europe, even before the start of large-scale smelting operations in the United States coincided with the appearance of heavy damage in a number of areas (about 1890–1910). The instances of pollution receiving the greatest amount of public attention occurred in the areas of Anaconda, Montana; Ducktown, Tennessee; Selby, California; Shasta County, California; the Salt Lake Valley, Utah; and the Columbia River Valley of Washington. Damage in the state of Washington resulted from operations of the smelter at Trail, British Columbia. Years of litigation resulted. Damage appeared in other localities as well, but generally did not receive the same public notice.

Smelting companies have taken measures to prevent such damage. Emissions have been controlled to a greater or lesser degree. and the use of tall stacks for dispersion of effluents has become general. In agricultural areas, smelting companies have purchased land around the smelters or acquired easements for their effluents. In some instances, smelting operations are curtailed during critical periods of the crop growing season. Crop damage does occur around some smelters, but the smelting companies have established procedures for settling claims for agricultural damage with a minimum of litigation. Few damage claims or reports of smelter emissions have become a matter of public record since about 1940.

In this study, investigations were confined to estimates of the potential for air pollution problems in smelter areas, and no attempt was made to assess the extent of any actual damage that may have occurred. The air pollution potential of a smelter was judged qualitatively on the basis of the following considerations:

1. Topography and meteorology of the surrounding area

2. Land use: the presence or absence of agriculture; the presence of sensitive commercial, ornamental, or natural plants; the proximity of towns or of human population in general, etc.

3. The emission of sulfur oxides from the smelter.

4. Any plans for plant expansion or modification that might increase or decrease the sulfur oxide emission.

5. The height of the smelter stack and the elevation of the stack base with relation to the surrounding terrain.

6. Data from ambient air sampling programs, if any, conducted by public agencies.

7. Historical data: published or other publicly available information on the past or current environmental effects of sulfur oxide emissions in the area. These included reports by public health or agricultural agencies.

The information for the study was derived from existing data, supplemented by observations made by project personnel during brief visits to the smelter areas. Cursory observations were made of the conditions of crops, ornamental plants, and natural vegetation for any obvious signs of sulfur dioxide injury.

Inquiries were directed to state and county public health or air pollution control agencies. Information was requested concerning results of air sampling programs, records of vegetation damage, citizen complaints, or litigation related to sulfur oxide emissions from smelters. Most of the agencies were unable to supply any significant amount of information. Some had no information, particularly current data, even where other sources indicated that significant problems probably exist. In a few cases, however, the agencies reported instances of agricultural damage, denuding of timber land, complaints about damage and nuisance, and relatively high atmospheric concentrations of sulfur oxides.

During the brief inspection trips to the smelter areas, one or more of the following conditions were observed around some of the sites visited:

1. Reduction in visibility over an area due to accumulation of particulate effluents (solids or sulfuric acid mist).

2. Reduced visibility in specific areas (sometimes along highways) where stack plumes reached the ground.

3. Looping stack plumes reaching the ground in residential areas or along highways. Concentrations of sulfur dioxide high enough to produce odor and sometimes throat irritation.

4. Sulfur dioxide odor present throughout a town area.

5. Sulfur dioxide markings on sensitive plants, including ornamentals and commercial crops.

6. Damage to natural vegetation.

An analysis of the influence of meteorology and topography on the air pollution potential of smelters is presented in appendix D. Only the conditions in specified general regions are considered. Meteorological data for specific smelter sites are usually not publicly available. For the purpose of the analysis, the geographical areas containing smelters were grouped into five more or less homogeneous regions: (1) Appalachian, (2) Midwest, (3) Southwestern Desert, (4) Northern Rocky Mountains, and (5) Pacific Coast. The meteorological variables considered in the analysis were inversion frequency, mean maximum mixing depth, surface winds, and general air flow conditions. Topography was considered in relation to its role in modifying the influence of the meteorological variables.

There is a high frequency of inversions at night over most of the U.S. With nighttime vertical mixing of the atmosphere being generally limited, overnight accumulations of pollutants are part of a typical climatic pattern. The subsequent daytime breakup of these accumulations may under some circumstances produce relatively high ground-level concentrations of pollutants.

From the standpoint of potential air pollution, the areas of most unfavorable meteorological and topographic conditions are in the Southwestern Desert, Northern Rocky Mountain, and Pacific Coast regions. These are also the regions in which there are the largest number of smelters operating.

An estimate was made of the extent of smelter emission effects, based primarily on the number of persons and the number of square miles of commercial agricultural land on which the sulfur oxides in the atmosphere might have some influence. For the purpose of the estimate, sulfur oxide effects were defined as (1) noticeable human irritation, (2) apparent increased corrosion of metals, and (3) development of markings on vegetation ascribable to sulfur dioxide. All of these effects can appear in varying degrees. Effects on humans can range from severe throat irritation to a slight tickling sensation in the throat or to a barely detectable odor or taste. Effects on plants can vary from complete defoliation to an occasional mark on a leaf that may be found only by a careful search.

In the estimation of human populations that might be affected, towns within a radius of six miles from a smelter were usually considered as locations where at least slight throat tickling may be experienced at some time during a year when meteorological conditions are unfavorable. The populations of such towns, taken from the 1960 census, were totaled to give an idea of the number of people that might be at least mildly irritated by the sulfur oxide emissions from a given smelter. To this sum was added arbitrarily from 300 to 1000 to account for persons living outside the town, the number added being an estimate based on observations made during the visit to the area. In some cases where it was obvious that there would be channeling of winds in specific directions, the populations of towns at distances from the smelter greater than six miles were included.

The commercial agricultural areas were delimited on the basis of observations made during the visits to the smelter districts. These areas were then measured on topographical maps by use of a planimeter, and the planimeter measurements were used to estimate the agricultural area potentially affected. Within the area boundaries there were often rivers and nonusable land. In some cases the contiguous agricultural area would extend for many miles beyond the limits at which the effects of sulfur oxide effluents would be detectable. In such instances the boundary of the affected area was set arbitrarily on the basis of observations of the crops, the topography, the height of the smelter stack, the emission from the smelter, the wind patterns, and occasionally on personal knowledge of the personnel making the on-site examination.

It is estimated that about 610,000 persons and some 300 square miles (192,000 acres) of agricultural land may be affected by smelter emissions of sulfur oxides. The sense of the findings is that the persons affected may at some time or times during a year experience some degree of throat irritation, or encounter markings on their ornamental plantings, or accelerated corrosion of the metalwork on their property. In the agricultural area, leaf markings may appear on farm crops during the year, but the extent of the damage can vary widely.

Damage that affects commercial value does not occur to all of the crops in an area, nor is damage taking place continuously even where it does occur. The damage may occur only under certain weather conditions, and heavy fumigations may be several years apart. At the other extreme, under certain conditions, some areas near specific smelters might be denuded of vegetation.

In the foregoing analysis, the bases for defining the extent of sulfur oxide effects are far more conservative than those being used in assessing air pollution by sulfur oxides in most urban areas. For example, detection of odor and taste and the experiencing of throat or nasal irritation are associated with atmospheric concentrations of sulfur oxides greater than those normally encountered in urban areas, where the total contamination of the atmosphere may be high but the individual sources are usually smaller and more diffuse.

VI. SULFUR OXIDE CONTROL

a. Control methods now available

b. Effects of changes in metallurgical processes

VI a. CONTROL METHODS NOW AVAILABLE

A large number of processes have been proposed for control of sulfur oxides. A few appear to have possibilities of development to economic and technical feasiblity for controlling air pollution by sulfur oxides from primary copper, zinc, or lead smelters. Of this group, only five have been sufficiently tested and enough data made available so that costs can be estimated for their application to a range of smelter conditions.

One of the five processes, conversion of sulfur dioxide to sulfuric acid, is now being used by nearly half the smelters in this country. It is a practical and profitable method of control wherever there is a market for the acid relatively close to the smelter. Only one other process, DMA absorption, is in use in the United States but only on a small scale at two smelters. It is used for the purpose of making liquid sulfur dioxide, the market for which is small, and is not one of the processes for which costs could be estimated.

The processes are described in this section of the report. Estimated costs are presented and discussed in section VIII c, "Costs of Control by Available Methods".

Processes Presented

The five control processes are:

Contact sulfuric acid
Cominco absorption
Reduction to elemental sulfur, Asarco process
Lime wet scrubbing
Limestone wet scrubbing

Four of these processes cool the smelter gases to about 140 F or cooler and involve scrubbing with an organic solvent or water solutions or slurries. For the other process, reduction to elemental sulfur, the gas is cooled to condense and remove volatile impurities such as arsenic and facilitiate solids removal in an electrostatic precipitator or bag filter.

All the processes are most efficient when the smelter offgas is supplied at a steady flow rate and sulfur oxide concentration. The lime and limestone processes are probably least sensitive to variations, but the efficiency of any scrubber drops off at excessive flow rates. With highly variable feed conditions, either the equipment is designed for the maximum flows with resulting high capital charges, or it is designed for some lesser flow rate and any excess is bypassed to the stack.

Operation of these and other control processes, or purity of the byproducts, may be affected by some of the minor constituents found in smelter offgases. Possible offenders include arsenic, chlorine, and fluorine. Concentrations of such impurities probably vary widely from one smelter to another, and also in a given smelter according to the source of the offgas. Some of the impurities may poison catalysts and some will cause high corrosion rates in ducts and processing equipment. Information on this subject is not generally available, and in any case would have to be determined for offgas flows in each smelter in order to be useful in design of control processes and equipment for that smelter. Some study of process catalysts may be needed to provide alternative catalysts more resistant to interfering impurities not easily removed from the gases.

Some other processes are discussed briefly in this section, but no costs are given for them in section VIII c. Included are processes for reduction to elemental sulfur recovery and concentration of sulfur dioxide by the DMA process, and recovery and concentration by sodium sulfite-zinc oxide processes. References to the literature on these processes are given in the bibliography for control processes in appendix B.

Rejected Processes

Many of the processes that were considered but rejected for use in this study are briefly discussed under the heading, "Rejected Processes", in Appendix B. References to the literature on rejected processes are given in the bibliography.

Sulfuric Acid Manufacture by Contact Process

The total number of primary smelter plants included in this study is 38. Of this number, 16 plants recover sulfur dioxide from the smelter offgas. All convert the sulfur dioxide to sulfuric acid using the contact process. Two also produce some liquid sulfur dioxide as a byproduct, but for one this is actually an adjunct of pyrites roasting.

Flow diagrams showing typical sulfuric acid units handling smelter offgases having two, four, eight, and 12 percent sulfur dioxide are in appendix B (Plates B-1,-2,-3,-4). The diagrams give flow quantities and cooling and heating loads for acid units receiving 100 tons per day of sulfur dioxide in gases of these concentrations.

A contact sulfuric acid unit designed to use cleaned smelter plant gases usually has a humidifying tower, followed by a cooling tower over which a weak acid solution is circulated. The weak acid is cooled in heat exchangers. The gas leaving the tower goes through a gas cooler, where some excess moisture may be condensed, then through an electrostatic mist precipitator.

The gas always contains some sulfur trioxide and this is absorbed in the humidifying and cooling towers. The resulting sulfuric acid accumulates in the weak acid system. The weak acid concentration depends on the amount of sulfur trioxide in the gas and on the quantity of water condensed in cooling. When the amount of sulfur trioxide is relatively high, it is necessary to add water to the weak acid system to hold the acid strength below about 30 percent.

Solid material in the gas accumulates in the weak acid system and is removed in the weak acid bleed stream. This dirty weak acid may be filtered and added to the product system, but is usually either neutralized and wasted, or used for leaching or other purposes in the smelter area.

For best operating efficiency a contact sulfuric acid unit should be fed with a gas having a uniform analysis of sulfur dioxide. Fluctuating concentrations of sulfur dioxide require that the contact sulfuric acid plant be designed for the worst conditions and with adequate controls to handle changes in concentration. Changes in feed gas volume are less of a problem and can be handled by the contact sulfuric acid plant within reasonable limits.

Before reaching the acid plant converter, the gas is dried by direct contact with strong sulfuric acid in a packed tower. Gas leaving this tower contains approximately five milligrams of water per standard cubic foot of gas. Acid strength in the drying acid system is maintained at above 93 percent by the addition of stronger acid from the product absorber. Diluted acid from the drying acid system is returned to the product system. All water removed from the gas stream by the drying tower dilutes the product acid from the plant.

The dried gas flows to the converter, where sulfur dioxide is converted to sulfur trioxide by beds of catalyst in three to four stages. On the way to the converter the gas is heated in a series of exchangers while serving to cool gas coming from the converter stages. This part of the acid unit is similar to the usual sulfuric acid plant operating on gas from a sulfur burner. The converted gas next flows through an absorption tower where sulfur trioxide is absorbed in strong sulfuric acid. Finally the gas is treated to remove droplets of acid and vented to the atmosphere.

Feed Gas Concentration

A contact sulfuric acid plant can be designed to operate on gases with sulfur dioxide concentrations from a fraction of a percent on up to the highest concentration feasible in a smelter offgas. Economic considerations, however, generally limit application of the process to gases with at least three percent sulfur dioxide.

Smelter gas containing more than seven percent sulfur dioxide usually does not contain enough oxygen for conversion of sulfur dioxide to trioxide. It is necessary to dilute such gas with air before it reaches the acid plant converter so that it will have the proper ratio of oxygen to sulfur dioxide.

Concentrations below three percent require added heat to keep the process in operation. All acid plants have a fired heater for startup of the converter section. When the waste gas feed has less than 3.5 to 4.0 percent sulfur dioxide, it is necessary to operate this heater continuously.

When the feed gas has less than five or six percent sulfur dioxide, extra cooling of the gas from the cooling tower is needed to condense more water. This is done to prevent dilution of the product acid below commercial grade, 93 percent or 66° Baumé. Acid plant feed gases of low concentration require cooling in inverse proportion to their concentration. With less than three percent sulfur dioxide, refrigeration may be needed to condense enough water.

Efficiency of Conversion of Sulfur Dioxide

The conversion of sulfur dioxide to sulfur trioxide is influenced by the concentration of sulfur dioxide in the converter feed gas. For a given set of conditions, a lower sulfur dioxide concentration results in higher percentage conversion of sulfur dioxide to sulfur trioxide. All unconverted sulfur dioxide is discharged in the tail gas. Tail gas from the contact sulfuric acid process contains on the order of 0.2 to 0.5 percent sulfur dioxide.

A typical smelter offgas contains decreasing amounts of oxygen as the sulfur dioxide content increases. For efficient conversion of sulfur dioxide to sulfur trioxide the feed gas to the acid plant converter needs to have about 30 percent more oxygen than sulfur dioxide, on a mole or volume basis. The typical waste gas containing more than seven percent sulfur dioxide does not have this excess of oxygen, and dilution air must be added to achieve the desired ratio. The result is that the sulfur dioxide content is reduced to between 7.0 and 7.5 percent before reaching the converter and the conversion efficiency is not decreased as would be expected. The tabulation on the next page shows the effect of this dilution, and the resulting conversion efficiencies as used for this study.

Feed Gas percent SO_2 (by volume)	To Converter percent SO_2 (by volume)	Conversion SO_2 to SO_3 percent
2	2	98.0
4	4	98.0
6	6	97.5
8	7.1	97.0
10	7.2	97.0
12	7.3	97.0

Overall recovery efficiency depends on how much sulfur is present in the waste gas as sulfur trioxide and is therefore lost in the cooling tower, as well as on the percentage conversion of sulfur dioxide to sulfur trioxide. The overall efficiency is expressed as the ratio of sulfur equivalent in the product acid to total sulfur equivalent in the feed gas. Recovery as strong sulfuric acid of the total sulfur equivalent in the feed gas entering a plant that has three stages of conversion is typically close to 89 percent for a two-percent sulfur dioxide gas, and 93 percent for an eight-percent gas. This is lower than the efficiency of conversion of sulfur dioxide to trioxide because the trioxide originally in the feed gas is extracted as weak acid, often a waste material.

Recovery from Weak Gases

When a smelter plant is equipped with a contact sulfuric acid unit for recovering sulfur dioxide, the offgas streams of higher sulfur dioxide concentration are used as main sources of feed for the unit. Weaker gases, such as those from the reverberatory furnace of a copper smelter, usually go to a stack and are vented to the atmosphere. The division between strong and weak gases is in the neighborhood of three to four percent sulfur dioxide.

Although many processes have been devised to accomplish the recovery and concentration of sulfur dioxide from weak gases, only two are known to be actually serving this purpose in commercial plants: DMA absorption and Cominco absorption. Each of these processes is economically satisfactory only under certain special circumstances.

DMA Absorption Process

The dimethylaniline (DMA) process was developed by American Smelting and Refining Co. (Asarco) about 25 years ago. Two or three small units were built in smelter plants in this country and two are still operating, but only on gases with over four percent sulfur dioxide. One new unit of this type has been installed in a European smelter, however, and is being used with xylidine instead of DMA to recover and concentrate gas as weak as 1.5 percent. The sulfur dioxide is liquefied. Production costs are said to be only $24 per ton of liquid sulfur dioxide at a rate of less than 100 tons per day. No other costs are known for this installation or the DMA units.

Cominco Absorption Process

This process was developed by the Consolidated Mining and Smelting Company of Canada Ltd. (Cominco), and the licensor for the process is Olin-Mathieson Chemical Corp. Plant units have been built by Cominco at Trail, B.C. and by Olin-Mathieson in Texas. The unit at Trail is part of lead and zinc smelter operations. The Texas units treat the tail gases from sulfuric acid plants. (See page VIII c - 16 for discussion of applications and costs.)

Two Cominco recovery processes for sulfur oxides have been mentioned in recent literature: the Cominco ammonium sulfate process and the Cominco exorption process. Only the ammonium sulfate process is considered to be a technically valid process by Cominco and Olin-Mathieson. The so-called exorption process was tested over 20 years ago and rejected because of high steam-stripping costs and other problems.

In this report the ammonium sulfate process is referred to as the Cominco Absorption Process. Gases with sulfur dioxide concentrations down to 0.5 percent, or even lower, can be treated with very good recovery. The sulfur dioxide is concentrated to around 24 percent by volume. Each of the three units that have been built delivers its sulfur dioxide product to a contact sulfuric acid plant. Ammonium sulfate is a byproduct, and some weak sulfuric acid is made when the smelter offgas is given its final cleaning and cooling before it enters the scrubbers.

The product gas from a Cominco unit could be a satisfactory feed gas for any of several kinds of conversion units, such as units to convert sulfur dioxide to elemental sulfur, or to liquid sulfur dioxide or sulfuric acid. However, the Cominco unit consumes some sulfuric acid and therefore serves most economically as part of a plant complex that includes a sulfuric acid unit. The cost of running the Cominco unit is high, which makes it most useful as cleanup equipment to prevent air pollution. For profitable operation, an acid plant or other conversion unit working with a Cominco unit should get a large fraction of its sulfur dioxide feed directly from the smelter operations, and only a small fraction should come from the Cominco unit.

Description of the Cominco Process

The principal chemical reactions taking place in the Cominco process are the following:

Absorbing:

1) $SO_2 + H_2O = H_2SO_3$
2) $H_2SO_3 + (NH_4)_2\,SO_3 = 2(NH_4)\,H\,SO_3$
3) $(NH_4)\,HSO_3 + NH_3 = (NH_4)_2\,SO_3$

Stripping

4) $2\,(NH_4)\,HSO_3 + H_2SO_4 = (NH_4)_2\,SO_4 + 2SO_2 + 2H_2O$
5) $(NH_4)_2\,SO_3 + H_2SO_4 = (NH_4)_2\,SO_4 + SO_2 + H_2O$

The gas containing sulfur oxides is scrubbed by a solution of ammonium sulfite and ammonium bisulfite. Sulfur dioxide in the gas reacts with ammonium sulfite to form the bisulfite. Ammonia is added to the recycled scrubbing liquor to reconvert bisulfite to sulfite. (See Figure VIa-1) The gas passes through two scrubber towers in series and vents to atmosphere. The vented gas contains no more than 0.03 percent sulfur dioxide by volume if the scrubber solutions are properly adjusted.

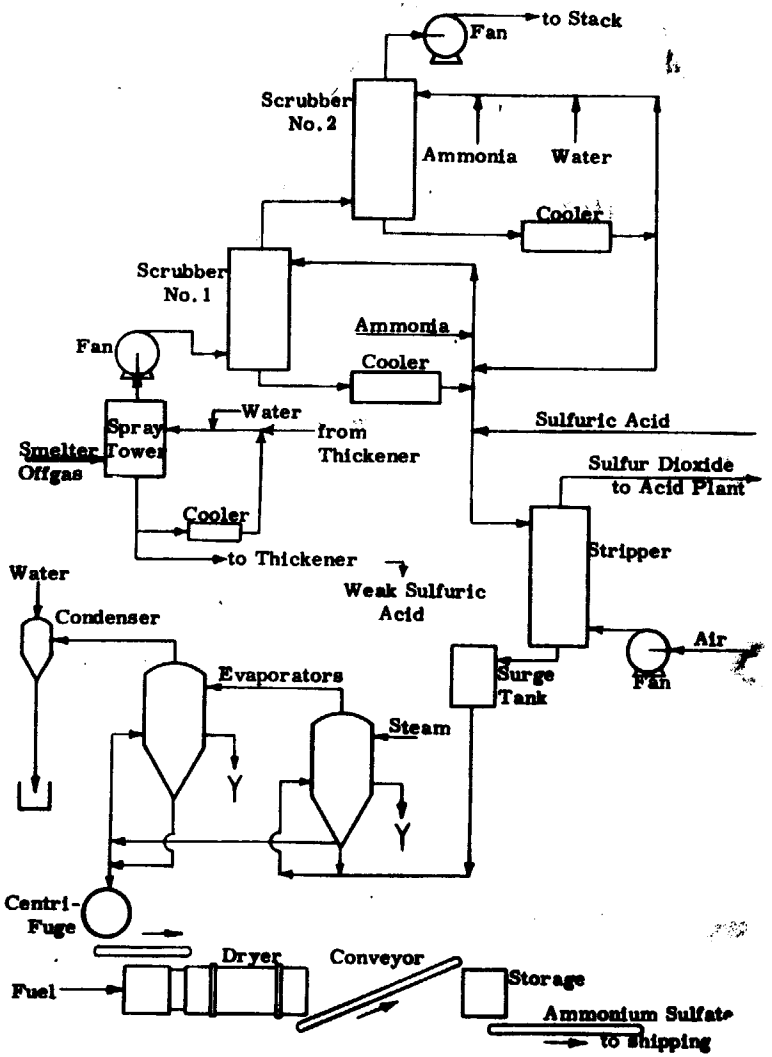

FIGURE VIa-1 Schematic Flow Diagram of Cominco Process

Hot smelter offgas is first cooled in a spray tower similar to those used to cool smelter offgases for a sulfuric acid plant. The spray of weak sulfuric acid cools the gas, washes out fine solids, and absorbs sulfur trioxide to form more sulfuric acid. The weak acid recycles to the top of the tower through a cooler and a thickener. Thickened solids and some weak acid are bled off from the thickener, with the rest of the weak acid returning to the tower.

Cooled offgas enters a scrubber tower where it is contacted with an ammonium sulfite-bisulfite solution. The solution in this first scrubber is maintained at low pH and high salt concentration. Sulfur dioxide is absorbed to form additional ammonium bisulfite. The solution from the bottom of this tower is cooled and recycled to the top of the scrubber together with some solution from the second scrubber. A portion of the solution from the tower bottom is diverted to the stripper.

Scrubbed offgas enters a second scrubber where additional sulfur dioxide is removed by contact with a solution that is at high pH and has a low salt concentration. The solution recycle stream is cooled and water and ammonia are added. Part of the scrubber solution recycle is diverted to the first scrubber. Offgas from this scrubber is released to the atmosphere. Careful control of pH in the scrubbing steps is necessary to assure highest recovery of sulfur dioxide.

The bisulfite solution diverted to the stripper is acidified with sulfuric acid and stripped with air to produce a sulfur dioxide gas stream suitable for feeding to the contact sulfuric acid plant. The solution leaving the stripper contains ammonium sulfate as a result of the sulfuric acid reaction and removal of sulfur dioxide. It is crystallized in a two-stage evaporator and the ammonium sulfate is recovered by centrifuging. This byproduct is dried in a rotary dryer and stored for shipment.

Reduction to Elemental Sulfur

The production of elemental sulfur from the waste sulfur oxides of the smelter plant offgases is an enticing prospect during times of high sulfur prices. Several processes have been proposed to accomplish this, and in fact sulfur dioxide reduction plants have operated at Trail, B.C. and elsewhere during periods when special conditions justified them.

Coke has been used as reducing medium for sulfur dioxide in processes developed by Consolidated Mining and Smelting (Cominco), Imperial Chemical Industries (ICI), and Bolidens. However, the lower cost and the availability of natural gas at most of the smelter sites make it a preferred reducing agent, and this study of reduction to sulfur begins with a natural gas process.

Reduction to Sulfur by the Asarco Process

The American Smelting and Refining Company (Asarco) operated a semi-commercial plant from 1940 to 1944 in which sulfur of high quality was produced by reduction from smelter offgas containing five to seven percent sulfur dioxide (Rd-2, 8)*. Natural gas was the reducing agent, and at the same time was burned to supply heat to bring the gases to the reaction temperature of 2200 F. Figure VIa - 2 is a schematic flow diagram of the process.

The Asarco process requires sufficient natural gas to react with all of the oxygen present in the waste gas and enough more to reduce the sulfur dioxide and trioxide to elemental sulfur. Some carbonyl sulfide and hydrogen sulfide are formed in the reactor, and these are subsequently converted to sulfur by catalytic reactions.

Description of the Process

The required amount of methane is mixed with hot offgas as it enters a brick-lined combustion chamber(a) that is packed with a checkerwork of refractory brick to assure complete combustion. The hot combustion gas is cooled in a heat exchanger(b) that

*Reference is to the bibliography for control processes in Appendix B.

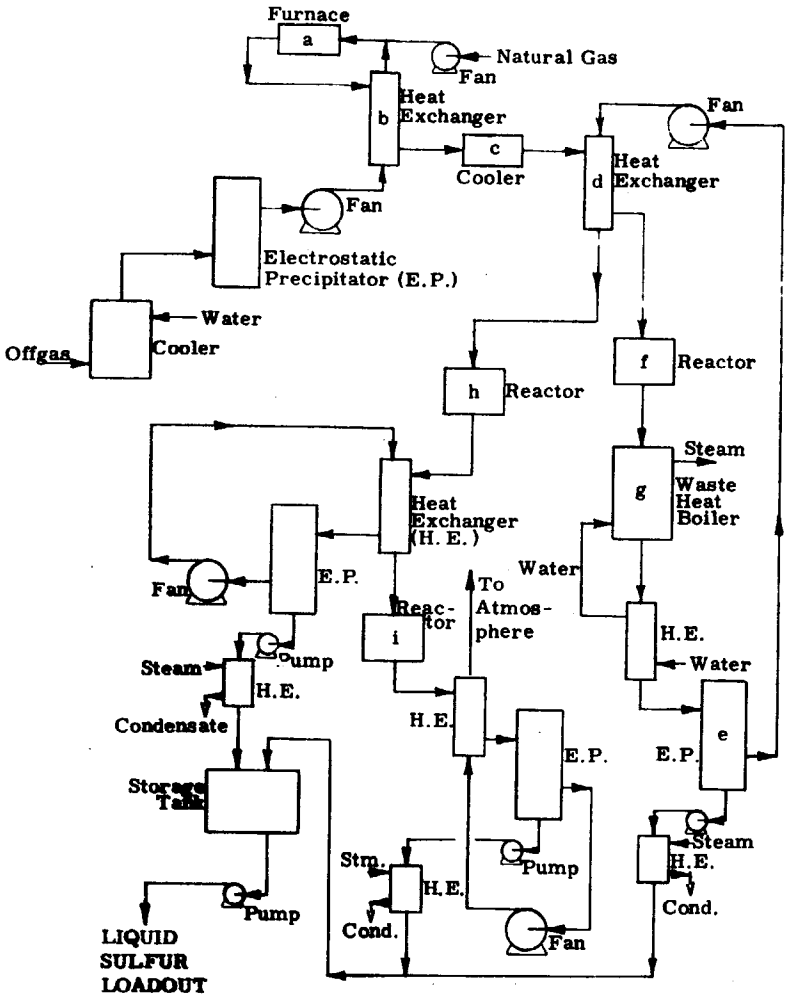

FIGURE VIa-2

Schematic Diagram of ASARCO Process for Reducing Sulfur Oxides to Sulfur

preheats the incoming offgas. The temperature in the combustion chamber is controlled by regulating this heat exchanger. Close temperature control is required throughout the process and counterflow gas-to-gas heat exchangers follow each reaction step.

The primary reaction between sulfur dioxide and methane in the combustion chamber reduces sulfur dioxide to sulfur with the formation of carbon dioxide and water vapor. Several side reactions take place, the chief products being hydrogen sulfide and carbonyl sulfide.

The partly cooled gas from the heat exchanger is cooled further by an aircooler(c), then passed through a second heat exchanger(d) where it is cooled by heating the gas from the first sulfur electrostatic precipitator(e). The cooled gases leaving this heat exchanger are at the proper temperature to enter a reactor(f) where contact with a bed of bauxite catalyst converts the carbonyl sulfide to sulfur. The exit gas from this reactor passes through a waste heat boiler(g) and a heat exchanger and is cooled sufficiently to allow separation of liquid sulfur in the electrostatic precipitator(e).

About 70 percent of the sulfur in the smelter offgas is recovered in this precipitator and is pumped to storage in liquid form.

The gas is next heated in the previously mentioned heat exchanger(d) to the proper temperature for further reaction to convert hydrogen sulfide to sulfur.

The remainder of the process consists of two reactors(h and i) in series, each with activated alumina catalyst, with heat exchangers and electrostatic precipitators to recover liquid sulfur. Portions of the gases are bypassed from previous steps to control the ratio of hydrogen sulfide to sulfur dioxide in each reactor.

Hot gases are also bypassed to periodically raise the temperature of each reactor to remove condensed sulfur.

Several blowers are required in the system because of high pressure losses through the reactors and heat exchangers. Gas temperatures through the system range from 2200 F leaving the

combustion chamber to 260 F in each of the electrostatic precipitators. Gas volume through the system remains approximately constant except for changes due to changes of temperature and pressure.

Tail gas containing a small amount of sulfur dioxide is discharged to the atmosphere. Sulfur recovery is 95 percent of the total sulfur in the offgas.

Feed Gas Concentration

A direct reduction plant can be designed to operate on offgas containing a fraction of a percent sulfur dioxide. Economic considerations limit application of this process, however, to offgases containing at least four percent sulfur dioxide. This is because of the high consumption of natural gas relative to sulfur produced at lower sulfur dioxide concentrations.

The process is best applied to an offgas containing from five percent sulfur dioxide and twelve percent oxygen to seven percent sulfur dioxide and nine percent oxygen. Within this range of concentrations, the production of 99.9 percent sulfur is technically feasible and economic considerations are most favorable.

The combustion reaction between methane and oxygen is highly-exothermic (generates a large amount of heat). The temperature reached in the combustion chamber depends primarily on offgas oxygen content as the reactions between methane and sulfur dioxide are only slightly exothermic.

Typical smelter offgases containing more than seven or eight percent sulfur dioxide do not have enough oxygen to assure a combustion temperature that will burn all of the methane to carbon dioxide and water vapor. Any unburned carbon discolors and lowers the grade of the recovered sulfur. If dilution air is added to avoid this deficiency of oxygen, the consequent greater dilution of the gas mixture by the nitrogen in the air increases the natural gas requirement per ton of sulfur to approximately the requirement for offgas containing six to seven percent sulfur dioxide.

Reduction to Sulfur by Other Processes

Several other processes for reducing sulfur dioxide to sulfur may offer advantages over the process just described, particularly for application to more concentrated smelter offgases. Most of them use some features of the Asarco process, but other features are varied to obtain some technical and economic advantages.

Claus Process Sulfur Plants

It should be noted that the pilot plant work on the Asarco process was done before the construction of large numbers of Claus process plant units in this country and elsewhere. Claus units produce elemental sulfur from waste hydrogen sulfide. Once the sulfur dioxide in a stream of waste gas has been even partly reduced by natural gas, there is considerable similarity between the process streams in the reduction plant and the Claus process plants. The equipment used in the Asarco and Claus plants, however, differs greatly. Where the Asarco plants use a number of large and expensive electrostatic precipitators, the Claus process plants are able to make an efficient recovery of sulfur at relatively low cost in condensers and packed towers.

It would seem that feed gases more concentrated in sulfur oxides should permit Claus sulfur plant methods to be used in the reduction plants with consequent large reductions in capital and operating costs. If such methods are not already being applied in the TGS and Allied processes, this should be a good area for research and development work.

Texas Gulf Sulphur Process

Patents have been issued to Texas Gulf Sulphur (TGS) for a process to recover sulfur from waste gas by direct, low-temperature (1500 F) reduction of sulfur dioxide with methane in the presence of an alumina catalyst. (Rd-4) It is claimed that the TGS process will produce a high grade sulfur when applied to a waste gas stream containing a high concentration of sulfur dioxide and a low concentration of oxygen. However, preheating may be necessary if the waste gas temperature is low.

For any given waste gas the TGS process requires enough methane to reduce the sulfur dioxide and combine with the oxygen in the same reactions as for the Asarco process. Only when the oxygen concentration is low does the TGS process require less methane, as air dilution of the waste gas is not necessary to the same extent as for the Asarco process.

The TGS process follows the first reactor with two reaction stages to convert carbonyl sulfide and hydrogen sulfide to elemental sulfur. This part is similar to the Asarco process except that heat exchangers condense the sulfur and the use of electrostatic precipitators is not specified.

The advantages of the TGS process, as compared to the Asarco process, should be most marked in applications where the sulfur dioxide content of the waste gases is above about eight percent.

A pilot plant using this TGS process has been operated by Texas Gulf Sulphur and International Nickel Company. No known commercial plants have been built.

Allied Chemical Process

Allied Chemical Canada, Ltd., is now building a plant near Sudbury, Ontario, to recover more than 100,000 tons per year of sulfur from offgas from a pyrrhotite roasting operation. (Rd-5, 6) No process details have been made public, but it seems likely that the process has some similarity to the Asarco and TGS direct reduction processes. (Rd-7) The offgas is estimated to contain more than ten percent sulfur dioxide with low oxygen concentration.

PCR Process

The catalytic reduction process developed by Princeton Chemical Research, (PCR,) is a variation of the methane reduction and the Claus processes. Elemental sulfur is reacted catalytically with natural gas to form hydrogen sulfide, which is then mixed with flue gas and reacts with the sulfur dioxide of the flue gas to form more elemental sulfur. The sulfur is recovered and a portion is diverted for conversion to hydrogen sulfide.

Not enough information has been made available on the PCR process to justify any conclusions now as to its economics, but it may be worth studying when the results of current testwork are published.

Reduction by Hydrogen

Sulfur can be recovered from gas containing sulfur oxides by direct reduction with hydrogen in the presence of a suitable catalyst. A second catalyst stage is required to react hydrogen sulfide formed in the first reactor with additional sulfur dioxide to form sulfur (Rd-3).

The first reactor is operated at approximately 600 F with an iron sulfide catalyst. Sulfur formed by reduction of sulfur dioxide reacts with hydrogen to form hydrogen sulfide. The second reactor is operated at approximately 400 F with an activated alumina catalyst. This is equivalent to the final stages of the Asarco and TGS processes.

It is considered to be impossible to reduce sulfur dioxide to sulfur with hydrogen without formation of hydrogen sulfide. The volume of hydrogen required to produce a ton of sulfur by the hydrogen reduction process is four times the natural gas volume required for the methane reduction process. Any oxygen present in the waste gas causes problems because of its reaction with the first stage catalyst. A typical waste gas requires a combustion operation ahead of the first reduction stage to react the oxygen with a suitable fuel.

In spite of these various problems, the hydrogen reduction process may be attractive for recovery of sulfur from waste gas containing a high concentration of sulfur dioxide and a small amount of oxygen. Sufficient information is not available on this process to permit further evaluation. However, a few copper smelters are now using hydrogen in place of green poles in the fire refining of blister copper from the converters. The hydrogen is obtained in a concentration of 45 to 50 volume percent by partial-oxidation reforming of natural gas. Steam reforming can give a reformed gas that has 80 percent hydrogen.

Reduction with Coke

Several processes have been developed for the recovery of sulfur from waste gas by direct reduction of sulfur dioxide with coke. Sulfur was produced at Trail, B.C., from 1935 to 1943 by this method. (Rd-1) The Imperial Chemical Industries (ICI) process was operated at about the same time, as was the Boliden process in Sweden. (Rd-3)

All of these processes pass the hot waste gas through a bed of coke, followed by heat recovery and reaction stages to control side reactions and produce elemental sulfur. Water vapor in the waste gas reacts with coke and sulfur dioxide to form hydrogen sulfide, requiring converters similar to other direct reduction processes.

Conclusions about Reduction Processes

Several companies have built and operated pilot plants that used natural gas to reduce sulfur oxides to sulfur. The fact that a plant is now being built in Canada to use such a process on a commercial scale indicates that the stage of economic feasibility may have been reached.

Unlike the sulfuric acid byproduct, elemental sulfur is a byproduct that can be stored indefinitely at low cost. Freight costs are relatively low. Sulfur weighs less than a third as much as the sulfuric acid that can be made from it, and half as much as the liquid sulfur dioxide it can be used to produce.

As has been well-proved in the smelter industry, it is technically possible to reduce sulfur oxides to sulfur by means of natural gas, or by using coke or hydrogen. Few smelters are in areas that have an abundance of low-cost coke. The use of hydrogen presents difficulties, as stated, and in nearly every case would require the construction of a gas reforming plant to make the hydrogen from such raw materials as coke, natural gas, or other hydrocarbon products or byproducts. While natural gas would be the convenient reducing agent for conditions prevailing at most smelters, it is possible that the specific situations of one or two smelters might be found to be economically favorable to the use of coke or of hydrogen.

In any case, more development work is necessary for the application of these processes to a specific smelter offgas, and any extensive general economic evaluation now is of limited value for this reason.

Lime and Limestone Processes

Several different versions of these processes have been proposed.

In the Howden-ICI Cyclic Lime and the Mitsubishi Simplified Lime processes (Re-1, 4, 9, 10, 11), lime or powdered limestone is made into a dilute slurry that serves as the scrubbing medium. The Combustion Engineering approach is to add crushed dolomite or limestone to the fuel in a coal-fired power plant. The calcine is carried through with the flue gases, combines with any sulfur oxides present, and is picked up in a wet scrubber (Re-2, 3, 5, 6, 7, 8). A dry lime process under investigation by Battelle Memorial Institute, Combustion Engineering, TVA, and others, injects dry, powdered oxides of magnesium or calcium into the flue gases and then removes the products in a dry collector that may be either a precipitator or a bag house (Re-2, 8, 12).

Choice of Process Versions

The process involving injection of dry lime or limestone into the gas stream, followed by recovery of the solids in precipitators or baghouses, is not considered in this study because efficiences reported for this method by various researchers have been very low (Re-2, 8, 12). The Combustion Engineering process for coal-fired power plants is not suitable for the smelting industry because limestone or dolomite injected into the firing zones of smelter equipment would fuse or become slag, except possibly in the case of roasters. Roasters, however, generally give off a gas strong enough in sulfur dioxide to serve as feed to a sulfuric acid plant.

The remaining alternatives are to contact the gases with a slurry of either lime or limestone in a wet scrubber, removing the sulfur oxides as a mixture of calcium sulfite and sulfate. These two versions seem more suitable for treatment of smelter offgases, and

since either version may be used under certain conditions, each has been studied. The limestone process has lower capital and operating costs than the lime process, but these advantages are partly offset by a lower efficiency and the larger stoichiometric excess of reagent needed. The limestone process may not be suitable for gases lacking carbon dioxide or oxygen.

Efficiencies reported for the wet lime or limestone processes vary widely. It seems probable that, with good scrubber design, the wet lime process could remove 90 percent of the sulfur dioxide from the gas. The wet limestone process probably can be expected to remove between 80 and 90 percent.

Wet Lime Process

Crushed limestone is delivered to the plant, screened into three sizes, and then placed in intermediate storage. See Figure VIa-3. From there it is conveyed to a rotary kiln or kilns and calcined to form quicklime which is then cooled and slaked. The hydrate is diluted with water to form the dilute lime slurry used in the wet scrubber to absorb sulfur oxides from the smelter gases. The scrubber effluent slurry is pumped to a thickener from which the overflow is returned to the scrubbing system. The thickener underflow can either go directly to a pond or be filtered. Solids are expected to be about half and half calcium sulfite and sulfate. In most cases they will be discarded.

Application of the Wet Lime Process

The wet lime process has most favorable application where small quantities of dilute sulfur dioxide gases have to be treated to alleviate air pollution problems. It is less suitable for situations where there are large volumes of offgas, or where the concentration of sulfur oxides is high. Also, it can be used to treat the effluent gases from the wet limestone processes to ensure high sulfur recovery, again to minimize air pollution.

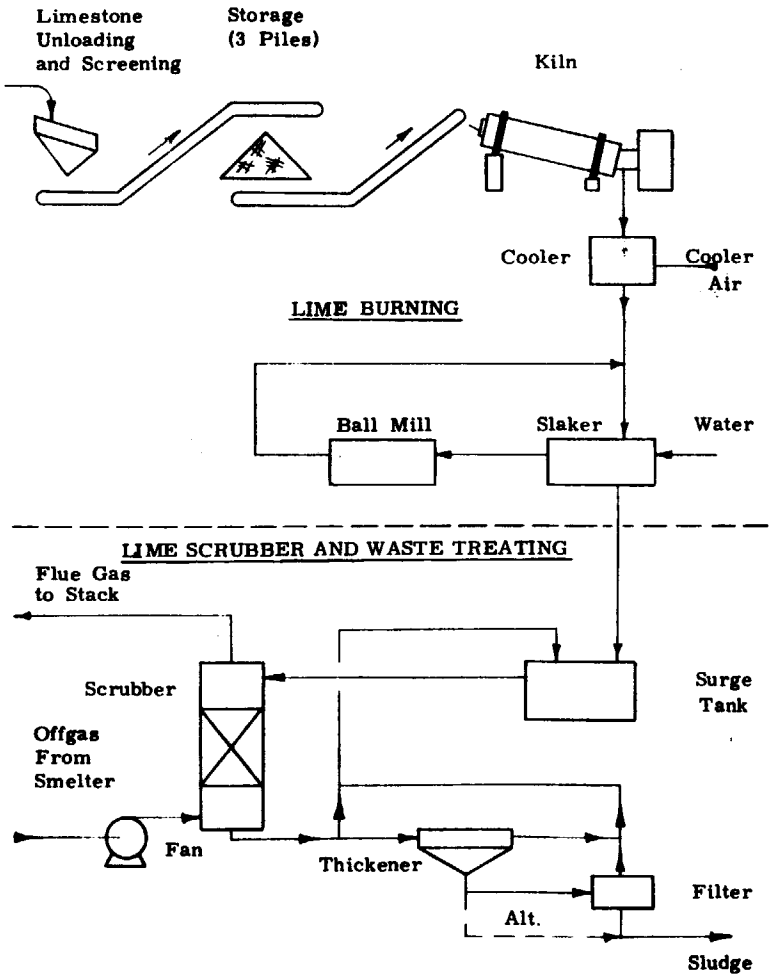

FIGURE VIa-3

Schematic Flow Diagram of Lime Wet-Scrubbing Process

A major operating problem arises in the scrubber and associated lime slurry facilities. The various solid constituents; namely lime, limestone, calcium sulfite, and calcium sulfate are all well known for their scaling tendencies. Severe plugging of lines and equipment will occur due to the hard deposits that build up on surfaces exposed to the liquid.

Wet Limestone Process

In this process, crushed limestone is delivered to the plant and placed in intermediate storage until needed to fill scrubber requirements. (See Figure VIa-4) From storage it is sent to a hammer mill and then to a wet, fine-grinding system consisting of a ball mill and classifier operating in closed circuit. The limestone is reduced to a minus-200-mesh slurry. The slurry flows into an agitated surge tank, from which it is pumped to the wet scrubber and used to absorb sulfur oxides from the smelter gases. The effluent slurry from the scrubber is pumped to a thickener, from which the overflow returns to the scrubbing system. The thickener underflow can either go directly to a pond or it can be filtered. The filter solids are expected to consist of approximately equal quantities of calcium sulfite and sulfate, plus unreacted limestone. In most cases the solids will be discarded.

Application of the Wet Limestone Process

This process has application similar to the wet lime process, except that it is less efficient at removing sulfur oxides from the gases and has somewhat lower capital and operating costs. Similar problems arise from plugging of pipelines and equipment openings by hard scale deposits that build up on surfaces exposed to the liquid.

Sodium Sulfite-Zinc Oxide Process

This process has been extensively investigated by many researchers over a period of years. The most important work was done by Johnstone and Singh (Rf-1) in 1940.

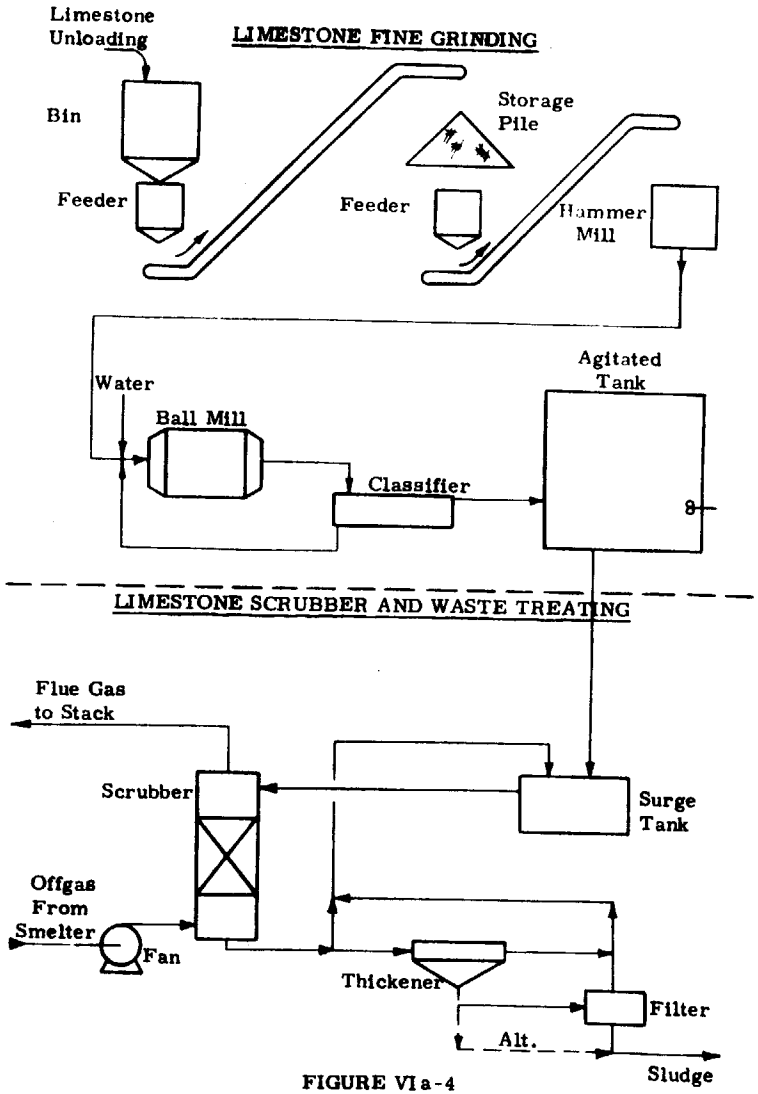

FIGURE VIa-4

Schematic Flow Diagram of Limestone Wet-Scrubbing Process

The process is similar to the Cominco absorption process in that sulfur dioxide is absorbed in an alkaline sulfite solution to form the bisulfite; the bisulfite is then treated to release sulfur dioxide. The absorbing solution is regenerated, although this step is omitted in some variations of the process.

Process Description

Sulfur dioxide is absorbed from the offgases by a solution of sodium sulfite, and sodium bisulfite is formed. The spent liquor goes to a mixer, where zinc oxide is added to precipitate zinc sulfite and regenerate the sodium sulfite solution. The resultant slurry is filtered, with the filtrate being returned to the scrubber. The filtered zinc sulfite is dried, milled, and then calcined to drive off sulfur dioxide and regenerate zinc oxide.

Advantages and Problems

Several problems occur because of formation of byproducts. Sodium sulfate forms by oxidation of sulfite to sulfate, and also by absorption of sulfur trioxide from the gas stream. The sulfate must not be allowed to build up, and is removed by adding lime to a sidestream drawn off for this purpose.

In their article, Johnstone and Singh state that this formation of sulfate is the most serious difficulty connected with the process. They consider that the process would have economic advantages as compared with lime neutralization whenever gas concentrations exceed 0.1 percent sulfur dioxide by volume, since at lower concentrations the ratio of sulfur trioxide to dioxide increases and more sulfate is formed.

Also serious is the formation of soluble polythionates, which are difficult to remove. Lime, for example, does not remove polythionates. Any formation of soluble sulfates or polythionates lowers the allowable concentration of sodium sulfite and hence the absorptive capacity of the scrubber liquor. This is a problem in some other absorption systems for sulfur oxides.

A further problem occurs with formation of soluble metal salts and complexes from dust in the smelter offgases. These are difficult to remove and tend to build up in the circulating absorption liquor.

Process Alternative

An alternative to the addition of zinc oxide for removal of sulfur dioxide as zinc sulfite is to steam strip the solution, decomposing the sodium bisulfite into sodium sulfite and sulfur dioxide. Since this involves absorbing sulfur dioxide into a cold solution in which its solubility is high, and desorbing it from a hot solution in which its solubility is low, it follows that an appreciable temperature difference between the absorption and stripping stages is required for maximum capacity of the system. Assuming that the smelter offgases approach their adiabatic saturation temperature in the scrubbing stage, the absorption will take place at temperatures of from 140 to 165 F, which does not leave much margin for absorption, even if stripping is done at 212 F. Consequently the gases should be cooled below 140 F, and this is costly. In addition, this alternative requires large quantities of stripping steam.

Further Investigation Needed

In a comparative cost study of three processes made by the U.S. Bureau of Mines in 1959 (Rf-2) capital and operating costs were lowest for the limestone wet scrubbing process, highest for the Cominco absorption process, and intermediate for the sodium sulfite-zinc oxide process before taking credit for byproducts. After making allowance for net receipts from sale of byproducts, the sodium sulfite-zinc oxide process has the lowest operating costs. Since this study was made, relative costs of raw materials and products have changed markedly. In addition, the study assumed that no gas cooling was required for the Cominco process, although cooling would definitely be needed for a smelter application. Since no fullscale plant utilizing the sodium sulfite-zinc oxide absorption process has been built, realistic capital and operating cost data are not available and hence cost estimates are not presented. The process appears to merit further investigation, however, and it may be that it could develop into a practical way to remove sulfur dioxide from weak smelter offgases and recover it in a more concentrated and therefore more economically usable form.

VIb. EFFECTS OF CHANGES IN METALLURGICAL PROCESSES

The cost estimates for sulfur oxide control processes reported on in section VIIIc show that costs of control are much higher when the gases are dilute than when they are concentrated. Costs rise sharply when concentration is below six percent sulfur dioxide for gases fed to the sulfuric acid process and the Asarco reduction process, below four percent for lime and limestone processes, and below two percent for the Cominco ammonium sulfate process. Any change in smelter operation that results in an offgas of smaller volume and higher sulfur dioxide concentration lowers the cost per ton for recovering the sulfur dioxide.

Some of the newer smelting methods include among their advantages the fact that they make possible production of offgases relatively rich in sulfur dioxide. The list of such methods includes the Outokumpu flash smelting process, oxygen enrichment of air for blowing copper converters, updraft sintering machines for lead smelters, and fluid-bed, suspension, or fluid-column roasters for zinc smelters. There is also the Hoboken copper converter, developed by the Belgians. Neither this converter nor flash smelting have been used in the United States, and no plans for such use have been made public. However, the other methods listed are now in use at some smelters here and increased application is planned.

Two processes being developed for copper smelting are reported to operate with fairly even flows of offgas at relatively high sulfur dioxide concentrations. These are the Worcra and the Noranda processes, now being tested in pilot plants in Australia and Canada, respectively. Since published articles claim that production of

blister copper is simplified and costs will be lower, information about the results of the test work is expected to be of considerable interest to the smelting industry here and abroad when it becomes available.

Cost estimates have not been released by either Worcra or Noranda, however. If the promise of either process is fulfilled, control of air pollution from copper smelters of the future could be simplified and made more profitable to the smelter owners.

Some work is being done in the smelter industry on copper extraction methods that avoid the pyrometallurgical operations that produce sulfur oxide emissions. One of these is the Treadwell acid-leach cyanide process that also can recover sulfur, gold and silver. There is promise of lower copper costs from work in this area.

Some smelters are not well located relative to markets for sulfuric acid. Development of local uses for the acid would tend to favor sulfur dioxide control by conversion to acid. Along this line, application of sulfuric acid leaching to ore or waste containing mostly oxides of copper is being facilitated by development on a small plant scale of processes using new ion-exchange liquids to concentrate the copper from dilute solutions. The copper metal is then recovered by electrolytic means. Sulfuric acid is regenerated in the cells but there is a net loss of acid in the leaching. However, the quantities of acid used in leaching are highly variable and often apparently inconsistent with the magnitude of operations.

VII. SULFUR OXIDE EMISSIONS AT U.S. SMELTERS

a. Current emissions and extent of control

b. Foreseeable emission trends

VII a. CURRENT EMISSIONS AND EXTENT OF CONTROL

Information obtained from visits to the primary copper, zinc, and lead smelters of the United States has been used to prepare tabulated material and drawings that present the state of sulfur oxide emissions in the smelter industry and the extent of control of these emissions in the first half of 1969.

The more detailed part of the presentation consists of 45 block flow diagrams, three large tables of gas flows and gas compositions at copper zinc, and lead smelters, and three large summary tables of current sulfur oxide emissions and extent of control. This material is in appendix A of volume II of this report.

Grouped together following this page are three single-page summaries that give a quick overall view of the subject. These are Tables VII a - 1, - 2, and - 3. A glance at them now is advisable before plunging into the discussion of the bases for the tables and diagrams.

Smelter Visits

The smelters were visited to gather fundamental data pertaining to sulfur oxide generation, emissions, and control. The object was to obtain information that would include average quantities and sulfur contents of ore concentrates, flux, and other raw materials, dust and other materials recycled, offgas flows, gases vented to stacks, gases treated for recovery of sulfur oxides, and recovered byproducts. Information was sought on cooling and cleaning of offgases, type of process equipment in use, and announced plans for changes or expansion in processing and in control of emission.

Table VII a - 1

SUMMARY OF SULFUR OXIDE EMISSION DATA*

	Sulfur Equivalent, tons per year	Percent of all smelters
Sulfur oxides generated at U.S. smelters:		
Recovered as sulfuric acid	848,300	30.5
Recovered as liquid sulfur dioxide	4,600	.2
Total recovered	852,900	30.7
Emitted to atmosphere	1,924,400	69.3
Total generated	2,777,300	100.0
Emissions to atmosphere - by source		
Copper smelters	1,471,700	76.5
Zinc smelters	321,100	16.7
Lead smelters	131,600	6.8
Total all smelters	1,924,400	100.0
Emissions to atmosphere - by location		
East of Mississippi River	49,900	2.6
West of Mississippi River	1,874,500	97.4
Total U.S.	1,924,400	100.0

*The figures given here represent approximate annual rates in the first half of 1969. They do not include sulfur oxides or byproducts from pyrites roasting or sulfur burning.

Table VII a - 2

SUMMARY OF SULFUR OXIDE GENERATION AND RECOVERY*

	Sulfur Equivalent, tons per year		
	Generated	Recovered	Percent Recovered
Copper smelters:			
Roasters	360,100	127,100	
Reverbs	391,100	0	
Converters	1,064,700	217,100	
Total copper	1,815,900	344,200	19.0
Zinc smelters:			
Roasters	697,300	461,600	
Sintering machines	22,700	0	
Sinter-roast machines	60,100	0	
Cokers & retorts	2,600	0	
Total zinc	782,700	461,600	59.0
Lead smelters:			
Sintering machines	170,300	47,100	
Blast furnaces	3,000	0	
Other	5,400	0	
Total lead	178,700	47,100	26.6
All eastern smelters	352,400	302,500	85.8
All western smelters	2,424,900	550,400	22.7
All smelters	2,777,300	852,900	30.7

*The figures given here represent approximate annual rates in the first half of 1969. Refer to Table A - 7 in appendix A for a more detailed analysis of sulfur oxide generation and recovery.

Table VII a - 3

SUMMARY OF CONTROLS ON
SULFUR OXIDE EMISSIONS*

	Number of plants	
Copper smelters		
With sulfur oxide recovery:		
Roaster gas, only	1	
Roasters and converters	2	
Converters, only	2	
Total with recovery		5
Without recovery		11
Total copper		16
Zinc smelters		
With recovery (from roasters, only)		9
Without recovery		**6
Total zinc		15
Lead smelters***		
With recovery (from sintering machines)		2
Without recovery		4
Total lead		6

*Represents conditions in the first half of 1969.
**Two use preroasted feed and have negligible sulfur oxide emission. One of these is being shut down.
***Does not include a slag fuming plant or two complete new smelters, one of which recovers sulfuric acid.

The data collected were used to prepare approximate material balances and block flow diagrams for each smelter plant. The complexity of operations required more than one flow diagram for several of the smelters. Preparation of the copper material balances required the use of a computer to adjust the differently averaged items of information to get a satisfactory balance.

Flow Diagrams

Smelter flow diagrams are included in appendix A. Copper flow diagrams are on Plates A - 1 to A - 17, zinc on Plates A - 18 to 35, and lead on Plates A - 36 to A - 45.

The flow diagrams are essentially sulfur balances. They show the principal smelter process steps and flows of material. Quantities of sulfur contained in the materials are given in short tons per 24-hour period.

The diagrams represent the best material balances obtainable with smelter data made available for this study. In some cases, the data was inadequate and judgement was needed in selecting bases for the material balance. Sometimes it was necessary to use figures from published literature. However, it is important to keep in mind that even when plentiful information is provided, the best, selected values cannot represent anything more than averages of quantities that may vary widely from one day to another.

Gas Flows and Compositions

Information on gas flows and gas compositions in copper, zinc, and lead smelters is in Tables A - 4, - 5, and - 6 in appendix A. Where available, the analysis of the gas is given, as well as volume, temperature, and duration of the flow in hours per day. As will be seen, much data was not reported.

Some figures in the tables apply to gas as it comes from the process equipment, with whatever air dilution is part of operation of the equipment. Air dilution that occurs after the gas leaves the equipment is not included in these figures. Data for stack

gas or gas to the acid plant apply to the gas with whatever air dilution it may have picked up by the time it enters the stacks or acid plant.

Current Sulfur Oxides Emissions and Extent of Control

Tables A - 1, - 2, and - 3 in appendix A give the total annual short tons of sulfur equivalent to the sulfur oxides in offgases generated at the smelters. The portions of this tonnage coming from roasters and other process equipment are also shown. Smelters east and west of the Mississippi river are grouped separately.

The tables give the tonnages vented to atmosphere from stacks, and tonnages recovered as byproducts of emission control operations. Estimated smelter capacities for production of metal are listed in one column. These capacities are engineering estimates that consider a number of factors, including the equipment in the smelter plant. The estimates will not necessarily agree with data published elsewhere.

The information in Tables A - 1, - 2, and - 3 is analyzed in the three single-page tables (VII a - 1, - 2, and - 3) in this section, and there is a more detailed analysis in Table A - 7 of appendix A. Smelters east of the Mississippi river are recovering a high percentage of the sulfur oxides that they generate. Over 97 percent of the emissions to atmosphere in this country occur west of the Mississippi.

The percentages show where the largest emissions to atmosphere occur, but they do not indicate the mixture of factors that produce this distribution: (1) There are more smelters in the west than in the east, (2) the eastern smelters are generally closer to markets for sulfuric acid, and (3) most of the eastern smelters are handling zinc, while the majority of western smelters handle copper and have to contend with the problem of fluctuating converter gas flows.

Sulfuric Acid

The tables do not isolate the data for sulfuric acid production. Omitting the 4,600 short tons of sulfur that is recovered as liquid sulfur dioxide, the annual sulfur equivalent recovered as sulfuric acid by the smelter industry is 848,300 short tons. This amounts to 2,594,000 tons when figured as 100 percent sulfuric acid.

Production of acid by smelters east of the Mississippi river is 925,000 tons or 36 percent of the U.S. smelter total. West of the Mississippi. 1,669,000 tons of acid is produced.

VIIb. FORESEEABLE EMISSION TRENDS

U.S. companies operating copper, zinc, and lead smelters are primarily producers of metal raw materials. As publicly owned companies, they must make a profit from marketable products within the structure of consumer demand. Also their plans and projections for the future must be made with consideration for possible effects on their relationship with the general public. With the ores and concentrates that are available, they attempt to produce enough metals to supply projected demands of the world market. Continuing research and development efforts are applied toward the accomplishment of better operational techniques, new processes, development of new products extractable from present processes, and greater efficiency of operations.

Major metallurgical changes in smelting systems are the result of efforts to improve production of metals or produce additional products. Such procedures as concentrate roasting and oxygen smelting are modifications of smelting processes that were developed to improve production capacity and efficiency. Modifications made for recovery of sulfur represent efforts to recover additional products available within the existing smelter system.

An increasing trend is developing for production of metals by process systems that are completely different from those presently in operation. Flash smelting and continuous smelting procedures represent major departures from systems now in use in the U.S., but are still within the general category of pyrometallurgical technology. Recent new operations in hydrometallurgy indicate a developing trend toward extractive systems that are new to the smelting industry. Procedures are already well established for specific kinds of ore and account for a substantial portion of metal production.

Direct reduction of metals from concentrates and solutions has gained some prominence in recent times and a trend appears to be developing toward metal production by such systems. Some of these new procedures will yield sulfur byproducts, but others will not have such capability. Production of sulfur byproducts from the processes that do yield them will be simpler than with present smelter systems.

As the consumption of metals has increased, it has become necessary to extract them from ore deposits of lower grade. In order for these operations to be profitable, the size of the mines and concentrators has had to grow to proportions that would have been considered impossible a few years ago. Individual mines and concentrators today produce volumes of metal concentrates sufficient to induce a trend toward local metal production. There appears to be a growing tendency to plan for new smelter systems where costs of transportion of concentrates will be less. As older, less efficient smelters are retired from service and replacements are considered, a trend has developed to make these replacements in the areas where the concentrates are produced.

In the last few years there has been a trend toward manufacturing finished metal products in the areas producing the copper, zinc, and lead. In 1968 mills for copper wire rod and copper wire drawing have been placed in production in the state of Arizona, closer to the source of metal production. It is to be expected that there will be a continuing trend to migration of metal fabrication industries closer to the sources of metal production.

Projects presently under development or recently placed in production will increase the metal capacity of the smelting industry by about seven percent of the capacity of 1968. These same projects will increase the recovery of sulfur in the industry by about 30 percent over 1968.

Projections to 1975

A study was made of the markets for copper, lead, and zinc (see appendix E), and from this projections were made of the probable additions to smelting capacity that may be required up to 1975.

The lead industry is now undergoing its largest expansion in smelting capacity in many years. One of the six lead smelters covered in this study is being expanded. Two new smelters not included in this survey are now going into service; these are the first entirely new lead smelters to be constructed in the U.S. in about 40 years. One of these new plants will incorporate sulfuric acid recovery, but the other apparently will not. It is not expected that any further additions to lead smelting capacity will be required before 1975, at least. If any new smelting capacity is constructed, it will probably be balanced by the shutdown of one or more obsolete existing plants.

Consumption of zinc is expected to increase by about 350,000 to 400,000 tons per year by 1975. If all of this additional amount of zinc were to be derived from smelting of sulfide ores, and the sulfur-to-zinc ratio were to remain the same (0.60) as the present average for all zinc smelters, the equivalent incremental amount of sulfur released as sulfur oxides would be about 210,000 to 240,000 tons per year (420,000 to 480,000 tons per year as sulfur dioxide). However, zinc smelting capacity is considered to be in oversupply at present. Some additional zinc smelting capacity is now being constructed, but part of this is in the form of zinc fuming plants for recovering zinc from lead blast furnace slag. The fuming plants are not a significant source of sulfur oxides emissions.

There appears to be no present inclination within the zinc industry to add to smelting capacity within the next several years. Up to 1975, any new primary smelting capacity constructed will probably be a replacement for obsolete equipment being retired.

The copper industry is currently opening new mines as well as increasing output from existing ones, and a shortage of smelting capacity is developing in the Arizona area. Expansions, or plans for expansion, have been announced for at least ten of the sixteen copper smelters covered by this study. Most of the new capacity is being installed in the area (Arizona, Utah, and Montana) that already smelts the most copper. At four of the plants, the expansion of smelting capacity coincides with installation of new or additional sulfuric acid recovery capacity.

It is estimated (see appendix E) that by 1975 the U.S. consumption of copper will have risen by about 500,000 tons per year. If all this copper were to be produced by smelting, and the sulfur-to-copper ratio remained the same (1.23) as the current average for the copper smelters, the additional amount of sulfur released as sulfur oxides would be 615,000 tons per year (equivalent to 1,230,000 tons of sulfur dioxide). However, there are indications that a very substantial part of the added output of copper may be produced by use of hydrometallurgical processes that do not involve generation or release of sulfur oxides.

The expansion of copper mining in Arizona, in particular, will result in production of more ore than can be handled by the existing smelters in the area. The anticipated shortage of smelting capacity is estimated to be equivalent to 100,000 tons of metal per year. Expansions have been announced for five of the eight smelters in the state, but part of the metal will be recovered by a combination of leaching and electrowinning. Kennecott Copper Corporation will use direct leaching and electrowinning on its silicate ores. The economical use of electrowinning to recover the copper from the dilute liquors produced by treatment of low-grade ores depends upon concentration of the copper by solvent extraction (see appendix G). Successful operation of a commercial solvent extraction-electrowinning plant has recently been announced by Ranchers Exploration and Development Corporation. This success may lead to much more extensive use of the electrowinning process to replace the more conventional cementation and smelting steps to copper recovery.

VIII ECONOMICS OF CONTROL

a. Markets for smelter - produced sulfur byproducts.

b. Market analysis summary.

c. Costs of control by available methods.

d. Control method evaluation with plant models.

VIII a. MARKETS FOR SMELTER-PRODUCED SULFUR BYPRODUCTS

The purpose of the market study phase of the project was to estimate the amount of each of four sulfur byproducts from smelters* -- elemental sulfur, sulfur dioxide, sulfuric acid, and ammonium sulfate -- that might be sold and the probable selling prices. Two base years are considered in the market study: 1965 for current markets and 1975 for future markets. Where shown, current and potential production rates are for first half of 1969. It would have been preferable to determine current markets for 1969 instead of 1965 but the necessary market data for that year were not available. From the market information it is possible to

- Determine the extent to which it is economically possible to dispose of sulfur byproducts from smelters by sale of byproducts producible with existing recovery processes.

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*The four salable byproducts can be considered as primary because each is formed in one of the processes available for recovery of sulfur from smelter offgases. Ammonium sulfate is actually a derivative of sulfuric acid, but is considered primary in this study because it is the unavoidable byproduct of the Cominco absorption process, in which it is formed in regenerating sulfur dioxide by reaction of sulfuric acid with the absorbent liquor. The Cominco process is the only one currently available for treatment of lean sulfur dioxide streams. Hence, the amount of ammonium sulfate that might be produced at smelters and have to be sold, is related to the potential application of the Cominco process rather than to an independent decision to produce the material.

- Indicate which byproducts are preferred for ease of marketing, so that research on new processes can be directed to production of these byproducts.

- Show what production cost levels must be achieved with existing or new processes if they are to operate at no net cost to the producer.

The development of the necessary market information was accomplished by:

- Estimating consumption of each of the byproducts in regions where the market might be supplied from smelters, the price of the byproduct in that market, and the cost of transportation to the markets.

- Identifying those smelters where production of smelter byproducts could either be absorbed by the existing market or where production would exceed the capacity of the market.

- Examining the areas around the smelters where production would exceed existing markets to determine if markets that might develop in the future could take potential production.

The country was divided at the Mississippi River for the regional analysis of the markets. As will be shown later, further division of the eastern region into specific areas was not required. The western region, however, was divided into 9 to 13 subregions or marketing areas -- depending upon the byproduct -- that could be supplied with smelter byproducts. The western smelters that could supply one or more of these areas were divided into seven groups that were treated as marketing entities.

The identification of the market for a smelter byproduct consisted of determining the size of the market in each market area and of determining the price, termed the competitive market price, at which smelter operators might have to sell their byproduct in order to capture all of the available portion (defined below) of that market.

The quantity of byproducts potentially available from some smelters is larger than the total market in the marketing areas that might be served by these smelters. These markets could easily be flooded with smelter byproducts. In that event, competition in the marketing areas could become so intense and chaotic that it would be impossible to estimate either the size of the market for the byproducts or the price level at which they could be sold.

In order to set practical limits on the possible extent of market enetration, reasonable assumptions were made concerning probable long-term marketing practices by smelter operators. The first assumption was that, at the extreme limit, smelter operators might be obliged to dispose of their byproducts at no return beyond the cost of transportation to the market plus the cost of any purchased raw materials (such as ammonia); they would not, however, ship byproducts to a market where the shipping cost would exceed the delivered selling price, and thus add shipping charges to their other losses. The second assumption was that smelters would not seek to sell to a segment of the market held by suppliers who are obliged to continue production regardless of price. A smelter near a marketing area is itself an example of such a supplier. On the basis of these assumptions, it is necessary to consider certain portions of the total market to be unavailable (or impenetrable).

The following tabulation defines those remaining markets for elemental sulfur, sulfuric acid, and ammonium sulfate that are considered to be available to the smelter operators:

Available Markets

	Sulfur	Sulfuric Acid	Ammonium Sulfate
Markets held by existing suppliers who can probably be displaced	All markets held by producers who do not use their sulfur in captive operations	All markets for acid made from purchased sulfur	Markets for 75% of the ammonium sulfate produced from virgin sulfuric acid

	Sulfur	Sulfuric Acid	Ammonium Sulfate
Markets that are within economic shipping distance	All	Those markets where transportation costs do not exceed the delivered selling price	Those markets where transportation costs plus the cost of the ammonia in the smelter product do not exceed the delivered selling price

The competitive selling price, defined as the price that the smelter operator would receive, fob the smelter, was determined by subtracting the cost of transportation* from the competitive market price for sale of the product in an available market. It is, in fact, different for each individual smelter supplying a given marketing area. In this report, however, it is generally presented as a range of values appropriate to the smelters of a given group.

The competitive selling price is also equal to the maximum production cost allowable for a byproduct if the byproduct is to be sold without incurring a net loss. The maximum allowable production cost can for convenience be termed the "breakeven production cost," and represents a minimum objective in development of a sulfur recovery process or system. Whether a smelter can attain or better the breakeven cost depends on both the recovery process and the transportation costs from the particular smelter considered to the byproduct marketing area. However, the definitions of the available markets presented above set minimum levels for the competitive selling prices, as shown on the next page.

*In most instances, freight rates have not been established for shipment of the byproducts from the smelters to the potential markets. Therefore, these transportation costs have been estimated. The methods used to estimate transportation costs are described in detail in appendix F, including the graph used to determine transportation costs as a function of the rail distance between the smelter and the market.

	Minimum Competitive Selling Price of Smelter Byproduct Sold to Available Markets (fob Smelter)
Sulfur	$ 0/long ton
Sulfuric acid	0/short ton
Sulfur dioxide	0/short ton
Ammonium sulfate	13-18/short ton

Using the bases just described, the quantity of each of the smelter byproducts that might be sold and the competitive sale price were determined by comparing the available market for the byproduct in each area with the potential production of byproduct at each smelter that could serve the marketing area. If the available market exceeded the potential production, the quantity to be sold was the potential production and the price to be received was the competitive selling price for that byproduct sold to that market. If the production exceeded the available market, then the quantity to be sold was the size of the market. The price to be received in this case was established by determining which of the smelters could supply the market and, in so doing, get the highest competitive selling price. The total market for each byproduct was determined by merely adding these individual quantities to be sold. The selling prices are those that might be received by the smelters that supply the available markets.

In selling to the available markets as defined above, some of the smelter operators would necessarily have to sell at prices below their cost of production. If none of these operators elected to do this and thus failed to meet the competitive selling price, the size of the market would be smaller than that previously determined to be available. Knowing the extent of this contraction would be useful; however, the size of this market could not be determined because estimates of breakeven production costs could not be made for each byproduct at each smelter. As an alternative, single average values of production costs were assumed based on results of the model studies presented in section VIIId. The markets estimated for byproducts sold at these assumed prices were termed "justifiable markets."

	Price Used to Estimate the Size of the Justifiable Market ($/ton, fob smelter*)
Sulfur	$45 (via Asarco process)
Sulfuric acid	4 (via Contact process)
Ammonium sulfate	25

These production costs appear to be achievable by use of the indicated processes on rich gases from a large smelter. The actual costs of producing ammonium sulfate via the Cominco process are not clearly defined, but depend in part on some arbitrary division of the production costs for the ammonium sulfate and any coproduct such as sulfuric acid. The figure of $25 per ton was selected as an arbitrary minimum.

The quantities of the byproducts that might be sold to the justifiable markets were determined in the same manner as those that might be sold to the available markets.

The market analyses described above showed that the smelters in certain regions could produce more of some byproducts than could possibly be sold currently even to the available markets. The market areas around these smelters were examined to determine to what extent the development of potential future uses of the byproducts might absorb the potential production from the smelters.

The detailed results of the market study are presented in appendix F. An abbreviated recapitulation of the results begins on the next page.

*Dollars per long ton for sulfur. Dollars per short ton for sulfuric acid and ammonium sulfate.

1. Eastern Marketing Region

The estimated consumption of sulfur and sulfuric acid in the eastern part of the United States is shown in the following tabulation for 1965 and for 1975.

Estimated Sulfur Consumption
Eastern Region of the United States
(million long tons/yr)

	1965	1975	Increase from 1965 to 1975
As sulfuric acid	4.66	6.72	2.06
All other forms	0.81	1.03	.22
Total (all forms)	5.47	7.75	2.28

The maximum possible recovery of sulfur or sulfur equivalent in compounds from the seven operating smelters in the eastern region that might supply the above market is 0.31 million long tons of sulfur, a small fraction of the total consumption of nearly 5.5 million tons. Furthermore, 0.27 million tons of this equivalent sulfur is currently recovered and marketed as sulfuric acid by five of the seven smelters in the region, leaving only 0.04 million tons to be emitted to the atmosphere. Under the circumstances, the smelters in the eastern region should be able to sell all of the potential byproducts they might currently produce.

The increase in markets for sulfur compounds in the eastern region between 1965 and 1975 should easily outstrip the increases in smelter capacity that might increase the amount of sulfur available from smelters during the same 10 year period. Based on the growth rates in production of copper and zinc indicated in Section VII (no lead smelters are operating in the eastern region) and assuming that the increases in production will be proportional to present capacity and that the ratio of metal to sulfur will remain constant, 70,000 long tons per year more sulfur (or sulfur equivalent) would

be available from the smelters in the eastern region by 1975. The 70,000 tons increase is only three percent of the 2.28 million-ton increase in markets for sulfur (in all forms) that is anticipated for the eastern region by 1975.

Since five of the seven smelters already have established marketing channels for sale of sulfuric acid (and sulfur dioxide), the increase in acid production that would correspond to complete elimination of the emissions both in 1968 and in 1975 is relatively small, and since the quantity of sulfur dioxide actually being emitted from smelting operations is so small, a complete analysis of the markets in the eastern region was not undertaken.

2. Western Marketing Region

The estimated consumption of sulfur and sulfuric acid in the western part of the United States is shown in the following tabulation:

Estimated Sulfur Consumption
Western Region of the United States
(million long tons/yr)

	1965	1975	Increase from 1965 to 1975
As sulfuric acid	2.24	3.15	0.91
All other forms	0.39	0.57	0.18
Total (all forms)	2.63	3.72	1.09

The maximum possible recovery of sulfur (either as elemental sulfur or in sulfur compounds) from the 26 operating smelters in the western region is 2.14 million long tons; enough to supply over 80 percent of the market shown above for sulfur in all forms that existed in the western region in 1965. By 1975 these smelters should be capable of supplying 2.60 million tons of sulfur equivalent per year or 70 percent of the anticipated market for sulfur in the region in that year. Because the western smelters are able to supply such a large proportion of the total markets for sulfur, the market for each smelter-produced sulfur byproduct within a marketing area that can be served by one or a group of the western smelters must be examined carefully to determine how much of the byproducts can be sold by which smelters.

The following tabulation summarizes the data on western markets for each of the four potential byproducts.

	Estimated Markets - 1965 1,000 tons*
Sulfur, all forms	2,634
Sulfuric acid	7,445
Ammonium sulfate	997
Liquid sulfur dioxide	17

The state-by-state consumption of each of the first three products that provide the above totals is given in Table VIII a - 1. The consumption of liquid sulfur dioxide has not been considered further because it is so small that even if sulfur dioxide produced at smelters could capture the entire market, the amount sold would represent only a small fraction of the emissions from the smelters in the region. As can be seen from Table VIII a - 1, the bulk of the markets for all three products are in Texas and California. Major markets for sulfur and sulfuric acid also exist in Louisiana, Missouri, Idaho, and Washington. The major markets for ammonium sulfate (other than in Texas and California) are in Oregon, Washington, and Idaho.

Data on the potential production of the three sulfur products from western smelters are given in Table VIII a - 2. The 26 operating smelters in the western region have been arranged into seven groups that can be treated as marketing entities since the smelters in each group are geographically close to each other. The Group I smelters have been divided into A and B subgroups because one of the subgroups may be able to supply a given marketing area within the range of both better than the other can.

The bulk of the potential sources of smelter byproducts are concentrated along the western side of the Rocky Mountains in Groups I, II, and III. The 17 smelters in these three groups are potentially capable of making 90 percent of the elemental sulfur, 87 percent

*The quantity of sulfur is reported in long tons, the quantities of the other byproducts are reported in short tons.

Table VIII a-1

ESTIMATED CONSUMPTION OF SULFUR, SULFURIC ACID, AMMONIUM SULFATE IN THE WESTERN STATES

(1,000 tons/yr*)
1965

Subregion - State	Sulfur, All Forms	Sulfuric Acid	Ammonium Sulfate
North west central			
Minnesota	45	107	6
Iowa	26	79	2
Missouri	157	641	6
North Dakota	≠	≠	≠
South Dakota	≠	12	4
Nebraska	≠	21	8
Kansas	65	90	3
South west central			
Arkansas	66	155	2
Louisiana	344	751	24
Oklahoma	54	121	15
Texas	806	2,578	307
Mountain			
Montana	28	22	2
Wyoming	27	78	2
Colorado	23	69	20
New Mexico	37	104	10
Idaho	132	456	58
Utah	90	292	12
Arizona	59	188	19
Nevada	29	97	2
Pacific			
Washington	137	124	55
Oregon	32	33	100
California	477	1,427	340
Total	2,634	7,445	997

* Elemental sulfur quantities are given in long tons. Sulfuric acid and ammonium sulfate quantities are given in short tons.

≠ Less than 1,000 tons/yr.

Table VIII a-2

POTENTIAL PRODUCTION OF SULFUR BYPRODUCTS FROM WESTERN SMELTERS

(1,000 tons/yr*)
1969

Smelter Group	Number of Smelters in Group	Smelter Locations	Elemental Sulfur ≠	Sulfuric Acid	Ammonium Sulfate #
I-A	3	Arizona, New Mexico, Texas	374	1,457	224
I-B	7	Arizona	602	2,332	349
II	3	Utah, Nevada	205	1,198	219
III	4	Idaho, Montana	316	1,405	75
IV	2	Texas	60	206	31
V	5	Kansas, Missouri, Oklahoma	62	492	7
VI, VII	2	Pacific Coast	52	234	19
Total	26		1,671	7,324	924

* Elemental sulfur quantities are expressed in long tons. Sulfuric acid and ammonium sulfate quantities are expressed in short tons.

≠ Excludes those emissions currently recovered as sulfuric acid.

Ammonium sulfate from the processing of only waste gases that contain small concentrations (usually less than 3%) of oxides of sulfur.

of the sulfuric acid, or 94 percent of the ammonium sulfate* that could be produced by all of the nonferrous smelters west of the Mississippi River.

a. Elemental Sulfur. The markets for elemental sulfur from western smelters need not be restricted to the western United States. As indicated earlier, elemental sulfur is shipped to markets all over the world. Since many of the western smelters are as close or closer to ports on the Pacific Coast than any of the other major sources of sulfur, world markets -- particularly markets in countries bordering the Pacific Ocean -- could be supplied as well as the markets in the western United States. The export markets for sulfur supplied by major producing countries are shown below:

	1965 Exports From: (1,000 long tons)			
Exports to:	United States	Canada**	Mexico	Total
Pacific Basin countries	605	359	155	1,119
Another exporting country	0	0	848+	848
All other countries	2,019	309	528	2,856
Totals	2,624	668	1,531	4,823

*The potential production of ammonium sulfate is shown in Table VIII a - 2 as 924,000 tons. This is the tonnage that could be produced if the Cominco process were used to recover sulfur dioxide from the dilute offgases from zinc sintering machines and copper reverberatory furnaces. Approximately half of the sulfur dioxide so recovered would be converted to ammonium sulfate. The total available market for ammonium sulfate in the west is only 997,000 tons.

**From Vancouver B.C. only.

+Exports to the United States.

All of the export markets just shown are available because the competitive price in the market exceeds the cost of transportation, and because none of the sulfur now exported is used by the sulfur exporters in captive operations overseas. Similarly, the sulfur markets in the entire western United States are within economic shipping distance of the smelters. However, a portion of the western market is not available because some of the sulfur is used in captive operations. The sulfur markets available to the western smelters are shown in Table VIII a - 3. The total available market (at least 6.1 million tons) is over three and one-half times as large as the total potential production (1.67 million tons).* With such a large market available, smelters should be able to sell all the elemental sulfur they can make provided they can match or better the price offered by the present suppliers.

The price smelters might receive for elemental sulfur, or for any sulfur byproduct, will be affected by the world price of sulfur because the latter is an item of international commerce. World prices in turn are affected by world supply of and demand for sulfur. World prices have fluctuated from a low of about $15 per long ton to a high over $40 in the last ten years (fob Gulf Coast prices, which are frequently quoted as the basis for world prices). Price fluctuations of this magnitude make it extremely difficult to predict the price smelters might receive.

The project team examined the present and possible future sulfur supply-demand situation in considerable detail (see appendix F), and concluded that the average price for sulfur between now and 1975 will probably be around $ 30 per long ton fob Gulf Coast. This price was used as the basis for determination of the prices at which elemental sulfur from smelters could be sold and also of the prices at which smelter-produced sulfuric acid and ammonium sulfate could be sold.

*Markets in the eastern United States are also within economic shipping distances of the western smelters. These markets have not been examined because the export and western U.S. markets for sulfur are so large compared with the total potential production that shipments to the eastern market (where the western smelters would have more difficulty competing) would not be necessary.

Table VIII a -3

AVAILABLE MARKETS FOR ELEMENTAL SULFUR
FROM WESTERN SMELTERS
1965

Area	Market Size (1000 long tons/yr)	Competitive Selling Price of Smelter Product* $/ton
Export via Gulf Coast	3,705	$19.50 - 22.50
Export via Pacific Coast	1,118	25.50 - 34.50
Missouri, Kansas, and Iowa	232	≠ - 33.50
California	209	29.50 - 36.00
Louisiana	200	# - #
Texas	153	21.50 - 26.50
Oregon and Washington	142	29.00 - 35.00
Idaho and Montana	121	25.00 - 27.00
Arizona and New Mexico	68	25.50 - 34.00
Oklahoma and Arkansas	61	24.00 - 26.00
Colorado and Wyoming	39	20.50 - 33.50
Utah and Nevada	37	31.50 - 34.00
All other western states	12	# - #
Total	6,097	

* Price of smelter elemental sulfur, fob the smelter, that is required to compete with existing suppliers for the market in the area when the fob Gulf Coast price is $30/long ton.

≠ The lower selling price incurred between the market and smelters that are farthest apart has not been calculated because the marketing area can be better served from other smelters.

\# Not determined because adequate markets exist in other areas where a higher price could be received for smelter-produced sulfur.

Table VIII a - 4 shows the distribution of smelter sulfur by market and by smelter group that should permit the smelter to realize the greatest price for this potential byproduct. According to the data developed and presented in Table VIII a - 4, all of the western smelters could sell all of their potential production of elemental sulfur if the price, fob smelter, was $ 25.50 or less per long ton.

Some of the smelters could charge more for their sulfur, up to $ 35, and still sell all of their potential production. But since the highest price the smelters might expect to receive for their sulfur is $ 35, no sulfur produced by the Asarco process could be sold at or above the production costs of $ 45 or more per long ton, and no justifiable market exists. Even if the Gulf Coast price of sulfur remains at its present $ 40, there would be no justifiable market for smelter sulfur.

b. Sulfuric Acid. Unlike the available markets for sulfur, the available markets for smelter-produced sulfuric acid must be situated relatively close to the smelters. Otherwise, the smelter acid cannot compete with acid made from elemental sulfur. Sulfuric acid made from $ 30 per long ton elemental sulfur can be produced for about $ 12 per short ton. The transportation cost alone, for moving smelter acid to distant markets, could easily exceed $ 12 per short ton. The smelters, therefore, might have to give their acid away in order to compete for any distant markets where the acid is currently produced from $ 30 sulfur.

Available markets for smelter acid are also limited because of the sizable amount of acid produced from captive -- or what amounts to captive -- sources of sulfur. One example of such a source is the sulfur or hydrogen sulfide, recovered from refinery waste streams, that is converted to sulfuric acid to be used in the refinery.

If distant and captive markets for acid are eliminated, the market in the western region is reduced from 7.4 million to 4.4 million tons (see Table VIII a - 5). Not all of the markets shown on Table VIII a - 5 are available to the western smelter operators, ie, markets for smelter acid selling for $ 0 per ton fob smelter. For example, the smelters that could supply the Louisiana market could not produce enough acid to fill the needs of that market.

Table VIII a-5

MARKETS FOR SULFURIC ACID FROM WESTERN SMELTERS
1965

Area	Market Size (1,000 tons)	Competitive Selling Price of Smelter Product*, $/ton
Louisiana	865	$ 1 - $ 3
Missouri, Kansas, and Iowa	794	8 - 22
California	692	4 - 6
Idaho and Montana	479	5 - 13
Utah and Nevada	417	7 - 24
Texas Gulf Coast	350	0 - 3
West Texas and New Mexico	221	10 - 22
Arizona	183	15 - 23
Colorado and Wyoming	152	5 - 17
Oklahoma and Arkansas	121	5 - 8
Oregon and Washington	107	10 - 23
Total	4,381	

* Fob price of smelter sulfuric acid from nearest smelters that is required to compete with existing suppliers for the market in the area. (Fob price must be $ 0/ton or more.)

Table VIII a-4

SELECTED AVAILABLE MARKETS FOR SMELTER-PRODUCED ELEMENTAL SULFUR*
(1,000 long tons)
1965

Marketing Area	Smelter Group I-A	I-B	II	III	IV	V	VI-VII	Total
Export Pacific Coast	336	512		112				960
Missouri, Kansas, and Iowa					36	33		69
California		60	139				10	209
Texas					24			24
Oregon and Washington				100			42	142
Idaho and Montana			16	104				120
Arizona and New Mexico	38	30						68
Oklahoma and Arkansas						29		29
Colorado and Wyoming			13					13
Utah and Nevada			37					37
Total	374	602	205	316	60	62	52	1,671
Selling prices, fob smelter, ($/long ton)	$25.50- $31.00	$26.00- $34.00	$29.00- $34.00	$26.00- $35.00	$26.50- $31.50	$26.00- $31.00	$35.00	

* These selected markets could use the total potential production of sulfur from western smelters and would provide the highest selling price to the smelter operators.

Even fewer of the markets can be classed as economically justifiable, ie, markets for smelter acid selling for $4 per ton or more fob smelter. The largest available but not justifiable market is the one along the Texas Gulf Coast.

The available and justifiable markets for acid from the western smelters are shown in Table VIII a - 6. These data indicate that the smelters could sell only about 3.1 million tons or 43 percent of the acid they are capable of producing to the available markets. Also, the justifiable markets for smelter acid (in 1965) are nearly as large as the available markets (2.8 million tons). Justifiable markets could absorb 38 percent of the total potential production of smelter acid.

Some of the smelter groups could sell a higher proportion of their acid than others, as can be seen from Table VIII a - 7. The smelters in Groups II, IV, and V could sell nearly all of the sulfuric acid they might produce to economically justifiable markets for $4 per ton or more. The Groups VI and VII smelters might sell nearly half of their potential production at $13 or more. However, the Groups I and III smelters could sell only 798,000 tons of their 5.2 million tons at $4 or more and 1.1 million tons even if they were willing to charge nothing ($0 per ton) fob the smelter, for their acid.

The possible future use of smelter acid is of equal if not greater importance to the market study. The analysis of the future markets has shown (see appendix F) that the smelter groups that have sufficient markets now will probably have sufficient markets in the future. The future markets are adequate in this instance because the growth rate in consumption of acid is higher than that of the production of nonferrous metals. The higher growth rate of acid consumption will also mean that a higher proportion of the acid could be used from the Groups I and III smelters, which currently do not have sufficient markets to absorb their potential production. The potential future markets for acid from these two smelter groups are discussed on the following pages. The data on these future markets for acid from the Groups I and III smelters are summarized in Table VIII a - 8.

Table VIII a -6

JUSTIFIABLE (AND AVAILABLE) MARKETS FOR SMELTER-PRODUCED SULFURIC ACID*

(1,000 tons, 100% acid)
1965

Marketing Area	Smelter Group I-A	I-B	II	III	IV	V	VI	VII	Total
Louisiana									0
Missouri, Kansas, and Iowa					7	456			463
California		280	332					47	659
Idaho and Montana			337	142					479
Utah and Nevada			417						417
Texas Gulf Coast	0(318)								0(318)
West Texas and New Mexico	108				108	5			221
Arizona	37	146							183
Coloredo and Wyoming			112	40					152
Oklahoma and Arkansas					90	31			121
Oregon and Washington				45			62		107
Total	145 (463)	426	1,198	227	205	492	62	47	2,802 (3,120)
Selling prices fob Smelter ($/ton)	$10-$22 ($0-$22)	$4-$23	$4-$24	$6-$14	$8-$17	$5-$22	$13-$23	$18-$26	

* Justifiable markets: where the selling price of the acid is $4/ton or more, fob smelter.
Available markets: where the selling price of the acid is $0/ton or more, fob smelter.
Available markets include all justifiable markets but not vice versa. Where available market is greater than the justifiable market, the available market is shown in parentheses.
All numbers in parentheses refer to available markets.

Table VIII a-7

MARKETS FOR SULFURIC ACID COMPARED WITH TOTAL POTENTIAL PRODUCTION*

(By Smelter Group)

Smelter Group	Potential Production from Smelters in Group	Available market; at $0 or more/ton	Justifiable Market; at $4 or more/ton	Market as a Percentage of Potential Production	
				Available	Justifiable
I-A	1,457	463	145	32%	10%
I-B	2,332	426	426	18	18
II	1,198	1,198	1,198	100	100
III	1,405	227	227	16	16
IV	206	205	205	100	100
V	492	497	492	100	100
VI, VII	234	109	109	47	47
Total	7,324	3,120	2,802	43%	38%

* 1,000 tons of 100% H_2SO_4 except for percentage columns (1969 potential production, 1965 markets).

Table VIII a-8

POTENTIAL FUTURE MARKETS FOR SULFURIC ACID

1975 Acid Consumption
(1,000 tons/yr)

Acid Markets by End Use	Group I Smelters		Group III Smelters	
	Total 1975	Increase 1965-1975	Total 1975	Increase 1965-1975
Fertilizer production	500	215	1,000	870
Leaching of copper ores	800-1,000	605-805	*	*
Uranium ore processing	220	150	225	150
Other	40	20	35	13
Total potential market	1,560-1,860	990-1,190	1,260	1,033
1965 potential production	3,789		1,405	

* Part of "other" uses.

Based on the data in Table VIII a - 8, the potential markets for acid from the Group I smelters could grow rapidly in the period from 1965 to 1975. Leaching of copper ores could take the greatest quantity of acid by that time -- up to one million tons per year. The potential use of acid is also expected to grow significantly; from 285,000 to 500,000 tons per year for fertilizer and from 70,000 to 220 000 tons for uranium. Despite these large increases in acid demand, the total potential market for sulfuric acid from the Group I smelters would only be from 1.56 to 1.86 million tons, or 41 to 49 percent of the total potential production.

Potential markets for acid from the Group III smelters could also increase markedly by 1975 (1,033,000 tons per year.) Most of this increase (870,000 tons) would be for production of phosphatic fertilizers. Processing of uranium ores could also require additional quantities of Group III smelter acid: 225,000 tons in 1975 compared with 75,000 tons in 1965. The above uses along with other lesser uses could increase sufficiently to allow the Group III smelters to recover 90 percent of sulfur values that are currently being processed and sell them as sulfuric acid in 1975.

The smelters in Groups VI and VII are the only other ones in the west that currently have insufficient market around them to utilize their total potential acid production. Unfortunately the information on the amounts of acid that might be recovered from these smelters was received too late in the project to allow us to analyze their future market.

c. Ammonium Sulfate. All of the 835,000 ton market for ammonium sulfate identified in Table VIII a - 9 would be available to the western smelters if it were not for the 75 percent limit imposed on the penetration of these markets.* Under the circumstances, the available market for ammonium sulfate was 626,000 tons in 1965 at prices ranging from $19 to $36.50 per ton, fob the smelter.

*The reason for imposing the 75 percent limit on the penetration of these markets by smelter-produced ammonium sulfate is explained in Appendix F.

Table VIII a -9

MARKETS AND COMPETITIVE SELLING PRICES
FOR AMMONIUM SULFATE
1965

Marketing Area	Market Size 1,000 tons	Competitive Selling Price of Smelter Product* $/ton
Texas	307	$19.00 - $36.50
California	235	20.50 - 29.00
Oregon and Washington	155	28.00 - 34.50
Idaho and Montana	60	30.00 - 35.00
Arizona and New Mexico	29	25.00 - 35.00
Colorado and Wyoming	19	30.50 - 33.50
Oklahoma and Arkansas	17	27.50 - 32.50
Missouri, Kansas, and Nebraska	11	27.50 - 34.00
Utah and Nevada	2	29.00 - 29.50
Total potential market	835	
75% of total market	626	

* Fob price of smelter ammonium sulfate that is required to compete with existing suppliers for the market in the area. (Fob price, by definition, must be $13/ton or more.)

The area-by-area breakdown of the justifiable and available markets for ammonium sulfate is given in Table VIII a - 10. These data indicate that the smelters might sell about 621,000 tons of the maximum 626,000 tons or 74 percent of the 75 percent market penetration set for them. The justifiable markets (where the byproduct might be sold for $25 per ton or more, fob the smelter) are smaller, 435,000 tons, corresponding to a 52 percent penetration of the existing market. The smelter groups that could supply these available and justifiable markets are shown in Table VIII a - 11.

The smelters in Groups I - A and III through VII could sell most of their potential production to the available market. Similarly, all of these smelters except Group I - A could sell all of their production to economically justifiable markets. The Groups I - B and II smelters could sell from one-half to one-third of their potential production.

The future sales of ammonium sulfate from the Groups I - B and II smelters will depend on the future use of ammonium sulfate as a fertilizer. Since adequate markets exist for the potential production of sulfuric acid from the Group II smelters, the future markets for ammonium sulfate around this Group of smelters was not determined because, even if no additional markets can be found, the Group II smelters could still recover their emissions as acid.

Markets for ammonium sulfate that could be served from the Group I - B smelters could also be served from the Group I - A smelters. Under the circumstances, future sales to these markets are considered to come from Group I as a whole rather than just Group I - B.

The three markets for ammonium sulfate fertilizer from the Group I smelters are located in (1) California, (2) Arizona, and New Mexico, and (3) Texas. Available markets in these states should increase by 270,000 tons per year by 1975. This additional market combined with the current available market (409,000 tons) would be more than large enough to absorb the present potential production from the Group I smelters (573,000 tons).

Table VIII a-10

JUSTIFIABLE AND AVAILABLE MARKETS FOR SMELTER-PRODUCED AMMONIUM SULFATE (WESTERN REGION)*
(1,000 tons)
1965

	Smelter Group							Total Market	Market ↓ Justifiable	Market ↓ Available
	I-A	I-B	II	III	IV	V	VI-VII VII			
Texas	149(199)				31			180(250)	59%	75%
California		40(176)						40(176)	17	17
Oregon and Washington			24	73			19	116	75	75
Idaho and Montana			43	2				45	75	75
Arizona and New Mexico	8	14						22	75	75
Colorado and Wyoming			14					14	75	75
Oklahoma and Arkansas	11							11	75	75
Missouri, Kansas and Nebraska						7		7	65	65
Total	168 (218)	54 (190)	81	75	31	7		435 (641)	52%	74%
Selling price, fob smelter, ($/ton)	$25.00-30.00 ($19.50-30.00)	$28.50-35.00 ($20.50-35.00)	$28.00-35.00	$31.00-33.50	$34.00-36.50	$29.50-34.00	$33.00-34.50			

* Up to 75% of the total available market in each marketing area. Justifiable markets: where the selling price of the ammonium sulfate is $25/ton or more, fob smelter. Available markets: where the selling price of the ammonium sulfate is $18/ton or more, fob smelter. Available markets include all justifiable markets but not vice versa. Where the available market is greater than the justifiable market, the available market is shown in parentheses. All numbers in parentheses refer to available markets.

↓ Market as a percent of the total market.

Table VIII a -11

AMMONIUM SULFATE MARKETS
AND PRODUCTION

Smelter Group	Potential Smelter*≠ Production	Market*# Available @ $18 or more/ton	Market*# Justifiable @ $25 or more/ton	Market as a Percentage of Potential Production** Available @ $18 or more/ton	Market as a Percentage of Potential Production** Justifiable @ $25 or more/ton
I-A	224	218	168	97%	75%
I-B	349	190	54	54	15
II	219	81	81	37	37
III	75	75	75	100	100
IV	31	31	31	100	100
V	7	7	7	100	100
VI, VII	19	19	19	100	100
Total	924	621	435	67%	47%

* 1,000 tons of ammonium sulfate

\# But no more than 75% of the total market in 1965

≠ From dilute waste gas streams only (See appendix F)

** In 1969

Ammonium sulfate production from the Group I smelters could increase from 573,000 to 679.000 tons per year by 1975 and still not exceed the total available market for ammonium sulfate in the area.

The justifiable markets (sales at $ 25 per ton or more, fob the smelter) for ammonium sulfate from the Group I smelters should increase by 105,000 tons per year by 1975. The 105.000 tons per year increase for the three justifiable markets would provide a total market of 327,000 tons, or enough to absorb only about 57 percent of the total potential 1965 production of ammonium sulfate from the Group I smelters.

VIIIb. MARKET ANALYSIS SUMMARY

Eastern Region

The seven smelters in the eastern region of the country should be able to find markets for any additional byproducts they might recover.

Western Region

The data on potential markets for the three smelter byproducts and on their potential smelter production are summarized in Table VIIIb - 1.

a. Sulfur. The western smelters should be able to sell all of the elemental sulfur they might produce. A market for over six million long tons of sulfur per year is available to these smelters, which could produce no more than 1.7 million long tons. However, in order to sell 1.7 million tons, some of the western smelters could probably charge no more than $25.50 per long ton fob the smelter, and they would all have to charge less than $35. If the smelters tried to charge as much as $45, they could not be sure of developing any market (although they might sell a little at that price in periods of short supply).

b. Sulfuric Acid. The existing markets for sulfuric acid (2.8 million short tons per year) could use only about 38 percent of the current potential production (7.3 million tons) if the smelter operators would charge $4 to $26 per short ton for their acid. Even

if some of the smelters were willing to give away their acid to distant users (who would be willing to pay for transporting it to their plants) the current market for smelter acid would be increased only to 3.1 million tons per year.

The potential markets for smelter acid could grow rapidly between now and 1975. The smelter operators might be able to sell as much as 5.3 million tons per year by 1975 if all of the potential markets develop. Even so, the western smelters could still market only about 73 percent of their current potential acid production.

c. Ammonium Sulfate. Existing markets for ammonium sulfate might absorb 435,000 tons of the 924,000 short tons per year potential production that could come from the processing of only the lean waste streams. The smelter operators would have to sell their ammonium sulfate for $25 to $36.50 per ton in order to capture this market. If the operators were willing to sell ammonium sulfate for as little as $18 to the more distant users, their total potential market might increase to 620,000 tons.

Future (1975) markets could use more ammonium sulfate, 540,000 tons per year at a sale price of $25 or more per ton and 891,000 tons at $18 or more. Even so, the future market would still not absorb all of the existing potential production.

Table VIII b-1

BYPRODUCTS FROM WESTERN SMELTERS:
POTENTIAL PRODUCTION AND MARKETS
(1,000 tons*/yr)

	Elemental Sulfur		Sulfuric Acid		Ammonium Sulfate	
	Potential production		1,671	7,324	924 *	
Potential market	At $45/ton or more	At $25.50/ton to $35.00/ton	At $4/ton to $26/ton	At $0/ton to $26/ton	At $25/ton to $36.50/ton	At $18/ton to $36.50/ton
Existing (1965)	0	1,671	2,802	3,120	435	621
Future (1975)	0	#	5,343**	ϕ	540	891

* Long tons for sulfur, short tons for sulfuric acid and ammonium sulfate.

≠ Potential production only from waste gas streams containing less than 3% sulfur dioxide.

Not determined but should be adequate to utilize total potential production.

ϕ Not assessed.

** Maximum market.

VIII c. COSTS OF CONTROL BY AVAILABLE METHODS

Estimated costs are presented graphically in the figures of this section for the five principal control methods listed at the beginning of section VI a. Some additional detail showing the development of these costs is given in the large tables included in appendix B and referred to in the following pages.

Capital costs for each of the control methods are derived from quoted or estimated costs for the equipment that makes up the control unit. These equipment costs allow for use of alloys and other construction materials as needed to accommodate the corrosion potentials of the process.

Costs from the graphs of this section are applied to specific smelter situations in section VIII d, "Control method evaluation with plant models".

Effect of Sulfur Control Costs on Cost of Metal

There is no fixed ratio between sulfur and metal values contained in the material charged to the smelters. Copper smelters in the United States operate with average weight ratios that range from less than 0.4 to as high as 2.6. One lead smelter may have twice as high an average ratio of sulfur to metal as another. The feed to zinc smelters is more nearly uniform, but still may vary by 10 to 15 percent from one smelter to another.

Again, there is no fixed relation between the amount of sulfur in the smelter charge, and the amount of sulfur that could be present in the feed gas to a sulfur oxide recovery plant. In one plant, only the roaster gas might be rich enough in sulfur oxides to be fed to the recovery plant, while in another the feed gas might consist of a variable mixture of roaster and other offgases. Another variable is the efficiency of removal of the feed-gas sulfur values in the different recovery processes.

It should be obvious, then, that the cost of sulfur control by a particular process cannot be calculated in terms of cents per pound of metal until several factors have first been specified. These will include, besides the factors just mentioned, the volume of offgas to be controlled and its concentration of sulfur oxides, as well as the magnitude of variations in the flow of the offgas. The section following this one does apply various combinations of control processes to a number of clearly defined plant models, and produces estimates of cost per pound of metal that apply only to these specific models.

Sulfuric Acid Manufacture by Contact Process

Of the many factors that must be considered before the owners of a plant can make a decision to install a contact sulfuric acid plant, two factors stand out as of fundamental importance:

1) The concentration of sulfur dioxide in the gas that can be delivered to the acid plant, and

2) The market for the acid.

The effects of gas concentration on costs are demonstrated in the following pages. Markets were considered in the preceding section of this report.

Feed Gas Criteria

For the purpose of estimating the costs for this recovery process, the criteria for the feed gas are as listed on the next page.

Temperature:	600 F
Pressure:	Atmospheric
Dew point:	Approximately 110 F
Wet bulb temperature:	Approximately 150 F
SO_2 content:	2 to 12 percent by volume, dry basis
SO_3 content:	0.2 to 0.5 percent by volume, dry basis
O_2 content:	2 to 16 percent by volume, dry basis
Dust content:	0.1 grain per standard cubic foot
Waste gas flow:	24 hours per day

Estimation of Costs

The costs presented here are estimated on the basis of a uniform flow and analysis of the smelter offgas. Such conditions are characteristic of zinc and lead smelters, but unfortunately, the offgas from a typical copper smelter does not meet this ideal situation. The selection of the best design capacity for an acid plant for control of sulfur dioxide emission from a copper smelter requires careful consideration of the variations in both flow rate and analysis of the offgas.

If the contact sulfuric acid plant is sized for average flow conditions, it will be necessary to bypass part of the offgas during periods of maximum flow. If sized for maximum conditions, the acid plant will be operating at below its capacity for considerable periods of time. The production cost of sulfuric acid will be higher than if offgas flow conditions are reasonably uniform.

The estimated production costs shown in the figures and the tables should be considered as minimum costs for application of this recovery system to copper smelters.

Capital Costs

The capital cost curves are based on estimated costs for the construction of a complete plant for sulfur oxides control, designed to operate on smelter gas containing five percent sulfur dioxide. This is considered a typical application of this kind of plant. The gas is assumed to contain a uniform quantity of sulfur dioxide and enough oxygen to convert it to sulfur trioxide. The costs include

equipment purchase, shipment, unloading, and installation, plus site preparation, foundations, piping, ductwork, electrical, instrumentation, support structures, and necessary buildings, all as needed for a battery limits plant unit, ready to operate.

From the cost information on this plant, costs were estimated for other plants of similar physical size to handle waste gases containing two, four, eight, and 12 percent sulfur dioxide. These plants of nearly equal cost will handle equal volumes of waste gas and produce a daily tonnage of sulfuric acid in proportion to the sulfur dioxide content. Note that these are not the plants shown in the four flow diagrams of Plates B-1 to B-4 in appendix B. The capital costs are given by plant segments in Table B-1 in appendix B.

Plotting these plant costs on a log-log chart, a family of curves was established at a slope of 0.80 to give estimates of capital costs over a range of plant sizes for each sulfur dioxide concentration. (See Figure VIII c-1) The slope of 0.8 was selected as a suitable average for a wide range of plant sizes. It is probably high for small plants, where the typical "six-tenths factor" more nearly applies, and low for large plants where more multiple units are required. However, the curves are considered to be reasonably accurate order-of-magnitude estimates of plant costs for the range of 1.5 million to 8 million dollars.

The estimates show how the capital cost per ton of sulfuric acid increases when the waste gases are low in sulfur dioxide concentration. The following compares costs on this basis for the range of 200 to 400 tons per day of sulfuric acid:

Sulfur Dioxide in Waste Gas, percent	Estimated Plant Cost, $ per ton per day of H_2SO_4 capacity
2	23,000
4	13,000
8	10,000
12	9,000
brimstone plant	5,000

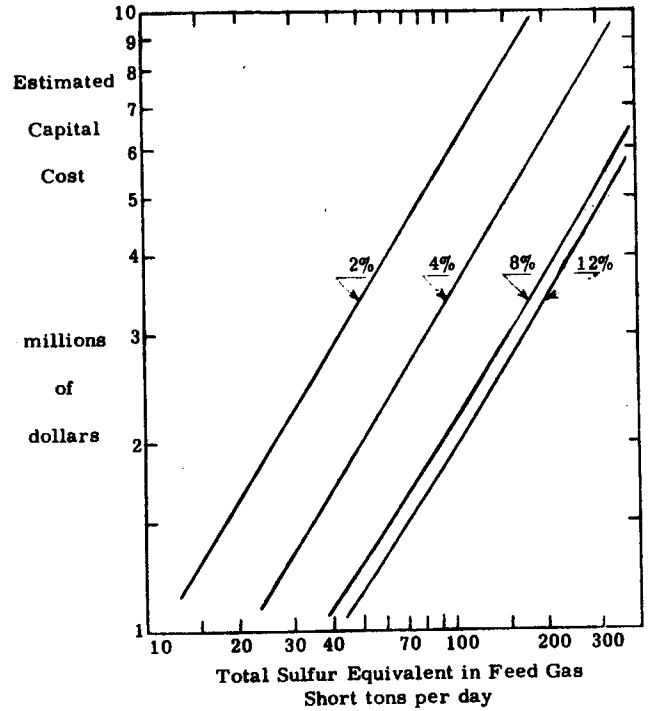

FIGURE VIII c-1

Capital Costs for the Contact Sulfuric Acid Process

Concentration of sulfur dioxide in the waste gas is indicated for each of the curves. Capital costs do not include working capital, cost of land, inventory, interest, offsite utilities, steam generators, plant access, equipment for preliminary cleaning of the gas.

Capital cost for a contact sulfuric acid plant fed with waste gas is considerably more than for an equivalent plant fed with brimstone. Additional equipment is required for cleaning the waste gas and for removal of excess water. When sulfur dioxide content is low, the larger volumes of gas add greatly to capital and operating costs.

Maximum Plant Size

The technological limitation on size of plants producing sulfuric acid from brimstone has not been reached. Several plants are operating in the 1600-ton-per-day range. One plant is reported to produce 2000 tons per day in a single converter system. The sizes of such plants are usually limited by flexibility requirements and by marketing limitations.

A 1600-ton-per-day sulfuric acid plant fed by brimstone has about the same physical size and cost as an 800-ton-per-day plant fed by smelter offgas containing six to eight percent sulfur dioxide. This is the maximum plant size to which these cost curves apply. Larger installations are likely to be multiple plants rather than single converter systems.

Operating Costs

Curves showing estimated operating costs are in Figures VIII c - 2, -3, and -4 for contact sulfuric acid plant units to handle smelter plant offgases containing two, four, eight, and 12 percent sulfur dioxide. The estimates used to prepare the curves were calculated for acid plants of three different feed gas capacities, for which the capital costs were approximately $2,000,000, $4,000,000, and $6,000,000. Operating costs were estimated for four plants at each capital cost level: one plant to treat a smelter offgas with two percent sulfur dioxide, one for a gas with four percent, one for eight percent, and one for twelve percent.

The operating costs given in the figures are typical for this type of plant. Direct and indirect costs are included, but not charges for sales expense or interest on investment. Details and cost criteria used are given in the production cost estimate, Table B-2

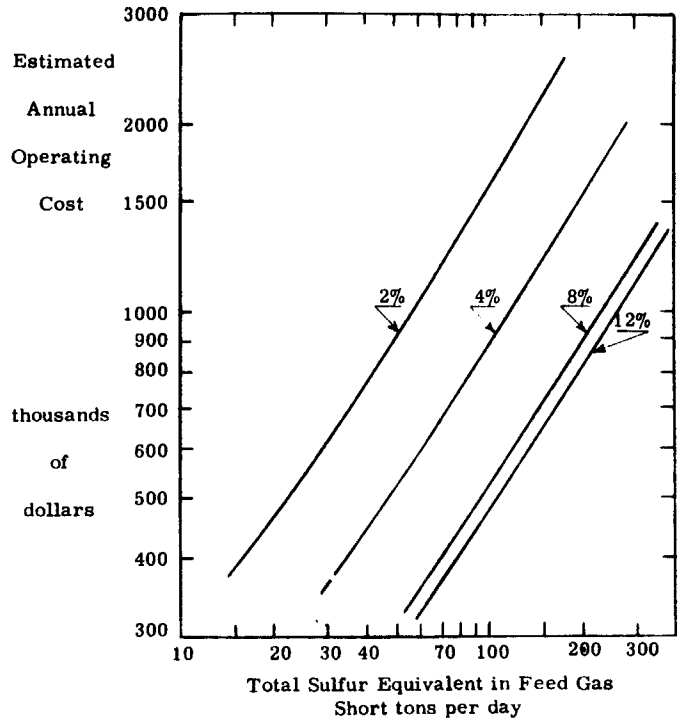

FIGURE VIII c-2

Annual Operating Costs for Contact Sulfuric Acid Process

Concentration of sulfur dioxide in the waste gas is indicated for each of the curves. Operating costs do not include interest on investment, sales costs, freight on product. There are 330 operating days per year.

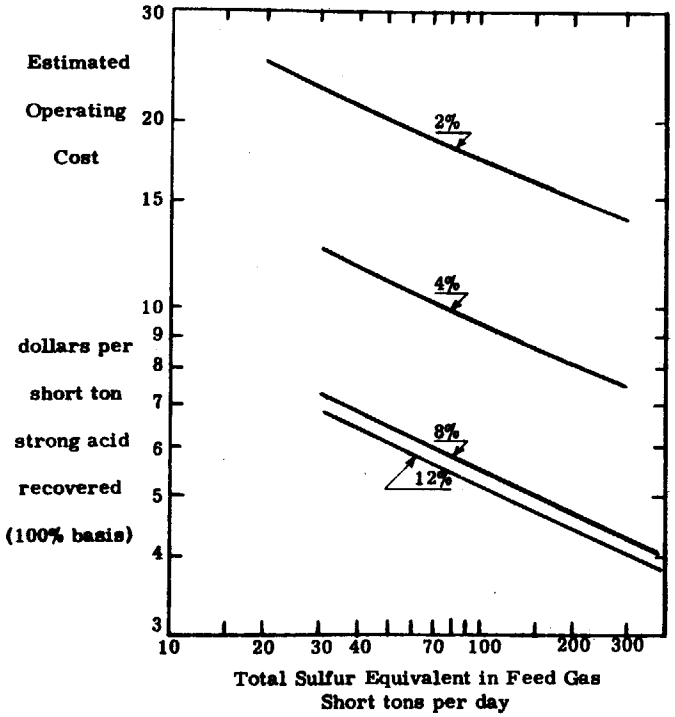

FIGURE VIII c-3

Operating Costs for Contact Sulfuric Acid Process (Acid Basis)

Concentration of sulfur dioxide in the waste gas is indicated for each of the curves. Operating costs do not include interest on investment, sales costs, freight on product.

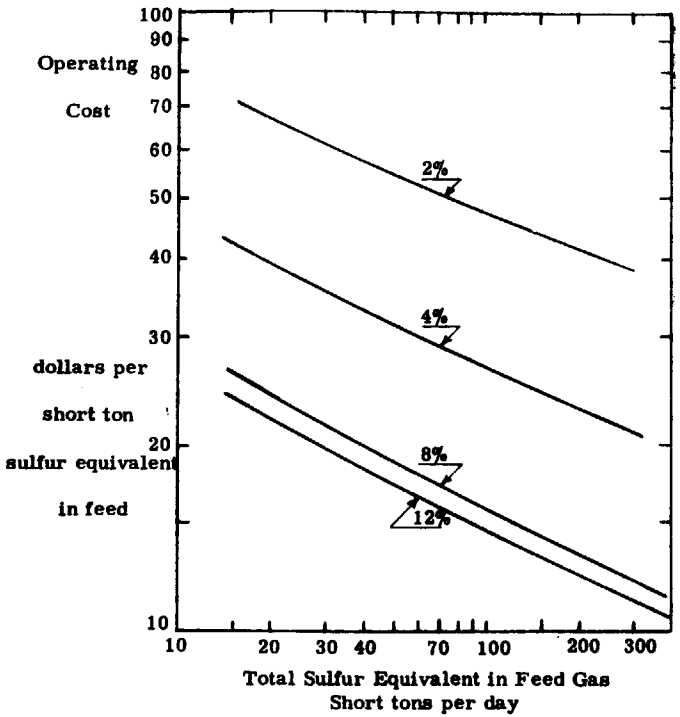

FIGURE VIII c-4

Operating Costs for Contact Sulfuric Acid Process (Sulfur Basis)

Concentration of sulfur dioxide in the waste gas is indicated for each of the curves. Operating costs do not include interest on investment, sales costs, freight on product.

in appendix B. This table indicates recovery and conversion efficiencies of 98 to 97 percent of the sulfur dioxide as marketable sulfuric acid of 66° Baume strength. Sulfur trioxide is recovered as a weak acid waste product.

Cominco Absorption Process

The feed gases to the Cominco units are assumed to have the same characteristics as the feed gases to the sulfuric acid units, except that the sulfur dioxide content is 0.5 to 3.0 percent by volume, dry basis, and the sulfur trioxide content is 0.05 to 0.23 percent. The Cominco units produce 24 percent sulfur dioxide gas, ammonium sulfate crystals, and a dilute acid waste.

Capital Costs

Estimated capital costs for Cominco process plants are given in Table B-3. These are the estimated battery limits capital costs for Cominco units if constructed in 1968. The costs are shown graphically in Figure VIII c-5. Costs for a cooling tower are included, but the costs do not include other offsite utilities, contingencies, working capital, inventory, interest, land, plant access, or gas cleaning equipment preceding the spray tower shown in the schematic flow diagram Figure VI a-1 of section VI a.

The cost estimates are based on a flowsheet and equipment list developed for a plant to handle smelter offgas containing 40 tons per day of sulfur dioxide at a concentration of one percent by volume. Preliminary quotations from vendors established the delivered and erected cost of the equipment, less foundations, as approximately $1,200,000 for this basic plant, escalated to the end of 1968. Rated horsepower of electric motors included totalled just over 1000. The delivered and erected costs of the equipment in each of the four sections of the plant were multiplied by experience factors to obtain the constructed plant costs. A different experience factor was used for each section. The sum of these costs is $4,800,000, which is the battery limits cost for the complete plant.

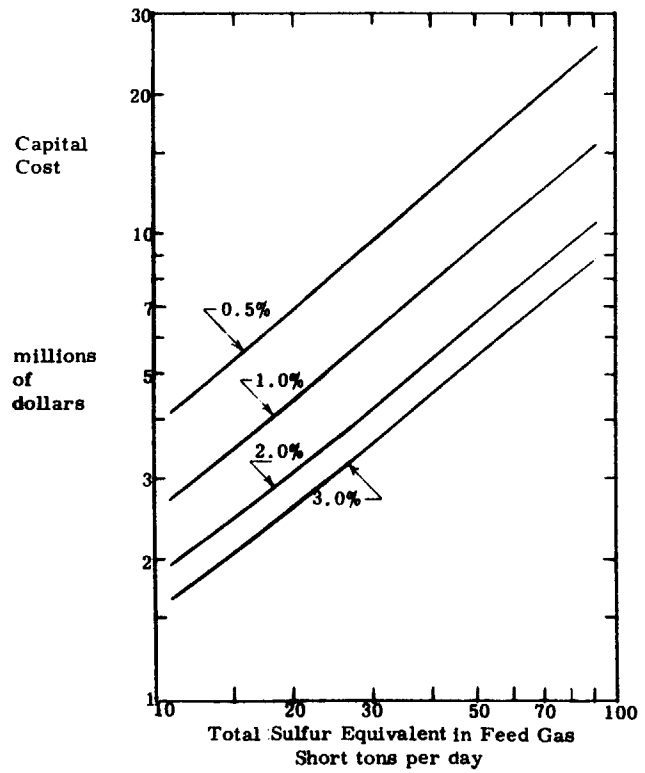

FIGURE VIII c-5

Capital Costs for Cominco Absorption Process

The four curves give estimated battery limits capital costs for absorption plants to treat smelter offgases of the sulfur dioxide concentrations indicated. The small amount of sulfur trioxide also present is included in the total sulfur equivalent. Costs not included are offsite utilities (except cooling tower), working capital, interest, inventory, contingencies, land, and plant access.

Note that changes in tonnage of sulfur dioxide or in gas concentration will affect the costs of the four plant sections in different ways. For example, a plant for 40 tons of sulfur dioxide daily at 0.5 percent concentration must handle twice the volume of offgas as the base plant at 1.0 percent. This requires a scrubber section, B in Table B-3, of twice the gas capacity, but makes no change at all in the costs of sections A, C, and D.

By considering each section separately to obtain installed equipment costs, and applying the appropriate experience factor, total plant costs were obtained for plants handling 20, 40, 80, and 160 tons per day of sulfur dioxide in gases of the following concentrations: 0.5, 1.0, 2.0, and 3.0 percent sulfur dioxide by volume.

Operating Cost Estimates

The results of calculations of operating costs are listed in detail in Table B-4 of appendix B for each of sixteen different conditions: sulfur dioxide content of feed gas at 20, 40, 80, or 160 tons daily, with concentration of the sulfur dioxide in the gas at 0.5, 1.0, 2.0 or 3.0 percent by volume.

The table gives operating conditions, such as percentage of sulfur trioxide assumed, feed gas volume, and the total sulfur equivalent of the sulfur oxides in the feed gas. The sulfur equivalent of the sulfur oxides recovered is given on the basis of 95 percent recovery of each oxide. Feed gas flow rates and concentrations are assumed to be uniform.

In calculating the yields of byproducts and required amounts of raw materials, the following criteria were used, derived from operating experience:

a) The Cominco unit receives the average feed gas flows and compositions listed in the table for 330 days per year.

b) The unit removes 95 percent of the sulfur dioxide from the feed gas and delivers it in the product gas from the stripper at a concentration of about 24 percent by volume.

c) The unit removes 95 percent of the sulfur trioxide from the feed gas and delivers it as weak sulfuric acid of 10 to 30 percent strength in a slipstream from the thickener overflow.

d) Sulfuric acid used by the unit equals two-thirds of a mol per mol of sulfur dioxide recovered.

e) Ammonia consumed equals two mols per mol of concentrated sulfuric acid used.

f) Ammonium sulfate produced for shipping equals 0.95 mol per mol of concentrated sulfuric acid used.

Recovered products are listed in the bottom lines of Table B-4: sulfur dioxide in tons of sulfur dioxide content in the product gas from the stripper, sulfur trioxide as tons of 100 percent sulfuric acid equivalent in the 10 to 30 percent weak acid byproduct, and ammonium sulfate as tons of dry crystals sent to shipping or storage, assuming a five percent handling loss of the ammonium sulfate.

The cost of the sulfuric acid used is taken as seven dollars per ton of 100 percent acid equivalent. Since the Cominco units would ordinarily operate in conjunction with a sulfuric acid plant, this would usually be an intra-plant cost and the actual charge against the Cominco unit for acid would depend on accounting procedures of the operating company. Ammonia, however, would be bought from the most economical outside source. The cost here is taken as fifty dollars per ton. Actual cost would be affected by smelter location relative to ammonia source, as well as by other factors.

Figures VIII c - 6 and VIII c - 7 present the estimated operating costs graphically. Figure VIII c - 6 gives the estimated annual operating cost for four different feed gas concentrations, plotted against the daily tonnage of sulfur that would be equivalent to the sulfur oxides in the feed gas. The costs included are those listed in the operating cost table in the Appendix with no credit given for the byproducts. In Figure VIII c - 7 the estimated operating cost is plotted as dollars per short ton of sulfur equivalent to the sulfur oxides recovered, again without credit for byproducts. Note that 95 percent recovery is assumed. The main product or byproduct is sulfur dioxide gas

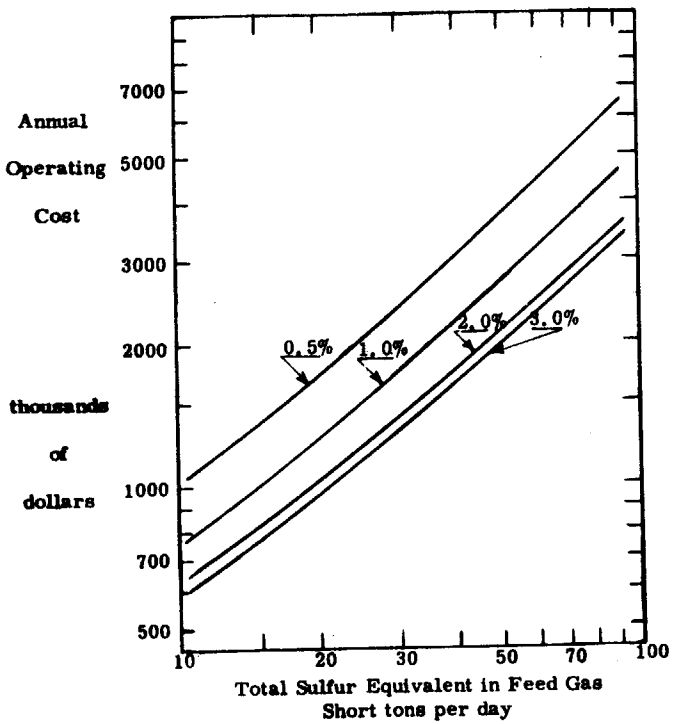

FIGURE VIII c-6

Annual Operating Costs for Cominco Absorption Process

Concentration of sulfur dioxide in the feed gas is indicated for each curve in volume percent. The sulfur trioxide also present is included in the total sulfur equivalent. Interest on investment is not included in costs, and no credit is allowed for value of byproducts. See detailed cost tables in Appendix. There are 330 operating days per year.

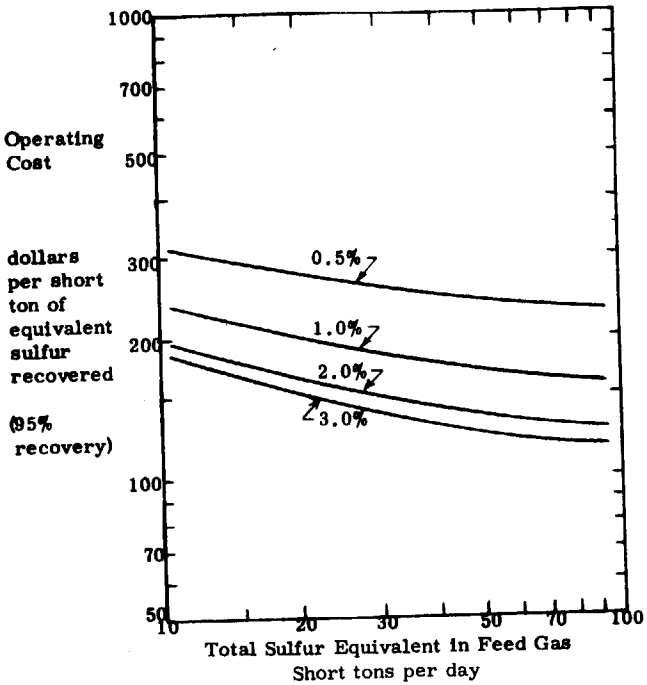

FIGURE VIII c-7

Operating Costs for Cominco Absorption Process

Concentration of sulfur dioxide in the feed gas is indicated for each curve in volume percent. The small amount of sulfur trioxide also present is included in the total sulfur equivalent. Interest on investment is not included in costs, and no credit is allowed for value of byproducts. See detailed cost tables in Appendix B.

from the stripper, but the minor byproduct, weak sulfuric acid, is also included as recovered sulfur. Ammonium sulfate is not included in the recovered sulfur equivalent since it is derived from the ammonia and sulfuric acid that are added.

Applications of the Cominco Process

A study of the figures and tables makes it apparent that the cost of recovering sulfur oxides by the Cominco process is high. Costs are lower with larger amounts of stronger gas, but even for 160 tons a day of sulfur dioxide in 3.0 percent gas the operating cost is $116 per short ton of sulfur equivalent recovered. The amount of credit that can be allowed for the three byproducts will be different at each plant. Value of the ammonium sulfate depends on market value, freight charges, selling costs, and overhead as discussed in section VIII a. Value of the rich sulfur dioxide gas depends on the same four factors and on acid plant costs. Weak sulfuric acid may have some value in the plant for leaching purposes, or it may be a liability that has to be neutralized and conveyed to a disposal area.

Examples of the costs of applying the process under certain specified conditions are given in section VIII d, "Control method evaluation with plant models". In general, the process does have value as part of a smelter plant where sulfuric acid is made from large flows of more concentrated sulfur dioxide gases, and only relatively small emissions of weak gases remain to be cleaned up. The Cominco process can then be used to avoid an air pollution problem that could become intolerable in some circumstances.

The process has even better potentials as part of a chemical plant that produces large amounts of sulfuric acid and ammonium sulfate and in which the Cominco unit operates on the clean, cool offgas from the acid plant. The costly initial gas cleaning and cooling stage, as well as the addition of equipment for crystallizing and handling ammonium sulfate, are unnecessary and operating costs are much less.

Asarco Sulfur Oxide Reduction Process

The cost calculations were based on 95 percent conversion of all sulfur oxides in the feed gas to recovered elemental sulfur. The plant operates 24 hours per day and 330 days per year. Characteristics of the feed gas are similar to those previously assumed for the feed gas to the sulfuric acid plant except for these items:

SO_2 content:	4 to 8 percent by volume, dry basis
SO_3 content:	0.26 to 0.38 percent by volume, dry basis
O_2 content:	13.2 to 7.6 percent by volume, dry basis

The feed gas is assumed to be of uniform concentration and flow volume. Sulfur oxides are recovered in the form of a 99.9 percent pure, salable grade of elemental sulfur.

Estimation of Capital Costs

The capital costs of Table B-5 in appendix B and the curves of Figure VIII c - 8 for reduction plants using this process are based on a cost estimate for a plant to recover 95 tons per day of sulfur from a smelter offgas containing six percent sulfur dioxide. The installed cost of each equipment item was estimated and the total multiplied by an experience factor of 3.0 to give the total estimated cost of the plant. The costs for plants of similar physical size to handle similar volumes of feed gas containing four, eight, or ten percent sulfur dioxide will be the same, since gas volume controls the size of the equipment.

With these estimates a family of curves with slopes of 0.80 were established on log-log graphs to show estimated capital costs over a range of plant sizes for each sulfur dioxide concentration.

Equipment costs for this process are increased considerably by the need to conserve heat and control temperatures as the gas stream passes through the several stages. This requires extensive use of gas-to-gas heat exchangers. The volume of gas handled does not decrease as sulfur is formed, and large electrostatic precipitators are used to collect small amounts of liquid sulfur from large volumes of hot gas. Multiple stages are required to reach reasonable recovery efficiency.

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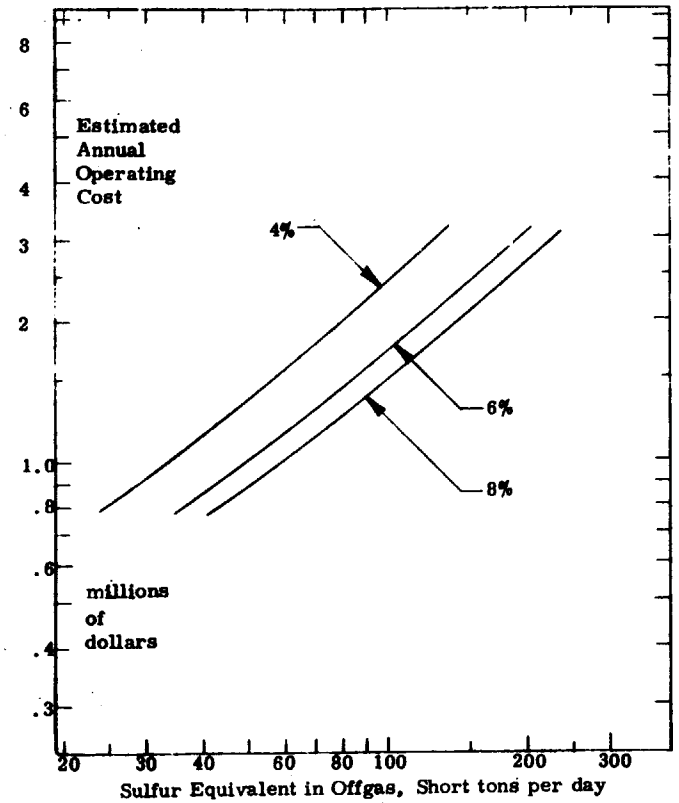

FIGURE VIII c-9

Operating Costs for the Asarco Reduction Process

Concentration of sulfur dioxide in waste gas is indicated for each of the curves. Operating costs do not include interest on investment, sales costs, or freight on product. The product is elemental sulfur. There are 330 operating days per year.

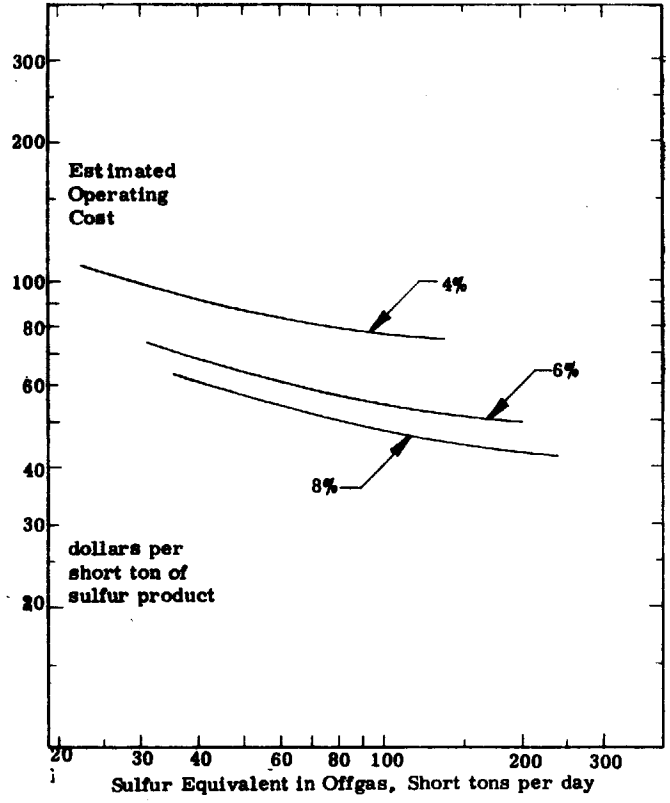

FIGURE VIII c-10

Operating Costs for the Asarco Reduction Process

Concentration of sulfur dioxide in waste gas is indicated for each of the curves. Operating costs do not include interest on investment, sales costs, freight on product.

Economics

The Asarco process never became commercial. The reason is apparent from the operating cost curves and the summary operating cost table. As the table shows, the cost of natural gas is an important element in the cost of the sulfur produced. In the calculations, the 1968 natural gas cost was assumed to be 40 cents per million Btu. Some plants may have to pay more, but some can obtain the gas for less than half as much. A natural gas cost of 20 cents per million Btu lowers the cost of the sulfur product by from five to ten dollars per short ton. The cost of the sulfur is cut by another two dollars per ton if a credit of 50 cents per thousand pounds is allowed for steam generated in the waste heat boiler.

Treatment by this process of 50 short tons per day of total sulfur equivalent in a smelter offgas containing four percent sulfur dioxide costs $1,360,000 per 330-day year under present conditions. The elemental sulfur produced totals 15,700 short tons and the cost of producing the sulfur is therefore $87.00 per short ton fob smelter plant. At the same 50-ton-per-day rate, if the offgas has eight percent sulfur dioxide, the annual cost on the curve equals a sulfur cost of $56.00 per short ton. When the offgas contains 100 tons per day of total sulfur equivalent at a sulfur dioxide concentration of four percent, the sulfur costs $83.00 per ton, and for eight percent gas and 100 tons per day the sulfur will cost $47.00 per ton. These costs do not include freight, selling charges, or interest on investment.

The process is presently unattractive as a money-maker, even with sulfur costs as high as they have been recently. It could be considered as an alternative if elimination of air pollution by sulfur dioxide is an absolute necessity. In such a case, the annual net operating cost of this process, after credit for the value of the sulfur, would be an addition to the production cost of the metal.

Lime and Limestone Processes

Costs for the lime and limestone processes were estimated for plants handling from 50 to 1000 tons per day of equivalent sulfur in offgases containing one, four, or nine percent sulfur oxides by

volume. Capital and operating costs were determined for the limiting cases as well as for one intermediate case at each concentration. Curves were then drawn on logarithmic charts to give estimated costs over this wide range of operating conditions. (Figure VIII c - 11 to VIII c - 20)

In any particular application it may be more advantageous to buy lime or finely ground limestone, rather than to construct and operate a plant to produce these materials. For this reason, capital and operating costs have been calculated and graphed separately for the lime-burning, limestone fine-grinding, and scrubber sections. The operating cost for the scrubber section varies depending on whether lime or limestone is used as the absorbing medium, since different quantities of waste are produced and the disposal charges differ. (See Tables B-7,-8,-9 and -10 in appendix B). Disposal costs of one dollar per ton of waste were used in the calculations.

Curves presented for the lime and limestone processes show costs for the reagent sections (lime-burning or limestone fine-grinding, Figures VIII c - 12 and VIII c - 17) separately from costs for the wet-scrubbing and waste-disposal sections. This takes care of the fact that capital and operating costs for the reagent sections depend on the amount of sulfur oxides in the waste gases, as expressed in tons per day, whereas the scrubbing and waste disposal section has to provide for gas flows that change inversely to sulfur oxide concentration changes when tons per day remain the same.

Design of the scrubbers must provide for maximum gas flow conditions that, in a copper smelter, may occur for only a few hours a day. With widely varying gas flows, the total amount of sulfur treated and of waste produced in a year will be less than the capacity of the scrubbing and waste treating section, and consequently operating costs will be higher per ton of sulfur equivalent than for units operating at full capacity all of the time.

All these curves give costs in dollars per short ton of sulfur equivalent in the offgas treated. The costs shown on the curves of Figures VIII c - 13 and VIII c - 18, have been calculated for units running steadily at 100 percent of capacity. Four of the curves

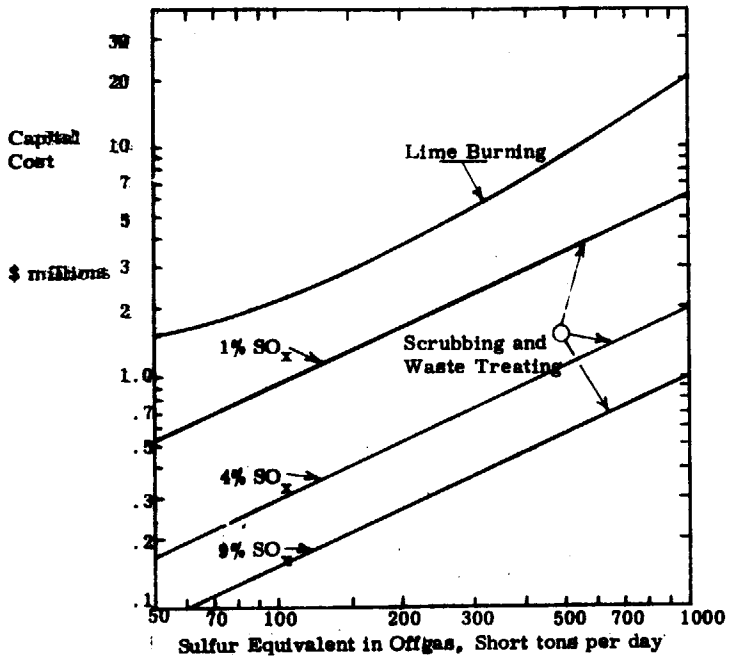

FIGURE VIII c-11

Capital Costs for Lime Wet-Scrubbing Process

Concentration of sulfur oxides in the offgas in percent by volume is indicated for the three lower curves. Capital costs do not include working capital, cost of land, inventory, interest, offsite utilities, plant access, or equipment for preliminary cleaning of the gas.

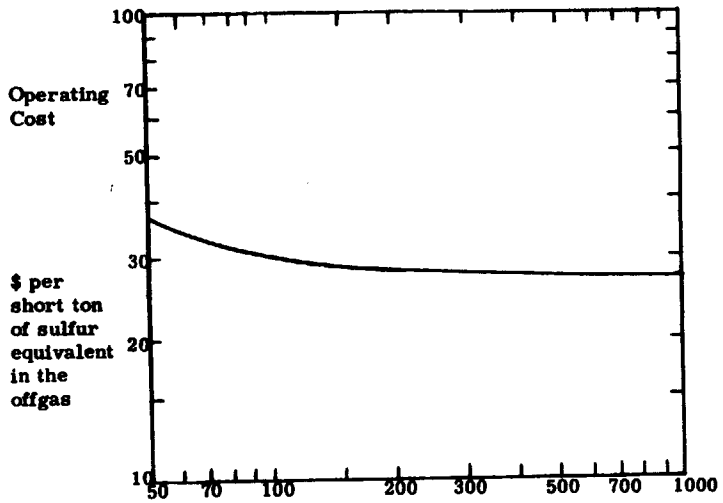

FIGURE VIII c-12

Operating Costs for the Lime-Burning Section of the Lime Wet-Scrubbing Process

Operating costs do not include interest on investment or credit for byproduct sales.

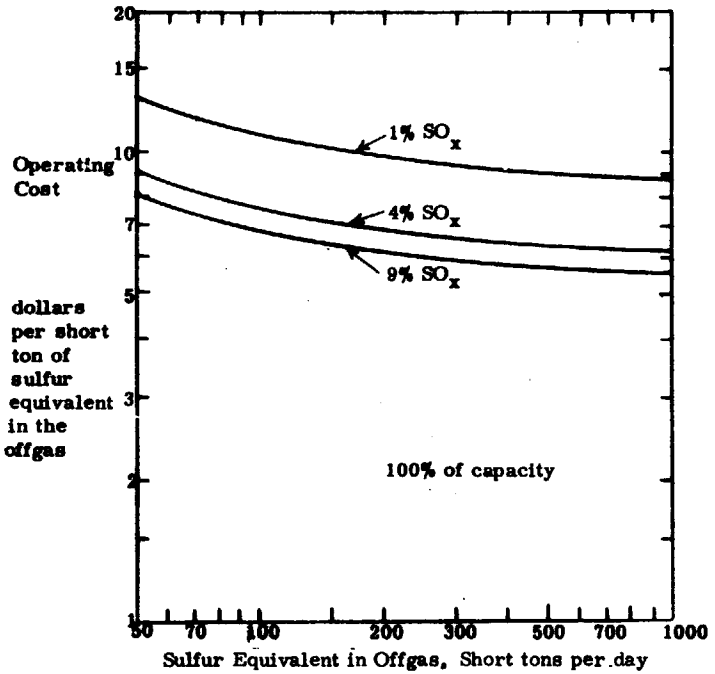

FIGURE VIII c-13

Operating Costs - Scrubbing and Waste-Treating Section of Lime Wet-Scrubbing Process at 100% of Capacity

Concentration of sulfur oxides in the offgas is indicated in percent by volume for each curve. Operating costs do not include interest on investment or credit for byproduct sales.

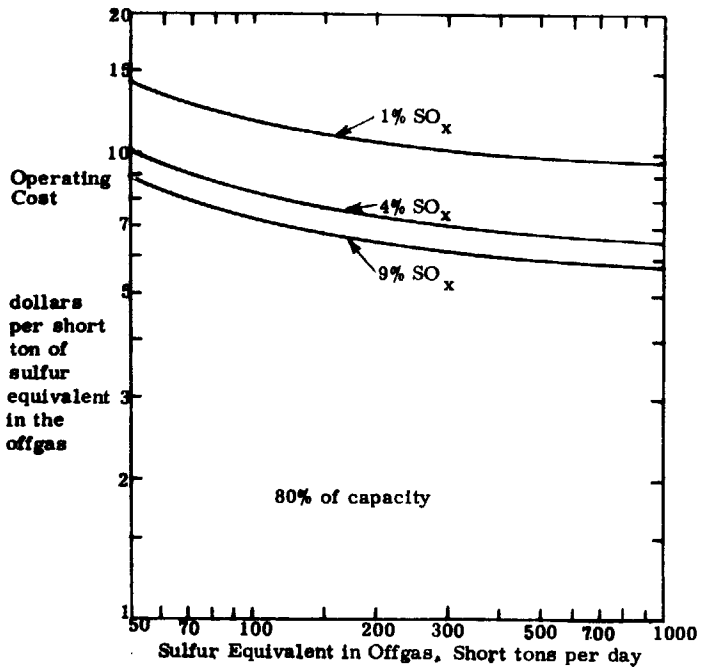

FIGURE VIII c-14

Operating Costs - Scrubbing and Waste-Treating Section of Lime Wet-Scrubbing Process at 80% of Capacity

Concentration of sulfur oxides in the offgas is indicated in percent by volume. Operating costs do not include interest on investment or credit for byproduct sales.

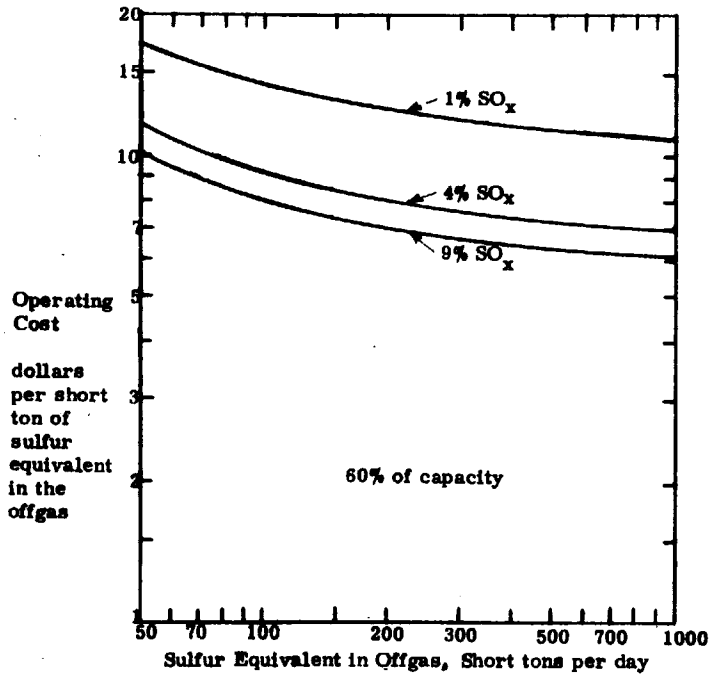

FIGURE VIII c-15

Operating Costs - Scrubbing and Waste-Treating Section of Lime Wet-Scrubbing Process at 60% of Capacity

Concentration of sulfur oxides in the offgas is indicated in percent by volume for each curve. Operating costs do not include interest on investment or credit for byproduct sales.

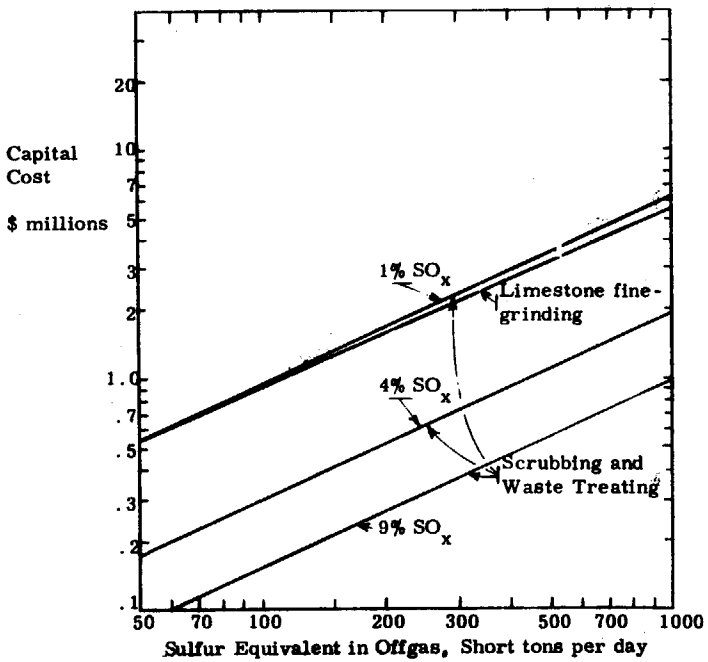

FIGURE VIII c-16

Capital Costs for Limestone Wet-Scrubbing Process

Concentration of sulfur oxides in the offgas is indicated in percent by volume. Capital costs do not include working capital, cost of land, inventory, interest, offsite utilities, plant access, or equipment for preliminary cleaning of the gas.

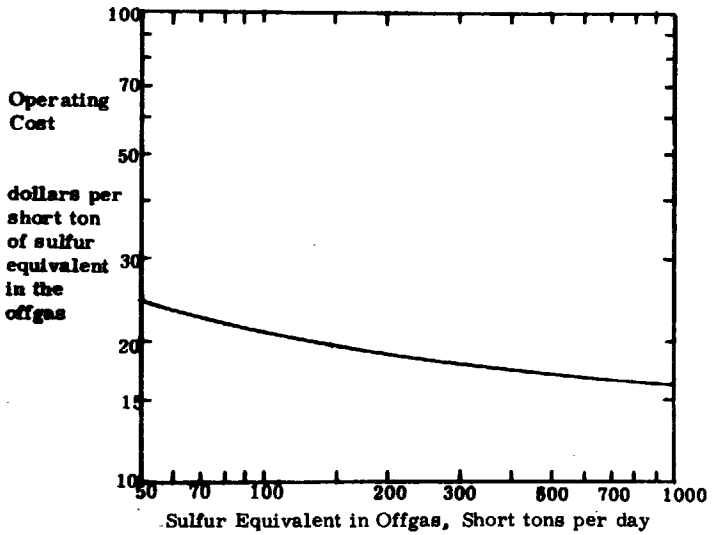

FIGURE VIII c-17

Operating Costs - Limestone Fine-Grinding Section of Limestone Wet-Scrubbing Process

Operating costs do not include interest on investment or credit for byproduct sales.

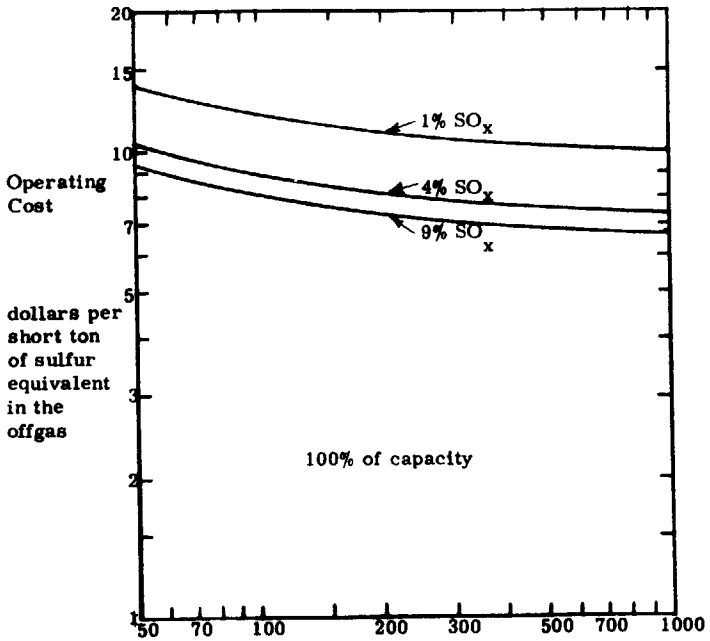

FIGURE VIII c-18

Operating Costs - Scrubbing and Waste-Treating Section of Limestone Wet-Scrubbing Process at 100% of Capacity

Concentration of sulfur oxides in the offgas is indicated in percent by volume for each curve. Operating costs do not include interest on investment or credit for byproduct sales.

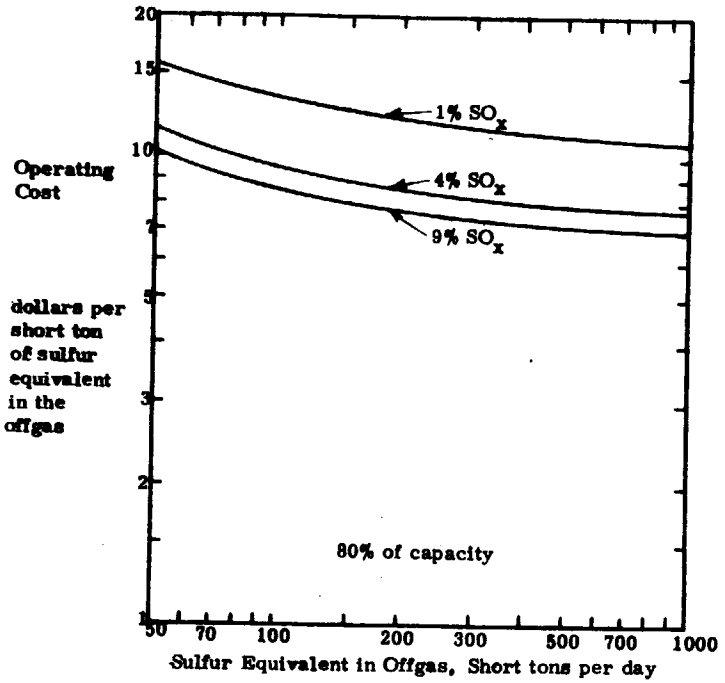

FIGURE VIII c-19

Operating Costs - Scrubbing and Waste-Treating Section of Limestone Wet-Scrubbing Process at 80% of capacity

Concentration of sulfur oxides in the offgas is indicated in percent by volume for each curve. Operating costs do not include interest on investment or credit for byproduct sales.

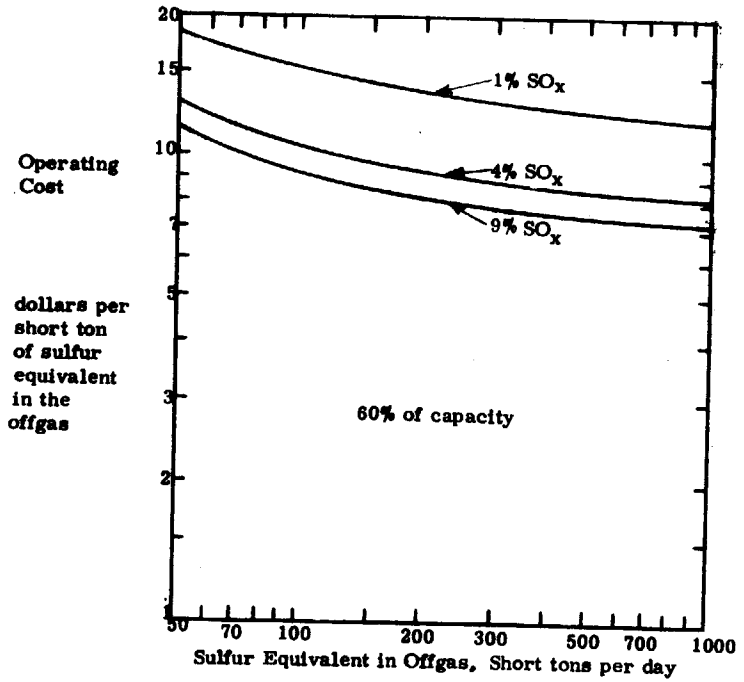

FIGURE VIII c-20

Operating Costs - Scrubbing and Waste-Treating Section of Limestone Wet-Scrubbing Process at 60% of Capacity

Concentration of sulfur oxides in the offgas is indicated in percent by volume for each curve. Operating costs do not include interest on investment or credit for byproduct sales.

give operating costs for the scrubbing and waste-treating sections of the two processes when these sections are operated below their design capacities. Figures VIII c - 14 and VIII c - 19 are for constant gas flows at 80 percent of capacity, and Figures VIII c - 15 and VIII c - 20 for flows at 60 percent. These curves for operation at 80 percent and 60 percent of design capacity used costs from the operating cost estimates for the scrubbing and waste treating section, (See appendix B, Table B-10,) with the exception that costs for electricity, plant water, and waste disposal were taken as 80 and 60 percent, respectively, of the costs for the unit operating at design capacity.

Capital Costs

Methods of estimating the capital costs for the three sections were as follows: (The capital cost graphs are in Figures VIII c - 11 and VIII c - 16)

1. A list of major equipment was drawn up for the lime burning section, and costs were estimated for each of the two limiting sulfur dioxide flows, as well as for an intermediate flow. The sum of the major equipment costs for each case was multiplied by an experience factor to determine the capital costs for this section.

2. The limestone fine grinding section was analyzed in a similar fashion, except that a different experience factor was employed.

3. For the scrubber and waste treating section, published figures (Re-8) were used to establish a median capital cost of $1,100,000 for a unit capable of treating 500,000 actual cubic feet per minute (acfm) of smelter offgas. Costs for larger and smaller units were estimated to be proportional to the 0.8 power of the gas flow, expressed in acfm. An estimate was obtained from a manufacturer for the cost of the fans needed to overcome pressure drop through the scrubber, and this was multiplied by the appropriate factor.

VIII d. CONTROL METHOD EVALUATION WITH PLANT MODELS

Models of copper, zinc, and lead smelters have been designed to serve as aids in evaluating sulfur oxide control methods. The smelter models correspond to the principal types of smelters now operating in the United States.

The models are described in the following pages and in Table C-1 and Plates C-1 to C-4 in appendix C. Matching the models with control processes and combinations of processes in the form of various schemes is discussed here, and estimates of capital and operating costs are presented in tables and graphs. The costs for the different schemes are based on the capital and operating cost tables and graphs for individual control processes as presented in section VIII c and appendix B.

By specifying certain definite ratios between sulfur and metals in these model plants, it is possible to present control costs in terms of cents per pound of metal. The quantities of metal and sulfur for each model are summarized with other data in Table C-1. (Note that all ton quantities given in this section and in the tables of appendix C are short tons unless otherwise specified.)

Offgas temperatures and sulfur oxides concentrations specified in Table C-1 apply to the condition of the offgas as it becomes the feed gas to a control process. The gas will have been diluted with air and cooled after leaving the designated smelting step, and entrained solids will have been removed to the point where not over 0.1 grain per standard cubic foot remains.

Conventional operation of the smelters that correspond to the various models is described in section V a of this report.

Control Methods Applied

The sulfur oxide control methods applied to the smelter models make use of the five principal processes described in section VI a of this report. Processes are applied singly or in combination as described in the schemes of Tables C-2, C-3, and C-4 (appendix C).

Schemes applied to the different models are not necessarily the optimum ones, rather they represent some illustrative choices among many possible alternatives.

The control methods that produce marketable byproducts are contact sulfuric acid, Cominco absorption, and Asarco reduction.

Sulfuric acid and Asarco reduction processes should have feed gases of around four percent sulfur dioxide concentration or better. Cominco absorption can take gases of lower concentration and deliver a concentrated sulfur dioxide gas byproduct. The first two of these processes require feed gases that are fairly uniform in concentration and without wide variations in volume of flow.

Lime and limestone slurry scrubbing processes produce only waste materials, their sole purpose being to control emission of sulfur oxides. These two processes and the Cominco process can handle gases of widely varying concentration, and flow volume can vary up to the top limits of the scrubber design.

For the purposes of this evaluation, the five control methods have been assumed to have the following control efficiences. These are the percentages of sulfur oxides removed from the offgas streams by each control method:

Contact sulfuric acid	95
Cominco absorption	95
Asarco reduction	95
Lime wet scrubbing	90
Limestone wet scrubbing	80

Unfortunately this report could present estimated costs for only one sulfur oxide reduction process, the Asarco process that was developed more than 25 years ago. The costs given by matching

this process to the models are high. Newer reduction processes that have not yet been fully described in the literature would probably yield byproduct sulfur at lower cost.

Model Copper Smelters

Two models of copper smelters have been prepared. The Model A smelter has reverberatory furnaces and Peirce-Smith converters but no roasters. Model B uses fluid-bed roasters, reverberatory furnaces, and converters. Smelters that are similar to Model A are treating concentrates rich in copper and relatively low in sulfur and iron. Smelters of the Model B type treat concentrates containing less copper and considerably more sulfur and iron. The ratio of sulfur to copper is 1.06 in Model A and 1.5 in Model B. Of the 16 copper smelters in this country, nine are similar to Model A and seven are similar to Model B. Actual average ratios of sulfur to copper vary from 0.4 to 2.0 in smelters of the Model A type, and 0.8 to 2.6 in smelters of Model B type.

The quantities of sulfur oxide gases generated by equipment in the two types of copper smelters are summarized in the following tabulation (from Table A-1, appendix A) as thousands of short tons per year of sulfur equivalent:

	Type A Smelters	Type B Smelters	Industry Totals
Roasters	0	360	360
Reverbs	242	149	391
Converters	682	383	1,065
Totals	924	892	1,816

Material balances have been calculated for a plant corresponding to each of the models. These are plants of relatively small size. The Model A plant has one reverb and two converters and produces 230 tons daily of blister copper. Plate C-1 has the flow diagram of this model. The small Model B has one roaster, one reverb, and two converters and produces the same amount of copper as Model A. A flow diagram of Model B is on Plate C-2.

In addition to the small model plants, medium and large sizes of each model were used in the matchings with sulfur oxide control processes. The medium size of each of these models has twice as many units of equipment as the small one and twice the sulfur oxide emission and copper production. The large size is three times the small one.

Concentrates fed to copper Models A and B have the following average compositions in percent by weight:

	Model A	Model B
Copper	24.8	19.2
Sulfur	31.9	35.0
Iron	27.8	29.0

Offgas Flows

Offgas flows from roasters, reverberatory furnaces, and converters differ from each other significantly. The reverberatory furnace gives off a steady flow of dilute gas, the roaster emits a steady flow of fairly strong gas, while the flow from converters is irregular and cyclical but has a high sulfur oxide concentration before dilution with air.

The important difference between Model A and Model B from the standpoint of control of sulfur oxide emission is that the flow and concentration of the combined offgases from Model B vary less than from Model A. The fluid-bed roaster of Model B generates more sulfur oxides than the converter in a fairly steady flow of gas that still has eight percent of sulfur oxides after it has been cooled by air dilution. This roaster gas can be mixed with the varying flow of gas from the converters to give a flow that is uniform enough to serve as feed gas to a recovery unit such as a sulfuric acid plant. Another feature favoring control of emissions from Model B over Model A is that the reverb of Model B generates less sulfur oxides. Since reverb offgases are consistently weak in sulfur dioxide, control is simplified and costs are reduced when reverb gas volume is smaller.

The problem of uneven volumes and strengths of offgas from the converters is illustrated by Plate C-3 in Appendix C. The rate of emission of sulfur oxides from each individual converter is traced in the profiles on the left. The uneven nature of the flow that results from the combined operation of two, four, or six converters is shown in the profiles on the right. Beginning at the bottom with only two converters, both flow rates and sulfur oxide emissions are sometimes at zero, and sometimes the overlapping converter cycles produce a maximum flow. Idealized flows are shown, without the frequent interruptions that occur for various reasons. Actual plant conditions are more uneven than the drawing indicates.

The advantage that a larger smelter has over a small one for control of sulfur oxides is brought out by comparison of the more moderate variations of the emission profiles of four or six converters with the wider swings of the profiles for two converters. This shows why some control options are not open to the operator of the small copper smelter. An acid plant, for example, requires a steadier flow and more uniform sulfur dioxide concentration than two conventional converters can provide.

Control Schemes Matched to Copper Models

Control processes have been matched to each of the copper models in six different arrangements or schemes. The schemes are described in Table C-2 in appendix C. Table C-5 gives the results of matching six schemes with Model A, and Table C-6 gives the results of the matchings with Model B.

The control process plants were sized to take care of maximum gas flows under the varying conditions that result from the cyclic nature of the converter offgas flows (Plate C-3). The design capacities of the plants for each of the schemes are tabulated on the next page as percentages of the capacities that would have been needed for the average gas flow in each case:

Scheme		Design Capacities small plant	medium plant	large plant
1	lime	125	125	125
2	limestone	125	125	125
3	Cominco, acid	137	130	130
4	Cominco, sulfur	137	130	130
5	acid, limestone		120	125
6	sulfur, limestone		120	125
7	lime	125	125	125
8	limestone	125	125	125
9	Cominco, acid	130	123	123
10	Cominco, sulfur	130	123	123
11	acid, limestone	132	125	125
12	sulfur, limestone	132	125	125

As stated, uneven offgas flows are more of a problem with Model A than with Model B, so much so that schemes 5 and 6 could be applied completely only to the steadier flows of medium and large Model A plants.

Tables C-5 and C-6 show that simple limestone slurry scrubbing costs the least to apply to each model (schemes 2 and 8) in capital and gross operating costs. However, sulfur oxide control is only 80 percent efficient and the byproduct is waste. Lime slurry scrubbing (schemes 1 and 7) also produces only waste material, but controls about 90 percent of sulfur oxides for two or three times the capital cost and only a little more operating cost.

Schemes 5 and 11, that send richer offgases to a sulfuric acid plant and only weak offgas to limestone slurry scrubbing, cost about the same as schemes 1 and 7 to install and a little less to operate. They are about equal in efficiency of control, but have the advantage of producing acid that can be sold to offset operating costs at some plant locations. The acid costs are low enough to permit sale of the acid at a profit for some smelters in each of the market areas of section VIII a. See Table VIII a - 6. Some smelters in each area except VI and VII will have a loss on these schemes, however.

Schemes that include either Cominco absorption or Asarco reduction (3, 4, 6, 9, 10 and 12) have high installation and gross operating costs. In schemes 6 and 12 the cost to produce the sulfur by the old Asarco reduction process far exceeds the highest selling price, fob plant, shown in Table VIII a - 4.

Figures VIII d - 1 and VIII d - 2 illustrate how the selling prices of the single byproducts of schemes 11 and 12 can increase or decrease the cost of copper produced by the smelter. Scheme 11 produces only a sulfuric acid byproduct and a waste material, and scheme 12 produces sulfur and waste. As shown, sulfuric acid must sell for from $4.50 to $7.50 per ton (100 percent acid basis) to break even on costs, depending on plant size and whether reverb gases are scrubbed with limestone slurry. At these prices, markets for the acid are available to all smelters in areas I-A, IV, VI, and VII (Table VIII a - 6) and to some smelters in each of the other marketing areas. Sulfur must sell for $60 to $75 per short ton ($67 to $84 per long ton) to break even. The prices are fob plant and do not cover sales costs and overhead. The graph form used in the above figures is not suited to illustration of net costs for schemes that yield two salable byproducts (schemes 3, 4, 9, 10).

To evaluate the schemes with two salable byproducts, selling prices can be used that are in the middle or low range of fob smelter prices stipulated in Tables VIII a - 4, - 6, and - 9 of section VIII a. Such prices could be $25 per ton for ammonium sulfate, $13 per ton for sulfuric acid, and $27.70 per short ton ($31 per long ton) for sulfur. At these prices, scheme 3 (Tables C-2 and C-5) does not show a profit; instead it costs 0.5 cents net per pound of copper produced by Model A large plants. Net costs for medium and small plants would be higher. Similarly, scheme 4 producing sulfur and ammonium sulfate costs 3.3 cents per pound of copper in large plants.

A model B large plant (Table C - 6) can make a profit from the sulfuric acid of scheme 9, and copper costs are cut by 1.2 cents per pound. Scheme 10 (sulfur and ammonium sulfate) costs such a plant 2.8 cents per pound of copper, however.

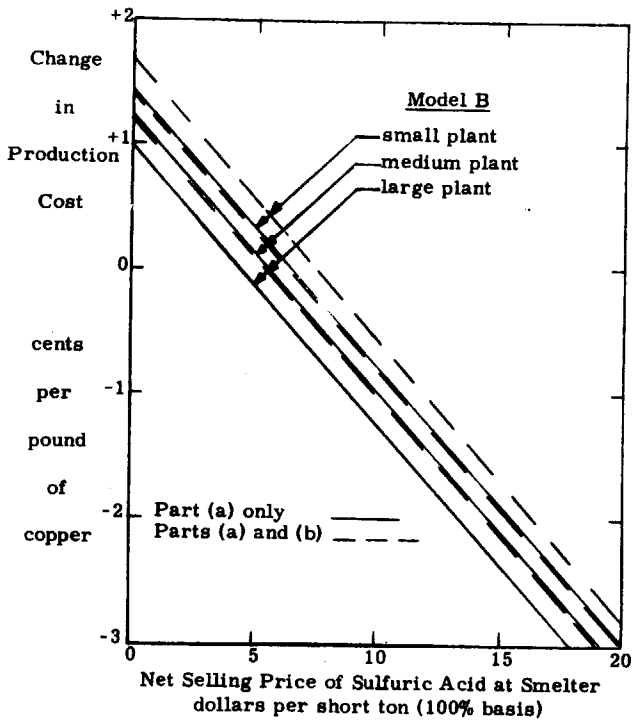

FIGURE VIII d-1

Effect of Scheme 11 on Production Cost of Copper

Credit allowed for sales of byproduct sulfuric acid. Net selling price equals gross price less sales cost and overhead.

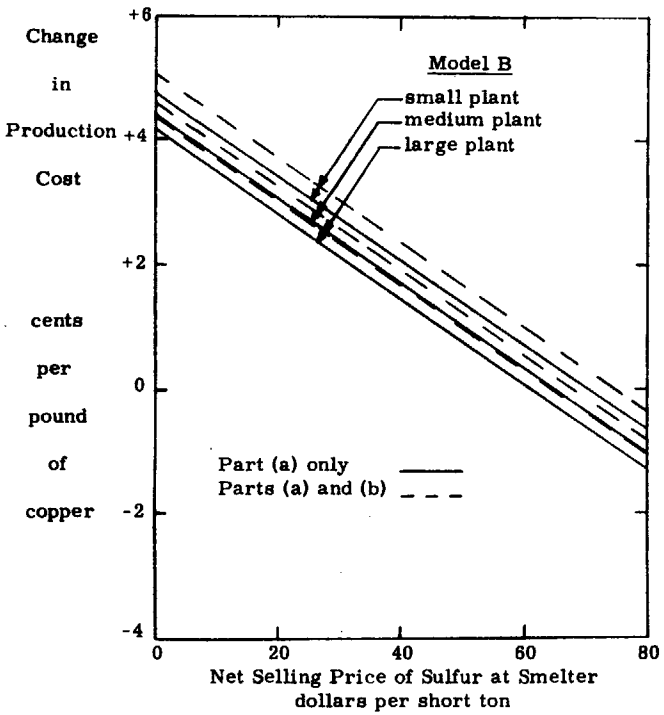

FIGURE VIII d-2

Effect of Scheme 12 on Production Cost of Copper

Credit allowed for sales of byproduct sulfur. Net selling price equals gross price less sales cost and overhead.

Model Zinc Smelters

Four different zinc smelter models have been prepared. Model A is representative of nine of the fifteen zinc smelters. These nine smelters have nearly three-fourths of the estimated production capacity of the primary zinc smelting industry, and all use fluidized or suspension roasters. Model B represents two smelters (326.31 and .32) of about the same size that are still using Ropp roasters. Models C and D represent one plant each. The Model C plant (326.21) uses multiple hearth roasters, and Model D represents a plant (326.25) that uses the sintering machine as a roaster. Two smelters that handle only oxide ores (326.26 and .37) are not represented by a model.

Characteristics of the different types of zinc roasters have been described in the zinc smelting portion of section V a of this report.

Control schemes for Model A were matched to plants of small, medium, and large size. For Model B, only small plants were matched to control schemes, and only medium size plants for Models C and D. Medium plants are twice, and large plants three times the small ones.

The Model A plant has drying, roasting, sintering, coking and retorting operations. The flow diagram is on Plate C-4. Only two (326.14 and .29) of the nine smelters it represents perform all of these operations. Four produce the metal by electrolytic methods and do not have sintering machines, cokers, or retorts (See Table A-2, appendix A).

The sulfur equivalents of the sulfur oxides generated in the zinc smelter industry are summarized by smelter types in the following tabulation. Quantities are thousands of tons per year:

Type	Roasters	Sintering Machines	Cokers & Retorts	Totals
A	578	9	2	589
B	54	14	--	68
C	66	--	--	66
D	0	60	--	60
Total	698	83	2	783

Offgas Flows

Unlike the copper smelters, offgas flows from zinc smelter operations are relatively stable in volume and sulfur oxide concentration. The temperatures and gas concentrations given in Table C-1 represent the condition of each offgas where it becomes the feed to a sulfur oxide control process. Because of the relative uniformity, control process plants matched with the zinc models are designed for 100 percent of the average offgas flows.

Control Schemes Matched to Zinc Models

The control schemes that are matched to the zinc models are described in Table C-3. There are four schemes for the principal model, A, and each is matched to a small, a medium-sized, and a large plant. Model B has four schemes matched to small plants, Model C has four schemes matched to medium-sized plants, and Model D has five schemes matched to medium-sized plants.

Results of the matchings are given in Tables C-7 to C-10. Since all but two or three percent of the sulfur oxides from Model A are contained in the 7.2 percent roaster offgas, an excellent degree of control is possible at a low gross cost by sending the gas to a sulfuric acid unit as in Scheme 1. This is actually done at all the type A plants, and only two of them recover less than 94 percent of the sulfur oxides generated. As Figure VIII d - 3 shows, if the acid sells for as little as $5.50 a ton at the plant (plus sales cost and overhead), the cost of operating even a small acid plant is returned. (Costs are based on 100 percent acid.)

In scheme 2 the roaster offgas is sent to a reduction plant. Costs are higher by the original Asarco reduction process, and Figure VIII d - 4 shows that even a large smelter has to get $46 per short ton ($51.50 per long ton) fob plant for the sulfur product to break even. This exceeds the selling prices of Table VIII a - 4 in all marketing areas.

It would be wasteful of potential profits for a type A zinc smelter, close to sulfuric acid markets, to use scheme 3 or 4 for control instead of scheme 1, even if the capital cost is less. The lime

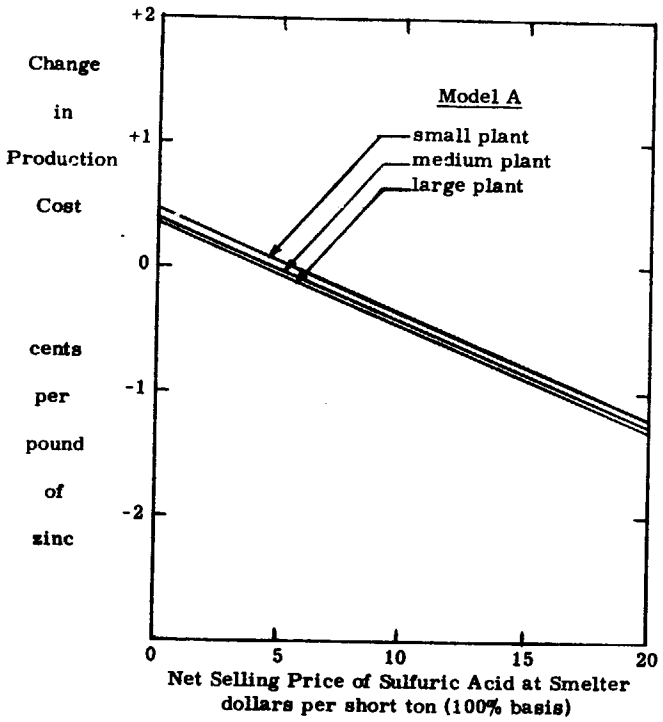

FIGURE VIII d-3

Effect of Scheme 1 on Production Cost of Zinc

Credit allowed for sales of byproduct sulfuric acid. Net selling price equals gross price less sales cost and overhead.

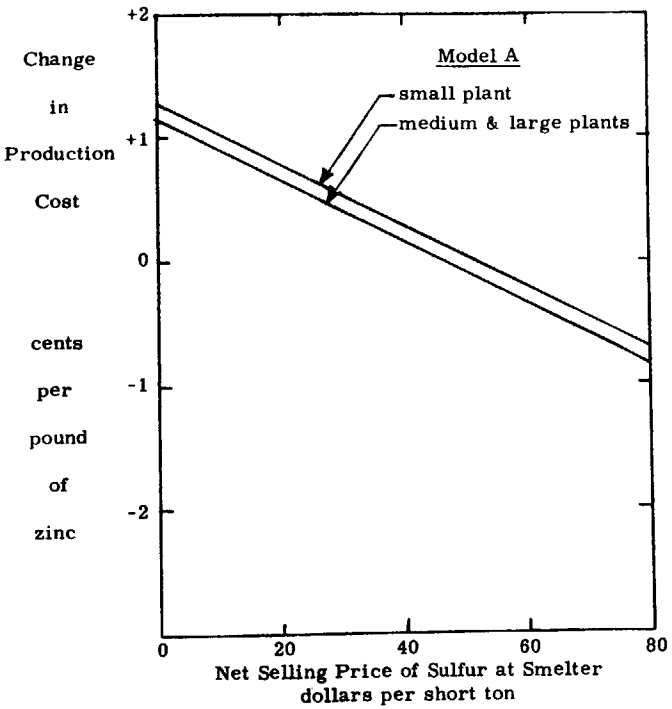

FIGURE VIII d-4

Effect of Scheme 2 on Production Cost of Zinc

Credit allowed for sales of byproduct sulfur. Net selling price equals gross price less sales cost and overhead.

and limestone slurry scrubbing schemes may cost less to install, but the byproduct is a waste material and the gross operating costs of 0.7 to 1.2 cents per pound of zinc for the four plant models are also the net operating costs. Zinc is not a metal that can easily absorb such increases in production cost.

Tables C-8 to C-10 show that Model B, C, and D schemes 5 to 16 all operate at high gross costs. The schemes that use Cominco absorption with either a sulfuric acid or a reduction plant cost 20 to 44 million dollars in estimated capital costs, and the gross operating costs are estimated at 3.1 to 5.6 cents per pound of zinc.

Byproduct selling prices used to evaluate copper model schemes making two byproducts can be applied to zinc model schemes making two byproducts. This allows $25 per ton for ammonium sulfate, $13 for sulfuric acid, and $27.70 per short ton ($31 per long ton) for sulfur. Of such zinc model schemes, not one shows a profit. Schemes 5 and 6, model B, cost 2.8 and 3.4 cents per pound of zinc, respectively. Schemes 9 and 10, model C, cost 2.6 and 3.3 cents. Schemes 13 and 14 of model D cost 1.2 and 2.0 cents.

Scheme 17 sends the two percent sinter machine gas from Model D directly to a sulfuric acid plant. This is a weaker gas than is normally used for acid, but a plant can be designed to handle it. Table C-10 shows that the gross operating cost is high, and Figure VIIId-5 shows that the net selling price of the acid, after deduction of sales and overhead costs, must be $14 per ton to break even. This price is obtainable by some smelters in each market area (Table VIIIa - 6).

As might be expected from the costs shown in the tables and figures, none of the type B, C, or D zinc smelters in this country make any recovery of sulfur oxides. (See Table A-2 in appendix A. The smelters referred to are code-numbered 326.31, .32, .21, and .25).

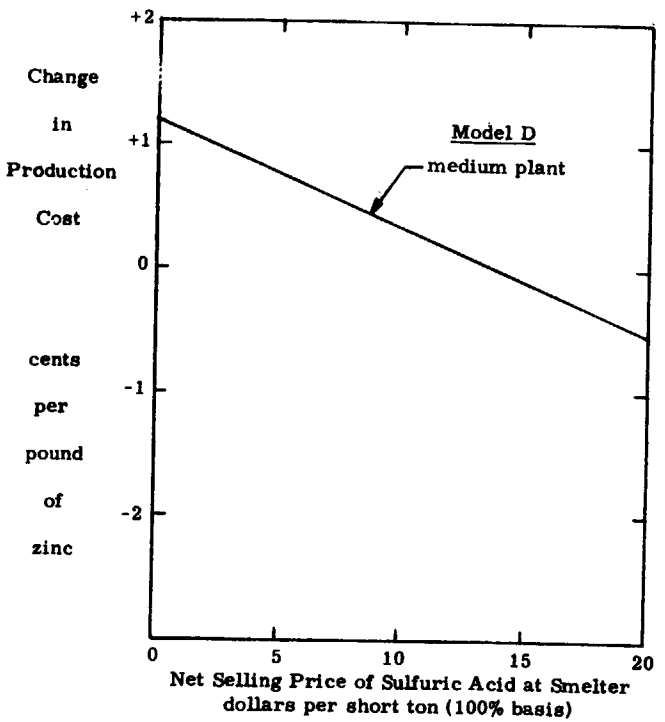

FIGURE VIII d-5

Effect of Scheme 17 on Production Cost of Zinc

Credit allowed for sales of byproduct sulfuric acid. Net selling price equals gross price less sales cost and overhead.

Model Lead Smelter

One model lead smelter, Model A, has been prepared that is representative of the three largest of the six smelters considered in this report (code numbers 326.10, .17, and .18). The smelters of this type use updraft sintering machines and generate 59 percent of the sulfur oxides generated by the smelters considered. They also have 68 percent of the estimated lead production capacity.

Not enough data on offgas conditions was available for preparation of a model to represent the other three smelters. All three use downdraft sintering machines and offgases are generally dilute. One smelter is able to recover about half the sulfur oxides by sending the stronger offgas from the first stage of a two-stage sintering machine to an acid plant.

Lead smelter Model A has updraft sintering machines that produce 98 percent of the sulfur dioxide generated in the smelter plant. The sinter machine offgas contains 5.0 percent sulfur dioxide by volume at the inlet to the control process plant, as stated in Table C-1. The table gives additional information about Model A. Offgases from the blast furnace and other smelter operations are very dilute, as described in section V a of this report.

The four recovery schemes that are matched with Model A lead smelter are described in Table C-4. In all the schemes, only the sintering machine offgases are processed for control of sulfur oxides. Other offgases are sent to stacks and vented to the atmosphere.

Sulfur oxides generated by the six lead smelters considered here are summarized by type of smelter in the following tabulation. Quantities are thousands of tons of sulfur equivalent per year.

Type	Sintering Machines	Blast Furnaces	Other	Totals
A	104	1	--	105
other	66	2	4	72
Total	170	3	4	177

Offgas Flows

Lead smelter offgases have fairly steady flow rates and sulfur oxide concentrations. Gas flow conditions given in Table C-1 apply to the offgas at the point where it becomes the feed gas to a sulfur oxide control process. As for the zinc models, the sulfur oxide control units that are matched to Model A lead smelter in the four schemes are designed for 100 percent of the average offgas flows.

Control Schemes Matched to Lead Model

Table C-4 describes the four control schemes matched to Model A lead smelter. Each scheme is matched to small, medium, and large smelter plants. The small plant is the one described in Table C-1, the medium plant is twice that size, and the large plant is four times the size of the small plant.

Table C-11 presents the results of the matchings. The lead plants generate about half as much sulfur oxides per unit weight of metal as the zinc plants. A similar high degree of control is possible, however, since the sinter machine offgas contains such a large portion of the sulfur oxides from the smelter.

Capital costs for schemes 1 and 3 are moderate, and for scheme 4 the capital cost is low. Gross operating costs, in cents per pound of lead capacity, are lowest for scheme 1, sulfuric acid, but the small amount of sulfur oxides handled boosts the cost per ton of acid. Reduction to sulfur by scheme 2, as would be expected, has the highest capital and operating costs. Schemes 3 and 4 produce only a waste material and the gross operating cost is also the net cost.

As shown by Table C-11 and Figure VIII d - 6, sulfuric acid from scheme 1 needs to sell fob plant at $7.30 to $10.60 per ton (100 percent basis), plus sales and overhead, in order to break even on the control operation. Some smelters in each marketing area (Table VIII a - 6) can sell acid in this price range, and any smelter in areas VI and VII (Pacific coast states) can do so.

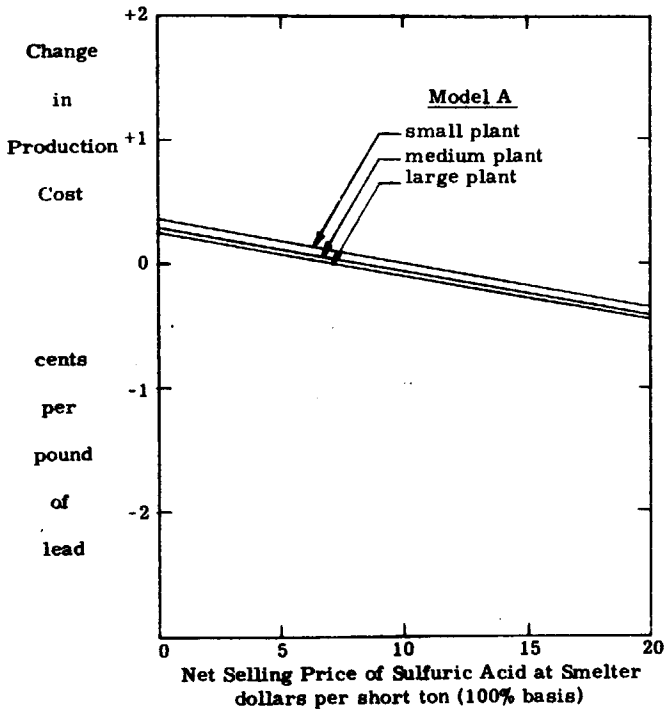

FIGURE VIII d-6

Effect of Scheme 1 on Production Cost of Lead

Credit allowed for sales of byproduct sulfuric acid. Net selling price equals gross price less sales cost and overhead.

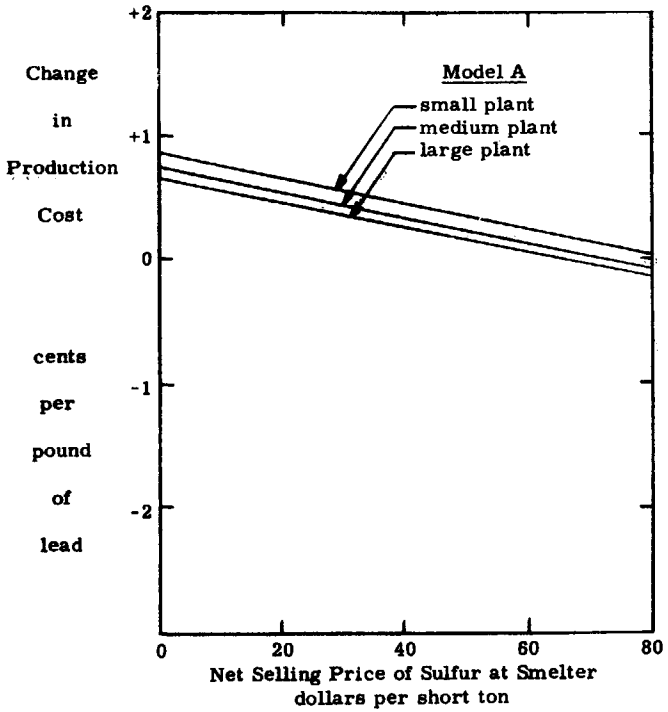

FIGURE VIII d-7

Effect of Scheme 2 on Production Cost of Lead

Credit allowed for sales of byproduct sulfur. Net selling price equals gross price less sales cost and overhead.

The table and Figure VIIId - 7 show that reduction to sulfur by scheme 2 requires unlikely high selling prices for the sulfur byproduct in order to break even. At these prices, there are no available markets (Table VIIIa - 4) when sulfur is selling at $ 30 per long ton, fob Gulf coast.

IX. CONCLUSIONS

The salient conclusions reached during the course of this study are:

1. That sulfur oxide offgases from smelters are now relatively well controlled in the eastern U.S., but due to problems of smelter location and the nature of the smelter processes, the much larger quantities generated in the west are only 23 percent controlled.

2. That there is and will continue to be a need for economically viable methods for concentrating the sulfur oxides of dilute process offgases, since such methods are not now available,

3. That sulfur oxide recovery and conversion to useful byproducts can be done at lowest cost when the gases enter the recovery process directly from the smelter at the highest concentrations,

4. That developments in the technology of smelting itself offer the most promise for production of sulfur oxide emissions as offgas streams that are rich enough in sulfur oxides for recovery and conversion at a profit,

5. That the most generally salable byproduct that can be made from smelter sulfur oxides is elemental sulfur,

6. That a low-cost process is needed to convert sulfur oxides to elemental sulfur,

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For concentration of sulfur dioxide from richer gases (generally four percent or more of sulfur dioxide), the Asarco DMA absorption process is available. The DMA process is fully cyclic and produces no product other than concentrated sulfur dioxide, except for a small amount of sodium sulfate. However, operating costs are believed to be high, and equipment costs excessive.

Effect of Sulfur Oxide Concentration on Costs

The one predominant factor affecting the cost of controlling sulfur oxide emissions is their concentration in the smelter gas that is to the conversion process (Section VIII c graphs). For a n quantity of sulfur oxide, low concentration means high me and high concentration means low volume. The costs of operation of gas cleaning and conditioning that precedes the conversion process are proportional to gas volume, and this is also true of the costs of most of the operations in the conversion processes themselves.

Reduction of the volume of gas, with attendant increase in the concentration of sulfur dioxide and decrease in oxygen concentration, will benefit all recovery systems. Additional air must be added to the gas fed to a sulfuric acid plant in order to provide the necessary excess of oxygen for oxidation of the sulfur dioxide. However, this air can be added downstream of gas cleaning and conditioning. The volume of the smelter gas should be kept at a minimum to reduce the cost of the gas cleaning and conditioning section of the system, which for an equal volume of gas handled will have about the same cost as the acid-making section. The minimum ratio of size to production capacity for the acid-making section is, of course, set by the necessity of adding air for oxidation.

There are smelters that are making sulfuric acid, for example, from gas with as little as 3.5 to 5.0 percent sulfur dioxide, but costs are high and they can make little or no profit from the operation (see pages VIII c - 2 to - 10). In contrast, smelters that make acid from 7.0 percent or stronger gas have a good chance for a profit if they are close to their acid markets.

Future success in upgrading offgas concentrations of sulfur oxides can come in large part from the continuing efforts of the smelter industry itself to remain competitive by developing improved smelting techniques that increase production of metal and reduce operating costs. A byproduct of such developments can be offgas flows of smaller volume and higher sulfur oxide concentration, particularly if gas collection systems are designed for cooling without air infiltration. A change in copper smelting, for example, that would avoid the varying offgas flows of Peirce-Smith converters or reduce the amount of weak offgas from reverberatory furnaces would make sulfur oxide control cost less. A step in this direction is the use of oxygen-enriched air in blowing the converters. Continuous smelting would be a still bigger step, if and when this becomes practicable.

The toughest technological problems are those involving (1) the large volumes of dilute gases produced by reverberatory smelting furnaces, sintering machines, and some types of roasters, and (2) the fluctuating volumes of offgas delivered by the copper converters, combined with infiltration of large quantities of air into the gas handling system. The problem of dilute gases from the reverberatory furnace can be reduced or avoided only by changing the smelting process; for example, by using oxygen-enriched air in the reverberatory furnace or by adopting flash smelting or other continuous process. Both oxygen-enriching and flash smelting are in commercial use abroad (see appendix G) and give more concentrated offgases.

Elemental Sulfur (Brimstone) as Byproduct

Markets are available for more sulfur than could be produced if western smelters made sulfur from all of the sulfur oxides now vented to the atmosphere. The conversion would have to be made at a cost that would permit sale at $25.50 to $35.00 per long ton, fob smelter. In contrast, not over about 42 percent of potential sulfuric acid production could be shipped, even if given away free at the smelter rail spur. Brimstone sulfur costs less to ship than the equivalent weight of acid, and it can be stored cheaply for indefinite periods. (Sections VIII a and b)

The sulfur oxide reduction process for which costs were estimated in this study is too expensive. The sulfur production cost for a plant making 200 long tons a day from smelter gas of eight percent sulfur dioxide strength is about $48 per long ton (Section VIII c). Costs are higher for weaker gases and smaller tonnages. The costs should be less from an up-to-date process using catalysts that reduce the sulfur dioxide at lower temperatures, and such processes may already have been developed by one or more U.S. corporations.

A commercial plant for reduction of sulfur dioxide to elemental sulfur with natural gas is being constructed at Sudbury, Ontario by Allied Chemical Canada Ltd. (see appendix G). It will operate directly on relatively rich gas from a pyrrhotite roaster. The adoption of this system was probably determined by the necessity for controlling air pollution in an area where the local market for sulfuric acid is limited and the distance from other potential markets is relatively great.

Manufacture of Sulfuric Acid

Almost all the sulfur oxides now being recovered from smelter gases in this country are converted to sulfuric acid. It is safe to say that this conversion is being made at nearly every smelter that can sell the acid at a profit, or even at no loss. The contact sulfuric acid process has the lowest costs of any process studied, and its technology is fully developed.

With the contact process, using smelter gases with at least 4.0 to 4.5 percent sulfur dioxide, it is possible to approach high levels of control of sulfur oxide emissions. Efficiencies of recovery of the sulfur dioxide can reach 96 to 97 percent or more with properly designed conventional equipment. The use of interpass absorption in the sulfuric acid plants, or application of absorption processes to the tail gases, can raise overall recoveries to over 99 percent, although considerations of economics would generally make these added refinements impractical.

X. RECOMMENDED RESEARCH AND DEVELOPMENT PROGRAM

The major obstacle to control of sulfur oxide emissions from smelters is the lack of economical methods for recovering and concentrating weak offgases and for reducing sulfur oxides to elemental sulfur. However, the potentially most important influence on sulfur oxide emission control could come from new developments in smelting process technology.

Smelting companies conduct extensive research and development in this area and technological modifications of processes are being instituted with regularity. Some of these improvements are announced and noted and some are not. These companies also conduct continuing programs for development of emission control and recovery systems. Nation-wide coordination and encouragement of these efforts seems appropriate.

The research and development projects described in the following pages are recommended for consideration as definite steps toward better control of emissions. Recovery and concentration of the sulfur oxides of weak offgases is an immediate problem and will continue to be a problem, even if a relatively diminishing one, in the foreseeable future. There is great need for a reduction process that can produce elemental sulfur from sulfur oxides at costs that allow sale of the sulfur at competitive prices. The problem of gas collecting and handling is important in any method of emission control because of its effect on gas volume, and information about gas constituents is pertinent because of potential effects on catalysts and on purity of byproducts. A recommendation is included for a long-range program to develop efficient new systems for metal recovery that could also alleviate the problems from sulfur oxide emissions. It is also recommended that a method be developed to clean smelter gases at high temperatures.

1. Develop to the point of commercial feasibility more economic cyclic absorption processes to absorb and concentrate sulfur oxides from weak smelter effluent gases that contain from 0.3 to 4.0 percent of sulfur dioxide by volume. The objective should be to obtain a process or processes with the lowest possible capital and operating costs. Necessary features will be minimum production of any secondary byproducts, minimum replenishment of reagents, and minimum degradation of absorptive capacity on continued recycling.

2. Develop to the point of commercial feasibility more economic cyclic gas absorption processes capable of concentrating sulfur dioxide from relatively rich gas streams (three to four percent sulfur dioxide, and higher) for subsequent reduction to elemental sulfur. To provide a baseline for these studies, an analysis should be made of the only currently operating commercial process in this category, the Asarco DMA process. The design of the DMA process has apparently never been optimized for use on large volumes of gas. It appears that the economics of the process may be radically improved if it is operated on gases containing eight percent or more of sulfur dioxide rather than three to five percent, the concentration range in which it is now being operated.

   Costs of the DMA process and any others studied should be estimated over a sulfur dioxide concentration range of from three percent to at least 20 percent. If the projected costs of any competitive process should appear significantly lower than those for the DMA process, complete development of the competitive process will be justified.

3. Develop to the point of commercial feasibility one or more sulfur dioxide reduction systems using natural gas, other hydrocarbons, or coke as the reductants. The systems should be designed conceptually, using the best elements of available technology from various related processes (such as the Claus process). The development should not necessarily be limited to systems that have been actually tested. One objective should be to obtain realistic estimates of the probable attainable production costs of elemental sulfur.

Costs should be developed as functions of the sulfur dioxide concentrations in the feed gas. The sulfur dioxide concentration range should extend from 100 percent down to perhaps 10 percent, or possibly lower. Identification should be made of the concentration level at which a one-step process (direct reduction of the smelter gas) becomes more economical than a two-step process (preconcentration of the sulfur dioxide from the smelter gas followed by reduction of the concentrated sulfur dioxide).

The results of these analyses should supply firm criteria for the development of new or improved reduction systems suitable for use on smelter gases from existing or anticipated new smelting processes.

4. Make an engineering study (technical and economic analysis) of smelting process enclosures and process equipment designed to limit introduction or infiltration of air to a practicable minimum. Estimated costs would be developed and compared with those for the conventional gas collecting and handling system, and would be related also to the economies achieved in the subsequent gas cleaning and sulfur recovery systems as the result of restricting air infiltration. The goal of the study should be to delineate practical designs that will provide offgas streams of uniformly high sulfur oxide concentration.

5. Initiate a project to obtain quantitative information about smelter effluent gases and their major and minor constituents. Gas measurements and analyses should be made at several smelters that are considered representative of the more advanced copper, zinc, and lead smelters in this country. This information is needed to more accurately define the nature and magnitude of the smelter emission problem at typical, well-managed plants. Data are needed on quantities of all constituents in order to determine what problems of catalyst poisoning, corrosion, and erosion must be considered in design of a sulfur oxide recovery and conversion system.

6. Institute a long range program to develop to the point of commercial feasibility efficient new systems for metal recovery that will be capable of producing metal at total costs equal to or less than those for existing processes, while at the same time producing any sulfur oxide offgases in such high strength as to be amenable to sulfur recovery. The systems could be among those known, at least conceptually, to individuals or companies but not yet generally reported.

7. Develop to the point of economical commercial application equipment capable of removing particulates from smelter gases at temperatures above 600 F.

   Advantages obtainable from this development will be (1) elimination of the need to cool the gas to 600 F or lower by cooling coils or jackets, waste heat boilers, or air dilution and consequent savings in costs of the offgas handling system, and (2) a saving in the cost of reducing sulfur oxides to sulfur by eliminating the need to reheat the cleaned gas before delivering it to the reduction process. By avoiding the need to cool the gas by dilution with air, a more concentrated offgas can be delivered to a plant unit for recovery of sulfur oxides.