

Sulfur Removal and Recovery from Industrial Processes

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FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in ADVANCES IN CHEMISTRY SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

In the last several years, much of the work in sulfur oxide emission control has been aimed at emissions from power plant stacks. However, there are many other stationary sources of sulfur emissions including non-ferrous smelters, sulfuric acid plants, and petroleum refineries. The papers in this collection are concerned with these "other" sources of sulfur-bearing off-gases. This volume is intended to be a consolidated reference source for those interested in the latest sulfur recovery methods.

After Mr. Semrau's introductory chapter follow four papers which present alternative techniques for recovering sulfur dioxide from the more concentrated smelter gas streams in the non-ferrous smelting industry. Presently, the only commercially available recovery techniques produce sulfuric acid or liquid sulfur dioxide. However, two of the discussions present developments in new processes for recovery of the sulfur values as elemental sulfur.

The next four papers concentrate on another emission source, hydrogen sulfide from Claus units. The Claus process has been used for several years to remove hydrogen sulfide from petroleum refinery waste gases. However, current environmental concerns require a more efficient recovery of the sulfur values. Some of the new technology to improve Claus plant efficiencies is discussed in these chapters.

The remainder of the book deals with scrubbing processes, the most publicized of the control methods. Process flowsheets for several absorbents are proposed and their applications in emission control are discussed.

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October, 1974

Controlling the Industrial Process Sources of Sulfur Oxides

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Industrial process or "noncombustion" sources of sulfur oxides emission are frequently more significant locally than fossil fuel combustion sources. The most important process sources are: primary copper, lead, and zinc smelters; Claus sulfur plants; sulfuric acid plants; coke plants; iron ore sintering and pelletizing plants; regenerators of fluid catalytic cracking units; and sulfite pulp mills. In the future, Claus sulfur plants will become still more important sources because of growing hydrodesulfurization of increasingly sour petroleum stocks and because of future coal desulfurization to produce clean solid, liquid, and gaseous fuels. Control of sulfur oxides emissions from the industrial process sources is closely related to the technologies of the sources themselves, and changes in the process technologies may greatly improve the effectiveness and economy of emission control.

During the past decade, the principal concern with control of sulfur oxides emissions has been focused on flue gases from fuel combustion, primarily the flue gases from power plants. Fuel combustion accounts for about three quarters of the estimated total sulfur oxide emissions in the United States. However, the emissions from industrial processes are frequently more significant than is indicated by their contribution (about one fifth) to the total emission. Whereas many of the combustion sources are individually small and widely dispersed, industrial operations are often relatively large and concentrated sources and may cause severe local pollution problems. Copper, zinc, and lead smelters, in particular, have a long and notorious history as pollution sources. It is only in recent years that individual power plants have become large enough that their sulfur oxide emissions compare with those from smelters.

The industrial processes present both special problems and special opportunities that are not encountered with fuel combustion gases. In most cases, sulfur dioxide concentrations in the waste gases are higher than in combustion gases, and there are greater opportunities to recover the sulfur dioxide in useful forms. The processes designed to treat combustion gases are not always well adapted to treating process gases. Finally, changes in the industrial processes frequently present opportunities for more economical control and recovery of the sulfur dioxide.

Emission Sources

Two sets of sulfur oxide emission estimates for the United States, drawn from Environmental Protection Agency sources (1, 2, 3) are presented in Tables I and II. The source categories in the two tables are not consistent nor are the estimates of the total emission, even allowing for a 3-yr difference in the base periods. It is also obvious that certain sources have not been accounted for in the compilations. Nevertheless, the estimates do identify most of the industrial sources and indicate their relative magnitudes. The distributions of sources in other nations are similar to those in the United States in a number of reported instances (4).

Table I. Estimated SO_x Emissions in the United States (1970)

<i>Source Category</i>	<i>SO_x Emission^a (10⁶ tons/yr)</i>	<i>Per cent of Total</i>
Transportation	1.0	2.88
Fuel combustion in stationary sources	26.5	76.42
Industrial process losses		
Pulp and paper	0.077	0.22
Calcium carbide	0.002	—
Sulfuric acid plants	0.474	1.37
Claus sulfur plants	0.875 ^b	2.52
Coking	0.474	1.37
Petroleum refining		
Fluid catalytic cracking	0.354	1.02
Thermal catalytic cracking	0.005	0.01
Nonferrous metals		
Copper	3.57	10.30
Zinc and lead	0.9	2.72
Iron ore sintering and pelletizing	?	—
Solid wastes disposal	0.1	0.29
Agricultural burning	0.1	0.29
Miscellaneous		
Coal refuse burning	0.2	0.58
Total	34.68	100.00%

^a From Ref. 1, except as noted.

^b Ref. 2.

Table II. Estimated SO_x Emissions in the United States (1973)

<i>Source Category</i>	<i>SO_x Emission^a (10⁶ tons/yr)</i>	<i>Per cent of Total</i>
Mobile sources	1.15	2.37
Stationary combustion sources		
Steam—electric power	28.15	58.04
Industrial boilers	7.77	16.02
Metals		
Primary copper smelters	4.45	9.18
Primary lead and zinc smelters	0.57	1.18
Fuels industries		
Petroleum refineries	4.40	9.07
Natural gas	0.54	1.11
Chemicals		
Sulfuric acid	0.83	1.71
Coking	0.44	0.91
Accidental fires	0.19	0.39
Total	48.50	100.00%

^a From Ref. 3.

The smelting of copper, lead, and zinc from sulfide ores is second only to fuel combustion as a source of sulfur oxide emissions in the United States. Petroleum refineries stand in third place in Table II. However, it seems clear that the greater part of the refinery emissions comes from the combustion of high-sulfur fuels in boilers or process heaters. From a process standpoint they should be classified as originating from the category of stationary combustion sources; this appears to have been done in Table I. The strictly process sources in refineries consist primarily of Claus sulfur plant tail gases and the regenerators of catalytic cracking units.

The tail gases of Claus sulfur plants are apparently the second largest process source after nonferrous smelters. The Claus plants convert hydrogen sulfide, which is mostly derived from petroleum refining or the treatment of natural gas. Most of the largest Claus plants in the United States and Canada are installed at natural gas-treating plants (2). It is ironic that although natural gas is our cleanest fossil fuel, its preparation for use is sometimes a major source of sulfur oxide pollution. In France, the Claus plants at the Lacq natural gas plant were estimated to yield 10% of the total sulfur oxide emission in the nation for 1970 (4) and have been a serious source of pollution and agricultural damage (5).

The emissions from Claus plants can be expected to present an increasingly serious potential problem in the future as petroleum refineries operate on increasingly sour crudes from the Middle East and elsewhere and as plants are built to desulfurize substitute natural gas (SNG) and liquid fuels from coal.

Sulfuric acid plants continue to be substantial sources of sulfur oxide emissions. The emissions estimates presented in Tables I and II presumably refer only to emissions from sulfur-burning acid plants. The emissions from plants producing by-product acid from smelter gases, sludge acid, and other such sources are probably classified with the emissions from the appropriate industries.

Relatively little direct information has been published on the sulfur oxide emissions from fluid catalytic cracking (FCC) unit regenerators (6, 7), although the estimate in Table I indicates that the total is substantial. The sulfur remaining in the coke deposited on the catalyst is related to the sulfur content of the petroleum feedstock. The sulfur oxide content of the regenerator flue gases from units treating relatively low-sulfur feedstocks is reported to be several hundred ppm. However, the author has been informed privately that units treating high-sulfur Middle Eastern feedstocks may yield flue gases containing 1% or more of sulfur dioxide.

In the steel industry the most common source of sulfur oxide emissions is the burning of coke oven gas that has not been desulfurized. However, emissions from iron ore sinter plants are receiving considerable attention in Germany and Japan, if not yet in the United States. Pelletizing plants are another potentially significant source. In Germany, sinter plants are estimated to be responsible for about 6% of the total sulfur oxide emission (8).

The paper pulping industry is reportedly not, in total, a very large emitter of sulfur oxides, although individual plants may present local problems. Kraft mills emit more malodorous reduced sulfur compounds, whereas sulfite mills are more important as emitters of sulfur dioxide. The pulping processes (particularly sulfite) are most interesting because the chemical recovery cycles use basic chemistry that could well be applied to recovery of sulfur dioxide and sulfur from the flue and process waste gases of other types of sources.

From the standpoint of sulfur recovery, recent experience has emphasized the desirability, in most cases, of processes that permit recovery of elemental sulfur. Sulfuric acid is the useful by-product that is usually most readily and economically produced from sulfur dioxide, but it cannot be economically shipped for long distances or be economically and safely stored for long periods. Elemental sulfur can be shipped long distances or stored indefinitely with minimal environmental problems.

Nonferrous Smelters

A large part of the pertinent literature to 1970 on control of sulfur oxides from copper, lead, and zinc smelters was reviewed by the author

in two previous papers (9, 10). The output of related publications has greatly increased since. The major new developments in smelter emission control have been related to process changes and have first appeared outside the United States. In the United States itself, control developments have consisted mainly of adopting or adapting systems or techniques pioneered abroad. The capability for a high degree of control by lead and zinc smelters is acknowledged (11, 12), but with respect to copper smelters, continuing disputes center on the availability of control methods for dilute gases from reverberatory furnaces and the alleged impracticality of attaining 90% or greater control of emissions from complete smelters (11, 13, 14). Inasmuch as both objectives have been attained at copper smelters abroad and are now being approached in some installations in the United States, the disputes must be regarded as more political than technical in origin.

Control Methods for Smelter Gases. The favored control method for smelter gases continues to be the manufacture of sulfuric acid by the contact process, either directly or after preliminary concentration of the sulfur dioxide in weak gases by some cyclic absorption process. As long as there is a use for the acid, this is unquestionably the most economical method available. Consumption of sulfuric acid for leaching of low-grade and oxide-type copper ores has increased greatly. However, it will ultimately be necessary to recover part of the sulfur dioxide in some other form, preferably as elemental sulfur. The Allied Chemical Corp. reduction process has been applied commercially and on a large scale to pyrrhotite roaster gases containing about 12% sulfur dioxide (15, 16). Application to richer gases will be more economical, and for leaner gases, use of a preliminary concentration step is indicated (9, 10).

The Allied Chemical process uses natural gas as the reductant, which is undesirable in the face of the diminishing supplies and increasing costs of natural gas. However, there is no obvious reason why the process cannot be operated on a producer gas generated from coal, as was done earlier with other processes (10). Another process using oil or pulverized coal as the reductant has been developed by Outokumpu Oy for use in conjunction with the Outokumpu flash smelting process (17).

The use of cyclic absorption processes for concentrating sulfur dioxide from smelter gases is still very limited. If and when sulfur dioxide reduction is practiced, concentration processes must be used more extensively unless metallurgical processes are used that deliver richer off-gases, probably with sulfur dioxide concentrations not lower than 20–25%. The Asarco DMA absorption process (9, 10) is coming into renewed use, partly to produce liquid sulfur dioxide and partly to provide enriched feed to sulfuric acid plants.

At the Tacoma smelter, the DMA process is being used on copper converter gas (18). At the Ajo smelter, it is also to be used to treat copper reverberatory furnace gases (19). The DMA process is not really well suited to treat gases as dilute as those from reverberatory furnaces. It is more economic for use on converter gases, or preferably, still richer gases (9).

At the Rönnskär works of Boliden AB in Sweden, which include both a copper and a lead smelter, a cyclic process using water as the absorbent concentrates sulfur dioxide both to produce liquid sulfur dioxide and for feed to acid plants (20, 21). The process is reported to give an absorption efficiency of about 98% on gas containing 2% sulfur dioxide. Water is not normally a favorable solvent for such an application but can be used in this case because it is available at a low temperature, less than 5°C for most of the year. Recovery of sulfur dioxide from the complete smelter is to be increased from 90 to 95% by applying water-cooled collecting hoods and waste heat boilers to all the copper converters (20).

The Cominco process, which uses a solution of ammonia as the absorbent, has been treating dilute gases (about 1% sulfur dioxide) from lead ore sintering machines on a large scale for more than 30 yr (10, 22). The gases must be cleaned and conditioned before entering the absorber. Thereafter, the original source of the gases is immaterial, and the process could be used to treat gases from copper reverberatory furnaces, although it has not actually been so used. Absorption processes for sulfur dioxide that use ammonia as the absorbent have been widely studied and applied commercially in processes such as pulp and paper manufacture (23, 24). The principal variations appear in the recovery cycles following the absorption step. In the Cominco process, the spent absorbent is acidified with sulfuric acid to release concentrated sulfur dioxide and to form ammonium sulfate as a by-product. Operation in conjunction with a sulfuric acid plant is generally necessary. Where it is desirable to conserve ammonia and reduce ammonium sulfate production, the sulfur dioxide can be steam-stripped from the rich solvent. This process variation was once used for a period by Cominco (10) and has recently been investigated by Electricité de France for use on power plant gases (25). If it is desired to use a throwaway process, the ammonia absorption process can be operated as a double-alkali system. Treating the spent absorbent with lime precipitates calcium sulfate and sulfite and releases ammonia for return to the absorption system. This procedure was used in part in the Guggenheim process studied in the 1930's (26) and has been recently revived in France and Japan (26, 27). The same ammonia recovery process is also used in the Arbiter process for leaching copper ores (28).

Other absorption processes using soluble bases, such as sodium, or adaptations of the contact sulfuric acid process (29, 30) are potentially available for treating dilute smelter gases. However, there is no reason to expect that any of them should be appreciably, if at all, less expensive than the ammonia-base processes.

The Onahama smelter in Japan illustrates the degree of emission control attainable at a conventional copper smelter, using conventional control techniques (31, 32). The converters are equipped with tightly fitted hoods and waste heat boilers, which minimizes air infiltration and raises the average sulfur dioxide concentration in the gas to 11% before it enters a new double-contact sulfuric acid plant. The average conversion efficiency is 99.8%. The gases from the reverberatory furnace are treated in the rebuilt single-contact sulfuric acid plant originally used to treat the converter gases. The sulfur dioxide concentration in the reverberatory furnace gas has been increased by minimizing air infiltration and by using oxygen. The furnace is fitted with oxygen-fuel roof burners similar to those used in open-hearth steel furnaces. The sulfur dioxide concentration in the gas entering the acid plant is 2.5%. This is too low to make the acid plant autogenous (10), so the gas is preheated in a fuel-fired heater. The conversion efficiency is 96.9%. The gas cleaning and conditioning system for the reverberatory furnace gas uses refrigeration for dehumidification so that concentrated acid is produced even from the dilute gas.

Even minor residual emissions from the Onahama smelter are treated. The tail gases from the acid plants are scrubbed with caustic soda to reduce the final sulfur dioxide concentration to about 20 ppm. The converter building is enclosed to prevent escape to the atmosphere of untreated gases that leak from the furnaces. Leaking gases are collected as close to the sources as possible and are scrubbed in a limerock tower before release. Virtually all of the sulfur dioxide from the smelter is reportedly contained (32).

After the system described above was devised, the Onahama smelter was expanded, and a commercial magnesia-base absorption system developed by the company was applied to the reverberatory furnace gases (27). As described (27), the process is essentially the same as the Chemico-Basic process (33) although equipment details are not reported. The magnesium sulfite is decomposed in a rotary kiln in the presence of added carbon. The magnesia is returned to the absorption process, and the rich kiln gas stream (13–15% sulfur dioxide) is sent to a sulfuric acid plant.

High degrees of sulfur oxides emission control are reported at the newer Japanese copper smelters, whether they use conventional or advanced smelting processes (31). All the plants using reverberatory or

flash smelting furnaces report recovery of at least 90% of the sulfur. Of three plants using flash smelters, Kosaka reports a sulfur recovery of 95% and Toyo and Saganoseki report 96%.

As illustrated by the Onahama smelter, it is essential to minimize the volume of the off-gases from a source. The capital and operating costs of a control system are determined primarily by the volume of gas that must be treated (9, 10). The growing application of emission controls has led recently to much more active development of methods and equipment for capture and cooling of waste gases as well as heat recovery from them (34, 35).

Smelting Processes. The experience of the Trail lead-zinc smelter (36) and the Onahama copper smelter (32) has demonstrated that high degrees of emission control can be attained even at conventional smelters that emit weak gas streams. Nevertheless, the relative costs of controlling such emission sources are necessarily high. Costs can be radically reduced only through process changes that reduce off-gas volumes and increase sulfur dioxide concentrations (9, 37). It is particularly desirable to produce off-gases rich enough to be fed directly to a sulfur dioxide reduction plant without using a preliminary concentration process.

The need for process modifications or changes does not arise only or even primarily from air pollution control considerations, even though these may affect the timing. The primary copper, lead, and zinc smelting industry in the United States is largely obsolete. A number of zinc and lead smelters were recently closed primarily because the installations were no longer economically competitive (38) with the more modern smelters operating abroad. New or renovated smelters are replacing the abandoned ones.

Although means are available for controlling the bulk of the emissions from the conventional lead and zinc smelters, new processes being developed offer greater economy as well as better emission control (9, 10). Cominco Ltd. recently announced the development of a new process to replace the conventional lead smelting process with its sintering plants and blast furnaces (39).

A great deal of new copper smelting technology has appeared in recent years, but mostly outside the United States (40, 41). This technology is being adopted in the United States only very slowly and with seeming reluctance, possibly because the cost of smelting has been a relatively small part of the total cost of copper production—at least until recently (42). The limits of cost reduction elsewhere are now being approached, however, and the expense of smelting is being increased by sulfur oxides control and the sharply increased cost of fuel (42, 43). The reverberatory smelting furnace, because of its poor heat and mass transfer characteristics, has a very high fuel consumption. The large volume of

combustion gases generated not only is a source of heat loss, but dilutes the sulfur dioxide produced and increases the gas cleaning problem that exists even without sulfur oxide control. Currently, the shortages of natural gas and fuel oil are leading the copper smelters to consider conversion to coal firing (44). Such conversion is itself expected to be a costly and time-consuming operation.

The Outokumpu flash smelting process (35, 45) and the Inco oxygen flash smelting process (46) were originally developed to reduce fuel requirements, but they have incidentally led to other process efficiencies and to more effective and economical pollution control. The Inco process is autogenous and produces a gas stream containing about 80% sulfur dioxide. The original form of the Outokumpu process is not completely autogenous, but produces off-gases containing about 10–14% sulfur dioxide, depending on the sulfur content of the ore concentrate treated. More recently, the air has been enriched with oxygen to make the process completely autogenous, reducing the gas volume and increasing the sulfur dioxide concentration to 17 or 18% (45). Outokumpu has also developed an associated process for reducing the sulfur dioxide to elemental sulfur with coal or oil. This process is now going into commercial application (17). The Outokumpu flash smelting process is widely used throughout the world, but the first unit in the United States will be in the new Tyrone smelter (18).

The electric smelting furnace has already had a long history of use abroad (40, 47) and has now replaced the reverberatory furnace in two U.S. copper smelters, Copperhill and Inspiration (18). The volume of off-gas from an electric furnace is determined by the tightness of the furnace enclosure, and it is practical to restrict air inleakage sufficiently to produce a gas rich enough for feed to a sulfuric acid plant (47). At the Inspiration smelter, an average sulfur dioxide concentration of 4–8% is anticipated (48). Heat transfer and control are good in the electric furnace, and the thermal efficiency is high (47, 49). However, electric smelting indirectly partakes of the thermal inefficiency of the thermal power plant, if that is the source of power. Hence, it may not be as generally favorable as autogenous flash smelting.

The conventional converting process, with its batch operation, inherently involves fluctuations in the volume and sulfur dioxide concentration of the off-gases and thus complicates sulfur recovery (42, 50). The problem has been partially alleviated by using improved hoods and waste heat boilers and by using oxygen in converting (9). The flash smelter produces a richer matte, which reduces the work that must be done by the converter (45). New types of converters are appearing that offer better facilities for gas containment than does the conventional Pierce–Smith converter (49). The Inspiration smelter is being fitted with

Hoboken siphon converters, the first used in the United States (48). The top-blown rotary converter, using oxygen, has been applied to nickel smelting and converting (51). It is applicable to copper smelting, both for autogenous concentrate smelting and for matte conversion (49). Tests have indicated that the average sulfur dioxide concentrations in the off-gases can be as high as 25–50% (49, 52).

Ideally, a continuous process incorporating both smelting and converting steps can yield a single, steady flow of off-gas that is readily processed for sulfur recovery. Three such processes, the WORCRA, the Mitsubishi, and the Noranda, have been tested on a semicommercial scale (44, 53, 54), and a full-scale commercial plant of the Noranda process is under construction (55). All the processes produce gas streams rich enough for feed to a sulfuric acid plant, and the use of oxygen can produce still richer gases. Wide application of any of these processes awaits completion of commercial development.

Another approach to copper smelting (oxide smelting), already in use abroad, is being incorporated into a new smelter in Arizona by Hecla Mining Co. (18). The sulfide ore is to be roasted to sulfate in a fluid bed roaster (56) and the rich off-gas fed to a sulfuric acid plant. The sulfuric acid will be used to leach the calcined ore, and the copper will be recovered by electrowinning. A related commercial process, the Brixlegg Electro-Smelting Process, employs dead roasting of the copper ore, followed by pyrometallurgical reduction of the oxide calcine with carbon in an electric furnace (57).

Among the various hydrometallurgical processes for copper recovery, those incorporating a controlled oxidation of the sulfide ore to elemental sulfur are of particular interest (9, 58). They avoid the production of possibly unneeded sulfuric acid or the costly collection and subsequent reduction of sulfur dioxide.

Sulfuric Acid Plants

The means for reducing the sulfur dioxide emissions from contact sulfuric acid plants are already relatively well developed. Any sulfur dioxide recovered as such can be recycled to the acid plant for conversion to acid. The most popular approach, at least in new plants, appears to be the double-contact process (59, 60) which is simply an extension of the basic contact process itself. In sulfur-burning plants, this presents no serious problems, but where the acid plant is operating on a relatively dilute process gas, it may not be possible to operate autogenously (10). In the latter instance, the double-contact process can still be used, but auxiliary heat must be supplied (61). Some forms of the double-contact process are reported capable of operating autogenously with sulfur di-

oxide concentrations as low as 5% (62). Applications now being made to smelter gases are assisted by measures to limit infiltration of air into gas collection systems.

The conversion efficiencies of double-contact systems reportedly range from 99.5% to as high as 99.9%, with exit sulfur dioxide concentrations ranging from about 500 ppm to as low as 100 ppm (60, 62). These conditions obviously depend on the initial gas conditions and system design factors.

Existing single-contact acid plants can also be converted to double-contact plants (63). In such cases, however, using add-on scrubber systems is an alternative, and several such systems have been used commercially. The Cominco ammonia absorption process has been used for many years (22, 64). The Lurgi Sulfacid process (65) and Wellman-Lord process (66) have had more recent and limited use. The Mitsubishi-JECCO process has also been applied to acid plant tail gases (27, 67, 68), but the gypsum by-product would be essentially a waste in the United States.

In Japan, open-cycle scrubbing of waste gases with sodium hydroxide or carbonate solutions has been popular for treating gas streams (including sulfuric acid plant tail gases) that contain relatively small total quantities of sulfur dioxide (27). Absorbent regeneration has been unnecessary because the sodium sulfite or sulfate could be sold to kraft pulp mills.

The Union Carbide Purasiv S is a fixed-bed adsorption process using a molecular sieve adsorbent. It removes sulfur dioxide from the clean, dry tail gases of contact sulfuric acid plants. Two or more adsorbers are operated in sequence; the loaded bed is regenerated by a stream of heated air that desorbs the sulfur dioxide and then is fed to the inlet of the sulfuric acid plant. The first commercial plant of this type is now operating on the tail gases of a single-contact acid plant that processes a mixture of spent alkylation acid and hydrogen sulfide from a refinery (69, 70). It is reported to reduce the exit sulfur dioxide concentration from about 4000 ppm (average) to 15–25 ppm (69).

Claus Sulfur Plants

The hydrogen sulfide present in natural gas, SNG, town gas, and synthesis gas must be removed for the sake of product gas quality. Hence, technology for removing hydrogen sulfide from gases has been extensively developed and is itself the subject of a voluminous literature (71, 72). From the standpoint of economic recovery of sulfur, the chemistry of hydrogen sulfide is substantially more tractable than that of sulfur dioxide. For the most part, these processes are not within the chosen scope of the present paper.

Once recovered from gas streams, hydrogen sulfide must generally be converted either to sulfuric acid or, more commonly, to elemental sulfur. The Claus process is the standard one for converting hydrogen sulfide to elemental sulfur. A few absorption processes, such as the Stretford (71, 72, 73), that also oxidize the absorbed hydrogen sulfide to elemental sulfur are used primarily to treat gas streams containing only relatively low concentrations of hydrogen sulfide.

The conversion of hydrogen sulfide to elemental sulfur in the Claus process is limited by a combination of equilibrium and kinetic factors. Over the past decade, the pressures of air pollution control requirements have resulted in major improvements in the design and operation of Claus plants, with consequent increases in conversion and reduction of sulfur oxides emissions (74–79). Nevertheless, emissions still commonly exceed the permissible limits coming into force both in the United States and abroad. Sulfur dioxide reduction plants present similar problems. Apart from the initial furnace or reactor, they are essentially Claus plants.

The effluent streams from Claus plants contain unreacted hydrogen sulfide and sulfur dioxide and elemental sulfur present as vapor and mist (77). They commonly also contain carbonyl sulfide and carbon disulfide formed by reactions with hydrocarbons present in the feed gas (77). It is usually required that the tail gas be incinerated, even though not otherwise treated, to convert the hydrogen sulfide, carbonyl sulfide, and carbon disulfide to the less toxic and malodorous sulfur dioxide.

Since the conversion limit even in improved Claus plants is not readily raised above about 97%, the emphasis in emission control has now passed to using tail gas-treating plants to attain overall conversion efficiencies of 99% or more. The economics of control at Claus plants are probably more favorable than in any other case requiring control of dilute gas streams (*i.e.*, those containing less than about 2–3% sulfur dioxide).

There are three principal approaches to tail gas treatment:

1. Continuation of the Claus reaction at lowered temperatures, on a solid catalyst or in a liquid medium.
2. Catalytic hydrogenation of the sulfur dioxide, carbonyl sulfide, and carbon disulfide in the tail gas to reform hydrogen sulfide, which is subsequently recovered by absorption.
3. Incineration of the tail gas and conversion of all sulfur compounds to sulfur dioxide, followed by one of the sulfur dioxide control systems.

The first class of systems is illustrated by the Sulfreen (80, 81, 82) and IFP (83, 84) processes. In the Sulfreen process the Claus reaction takes place on the carbon or alumina catalyst in a fixed-bed reactor. At the reduced temperature, the conversion equilibrium is improved, but the sulfur is retained on the catalyst as a liquid and must be removed by

hot inert gas in a regeneration cycle. In the IFP process the Claus reaction takes place in a high-boiling solvent (typically a polyalkylene glycol) containing a catalyst. Carbonyl sulfide and carbon disulfide are not affected. The product sulfur is drawn off as a liquid. The efficiencies of the Sulfreen and IFP processes are about 75–90%, so that neither process is economically suitable for attaining the very low exit concentrations reached with some of the other processes.

The second class of systems is illustrated by the Beavon (73, 85) and Shell SCOT (86) processes. In each process a cobalt molybdate catalyst promotes hydrogenation of the sulfur dioxide and elemental sulfur to hydrogen sulfide. It also catalyzes the hydrolysis of the carbonyl sulfide and carbon disulfide to hydrogen sulfide. The gas stream is then cooled, the water vapor is condensed out, and the hydrogen sulfide is recovered. In the Beavon process, the hydrogen sulfide is absorbed and oxidized to elemental sulfur by the Stretford process. In the SCOT process, the hydrogen sulfide is concentrated by absorption in an alkanolamine solution, and the concentrated hydrogen sulfide stripped from the absorbent is recycled to the Claus unit. Both the Beavon and SCOT processes consist of combinations of previously used and essentially conventional technologies. The Stretford system reportedly gives much lower exit concentrations of hydrogen sulfide than does alkanolamine scrubbing, but is chemically and mechanically much more complex.

The third class of control systems may use any of the sulfur dioxide control systems; among those used commercially are the Haldor Topsoe (5, 80), Wellman-Lord (27, 67), and Chiyoda (27, 67, 87) systems. The circumstances are generally highly favorable for recovery processes that produce a stream of concentrated sulfur dioxide, since this can be recycled to the Claus plant. The application of processes that produce sulfuric acid or solid wastes will be dictated only by peculiar local circumstances.

One subclass of sulfur dioxide recovery processes incorporates a liquid-phase variation of the Claus reaction for regenerating the absorbent and directly producing elemental sulfur. Processes of this type are the Stauffer Aqua Claus process (88), which was developed specifically for Claus plant tail gases, and the Bureau of Mines Citrate process (89). In each, the absorbent is the sodium salt of a stable, nonvolatile weak acid, which forms a basic solution by hydrolysis. The anion of the acid buffers the solution as acid is formed by the absorption of sulfur dioxide. The spent absorbent, which consists of a solution of sodium sulfite and bisulfite and of the weak acid, is contacted directly with hydrogen sulfide. The hydrogen sulfide reacts with the sulfite and bisulfite to yield elemental sulfur, and the regenerated basic salt solution is recirculated to the absorption step.

In the Bureau of Mines process the absorbent is sodium citrate; that used in the Aquaclus process has been identified as sodium phosphate (90). As is common in similar processes, some of the sulfur dioxide is oxidized to sulfate, which is not readily regenerated, and thiosulfate and polythionates are also formed (88, 89). Consequently, it is necessary to draw off purge streams of the absorbents, recover the citrate and phosphate for reuse, and discard the sulfate and thionates. Losses of citrate and phosphate in this operation can greatly affect the economics of the processes.

IFP has developed an ammonia absorption process (91) that is parallel to the Citrate and Aquaclus processes in some respects. The sulfur dioxide is absorbed in ammonia solution in a generally conventional manner. The spent absorbent containing ammonium sulfite and bisulfite is decomposed by heating in an evaporator, and the resulting ammonia, sulfur dioxide, and water vapor are sent to an IFP liquid-phase Claus reactor (83) into which hydrogen sulfide is also injected. The hydrogen sulfide and sulfur dioxide react to form elemental sulfur, and the ammonia, which is not affected, passes through the reactor and is recycled to the absorber. The nonvolatile sulfate and thionates from the sulfite evaporator pass to a sulfate reduction reactor where they are reduced to sulfur dioxide with hydrogen sulfide (27, 91). The sulfur dioxide from this operation also is sent to the IFP reactor.

It has been suggested (80, 88) that the Aquaclus or Citrate process might be substituted for the conventional Claus plant to convert all the hydrogen sulfide to elemental sulfur. One major factor determining the practicality of this approach is the problem of separating the sulfate and thionates from the phosphate or citrate. A secondary process system to recover sodium and sulfur from the purged absorbent will be a virtual necessity at any large installation.

The capital cost of a Claus sulfur plant strongly depends on the total gas flow (77), and the costs for a tail gas-treating system will be determined primarily by the gas flow. Consequently, reducing the gas flow can significantly reduce both capital and operating costs. A major, if not the largest, part of the gas in the Claus system is nitrogen which is introduced in the air used to combust the hydrogen sulfide, and into the tail gas when the latter is incinerated (72, 77). The gas volume could be greatly reduced by using oxygen instead of air to support the combustion (72, 77). The cost savings from the use of oxygen would probably not be sufficient to justify constructing an oxygen plant solely to supply the Claus plant, but if an oxygen plant were required for other purposes anyway, providing incremental capacity to supply the Claus

plant as well might have merit. In petroleum refineries producing intermediate-Btu fuel gas from oil or in SNG plants, such oxygen plants will generally be required.

Petroleum Refineries

Petroleum refineries, along with natural gas processing plants, are probably the best situated sulfur oxides sources with respect to emission control. The availability of hydrogen sulfide allows ready processing of recovered sulfur dioxide to elemental sulfur for disposal.

In U.S. refineries at least, the largest source of sulfur oxide emissions is undoubtedly the burning of high-sulfur fuels, including sour refinery gases, residual oil, heavy refinery residues, and petroleum coke. During refinery upsets, the flaring of large amounts of untreated refinery gas may also result in high short-term sulfur oxide emission rates. The pressure of air pollution control regulations is resulting in general treatment of refinery gases. Hydrogen sulfide is being removed by well established technology and converted to elemental sulfur in Claus plants. Desulfurized residual oil might be used, where available, to replace the liquid fuels, but it has been common practice for refineries to consume their lowest grade residues in their own operations. Flue gas scrubbing systems might be used to control the sulfur dioxide emitted from burning of such fuels. This is being done to a limited extent in Japan (27). However, an alternative approach is to gasify the residues to produce a low-Btu fuel gas, using a process such as the Shell Gasification Process, (SGP) (92). This would permit recovery of the sulfur as hydrogen sulfide, using the same processes employed to treat the refinery gases. The Shell Gasification Process has been applied on a fairly large commercial scale (93).

The sulfur oxide emissions from the regenerators of fluid catalytic cracking units may be controlled either by hydrotreating the feed to the catalytic cracker or by scrubbing the flue gas from the regenerator (7). Hydrotreating the feedstock presents several process advantages in addition to emission reduction and is already in use (7, 94, 95). Scrubbing the regenerator flue gas has been proposed (7, 96), but no such installations appear to be in service. It is reported (97) that the first known wet scrubber installation for regenerator flue gas will go into service at the Exxon refinery at Baytown, Tex. The scrubber will remove sulfur dioxide as well as collect catalyst fines, replacing the conventional electrostatic precipitator for the latter duty. It appears that the main duty of the scrubber will be particulate collection.

Steel Mills

The coke oven gas produced and used in integrated steel mills has very commonly not been desulfurized except where the combustion gases came in contact with molten metal. Consequently, the combustion of coke oven gas has been one of the principal sources of sulfur dioxide emissions from steel mills, even though adequate technology for control has long been available. Occasionally, the hydrogen sulfide in the gas has been concentrated by an absorption process and converted to sulfuric acid in a contact plant or to elemental sulfur in a Claus plant. The increasingly stringent air pollution control regulations are forcing installation of more such systems both in the United States and abroad (27, 98).

Because coke oven gas does not contain extremely high hydrogen sulfide concentrations of hydrogen sulfide, it can be effectively treated by processes such as the Stretford (73, 85) or Takahax (27, 72), which both absorb the hydrogen sulfide and oxidize it to elemental sulfur.

About half the sulfur oxides emission from steel plants originates in sintering plants (99), with much higher proportions at some mills (100). The quantity, of course, depends on the sulfur content of the ore being sintered, and the situation will be similar at pellet plants, which are generally located at the mines rather than at the steel mills. In the United States, concern with sinter plant pollution has been focused largely on particulate matter, but in Germany and Japan the sulfur oxides emission is of serious concern. It is likely that at some sinter plants, fluoride emissions are actually a more serious pollution problem than sulfur oxide emission. Fluoride emissions from sinter plants are receiving increasingly serious attention in Germany and the Netherlands.

In Japan, scrubbing systems are being applied to sinter plants to control sulfur dioxide and should also be very effective in removing hydrogen fluoride. Kawasaki Steel Corp. has tested Mitsubishi-JECCO lime scrubbing process on a demonstration scale (27) and will now install a full-scale system, handling 750,000 m³ gas/hr, on a new sintering plant that may be the largest in the world (100).

Nippon Kokan has developed and tested an ammonia-base double-alkali scrubbing process for sinter plants (27). Both in this system and the Mitsubishi process, lime will precipitate the sulfur oxides as well as the fluoride that is probably present.

The concentrations of sulfur dioxide in sinter plant gases are variously reported to range from about 0.02 to 1.5 vol % (8, 68, 101). There appears to be no way to increase the sulfur dioxide concentrations to levels suitable for economic recovery, and the presence of fluorides would be a hindrance in any case. However, it may be feasible to reduce the

waste gas volume by applying the techniques of updraft sintering and gas recirculation that have been used in the nonferrous smelting industry.

Pulp Mills

In the pulping industry, sulfur oxides emissions represent loss of pulping chemical, but the economic loss is apparently not regarded as very serious, at least in this period of relatively abundant and cheap sulfur. In current practice, much sulfur is evidently lost to become either a water or air pollutant (16, 53, 102), but pollution control regulations are forcing increased recovery and recycling of sulfur and other pulping chemicals. The need to increase heat recovery and use should also influence emission controls.

In the kraft process, the most serious air pollutants are hydrogen-sulfide and other reduced sulfur compounds (103). Even though their mass emissions may not be high, their extreme malodorousness constitutes the major problem. The emissions of sulfur dioxide from kraft recovery furnaces may range from small to substantial, depending on the composition of the black liquor and on the operating conditions in the furnace (104–109). Several recent studies have treated factors influencing the sulfur dioxide emission (104, 106, 107, 108).

The sulfur dioxide in kraft recovery furnace gases can be readily scrubbed with sodium carbonate to produce sodium sulfite or sulfate as makeup for cooking liquor preparation. The absorbent liquor can be used in the scrubber units that collect part of the sodium carbonate and sulfate particulates that escape collection by the electrostatic precipitator. Particularly in Sweden, such afterscrubbers are sometimes used also to recover low level heat (110), and they could be extended to recover sulfur dioxide as well (111). The use of afterscrubbers to collect sulfur dioxide from kraft recovery furnace gases appear to be fairly common in Japan (27).

Sulfur dioxide emission is a much more serious problem in sulfite mills. The sulfur dioxide may be emitted in the tail gases from absorption towers used to prepare cooking liquor, in blowpit gases, in digester relief gases, and in venting noncondensibles from multiple-effect spent liquor evaporators (102, 103, 112). Tail gas scrubbers are sometimes applied to reduce the emissions from absorption towers (113). Vent gases may also be sent to the absorbers to recover the sulfur dioxide contained (102, 103, 112). Blow pit gases can be scrubbed with water to recover both sulfur dioxide and heat (6, 114). Although this procedure is reported to be economically favorable, it is apparently not universally practiced in the United States even now.

The requirements for water pollution control have been forcing a shift to concentrating spent sulfite pulping liquor by evaporation, followed by incineration with heat recovery (102). When calcium-base liquor is burned, the sulfur emerges as calcium sulfate and is not available for recycle to the pulping process. The flue gas from such furnaces in Sweden is reported to contain 0.2–0.3% sulfur dioxide, and in one Swedish mill a Bahco wet limestone scrubber is used to treat the gases (115).

When ammonia-base sulfite liquor is burned, the sulfur is released as sulfur dioxide. However, it has not been the practice to recover the sulfur dioxide for re-use, although absorption systems were developed for the purpose (23, 24, 102, 103, 112). Nevertheless, recovery systems are now going into service with ammonia-base mills (116).

Most of sulfite mills using a sulfur dioxide recovery cycle have used the well established magnesia-base process (117, 118, 119, 120, 121). When the magnesia-base spent liquor is burned, or magnesium sulfite and sulfate are smelted in the presence of excess carbon, the sulfur goes off as sulfur dioxide, and the magnesium remains as the oxide. In the calcium system, the equivalent reactions take place only at much higher temperatures. Experience with the magnesia-base pulping process was undoubtedly the inspiration for development of the Chemico-Basic (33) and other similar processes using magnesia in cyclic sulfur dioxide recovery systems.

The sodium-base sulfite systems present experience with sulfur recovery processes that may have wide application outside the paper pulp industry. The basic chemistry involved is historically very old (122). Essentially, four steps underlie the various processes:

1. The spent sodium-base sulfite liquor is burned under reducing conditions, as in the kraft process, yielding a smelt of sodium sulfide.
2. The sodium sulfide is treated with steam and carbon dioxide. Sodium carbonate is formed, and hydrogen sulfide is driven off.
3. The sodium carbonate is used to absorb sulfur dioxide, producing fresh sodium sulfite or bisulfite for use as cooking liquor.
4. The hydrogen sulfide is burned to provide the sulfur dioxide for cooking liquor production, or in some processes, it is sent to a Claus plant for conversion to elemental sulfur.

Among the various pulping chemical recovery systems are the Stora (123), Sivola (124), and Tampella (125) processes, which have been demonstrated commercially. The first of the process steps given above can be accomplished with sodium sulfate or sulfite by smelting under reducing conditions, which is the oldest method for producing sodium sulfide (126).

The process composed of the above sequence of steps can be used to recover elemental sulfur from sulfur dioxide-bearing gases, using sodium carbonate as the primary absorbent. Alternatively, it can be used to recover sulfur and sodium carbonate from the sodium sulfate formed in the cyclic absorption processes, such as the Wellman-Lord, that are used for concentrating sulfur dioxide from dilute gas streams (10). A purge stream of the absorbent must be withdrawn to prevent buildup of excessive sulfate. Disposal of the sodium sulfate as such will probably become difficult if the sodium-base absorption processes are used on a large scale for sulfur dioxide recovery. Nittetu Chemical Engineering has developed a process using the same basic chemistry to deal specifically with the sulfate buildup in sodium-base absorbents used to desulfurize coke oven gas (127).

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The Allied Chemical Sulfur Dioxide Reduction Process for Metallurgical Emissions

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Allied Chemical technology for reducing sulfur dioxide to elemental sulfur was commercialized in 1970 as the emission control system for a Canadian sulfide ore roasting facility which received up to 500 tons/day of sulfur as 12% sulfur dioxide. In the next 2 yrs, this plant recovered more than 90% of the entering sulfur. Allied's sulfur dioxide reduction technology can now be applied to gas streams containing 4–100% sulfur dioxide, dry basis. Sulfur dioxide reduction may be used directly to control emissions from roasters and continuous smelting processes. Where sulfur dioxide concentration is below about 4%, and/or gas composition fluctuates widely, the reduction process is combined with a preliminary concentrating process.

Large-scale commercialization of technology for sulfur dioxide reduction to sulfur was accomplished by Allied Chemical Corp. in 1970 with the start-up of a prototype facility for a large new metallurgical operation at Falconbridge, Ontario. The technology, used initially for the emission control system at this plant, was developed through a major R&D program in the 1960's. Specifically over 90% of the sulfur dioxide was removed from a gas stream resulting from fluidized bed roasting of nickel-containing pyrrhotite ore at rates up to one-half million tons/year. The process installed in the Canadian plant has been discussed in detail in earlier papers (1, 2). The single-train plant design, which is capable of receiving sulfur dioxide equivalent to as much as 500 long tons/day of sulfur, and other operating experience in this unique emission control project have been described in previous publications (3, 4).

The reliability of Allied Chemical's sulfur dioxide reduction technology was proved during 2 yrs of successful operation in which the capability of achieving a 90% on-stream factor was established. All of the original process design and performance criteria were confirmed. Turn-down characteristics of the system were demonstrated during extended operation at as low as one-third of design capacity with nearly constant operating efficiencies (in terms of overall sulfur dioxide removal and reducing agent utilization) being achieved at all rates. Elemental sulfur produced in the process was used interchangeably with Frasch sulfur at various Allied locations to produce high quality sulfuric acid for the U.S. merchant market.

Commercial Plant Description

A flow diagram of the sulfur dioxide reduction process as it is applied to a sulfide ore roasting operation like that at Falconbridge is shown in Figure 1. The hot sulfur dioxide gas from the roasters is passed through hot gas heat exchangers (1) and (2) where part of the heat content of the gases is used to reheat other process gas streams. These will be described in more detail later. At this point the roaster gas still contains fine dust particles as well as gaseous contaminants which must be removed before the gas reaches the reduction reactor. This gas purification is accomplished in a two-stage aqueous scrubbing system consisting of a two-leg gas cooling tower (3) and a packed condensing tower (4). The bulk of the dust and other contaminants are collected in the gas cooling

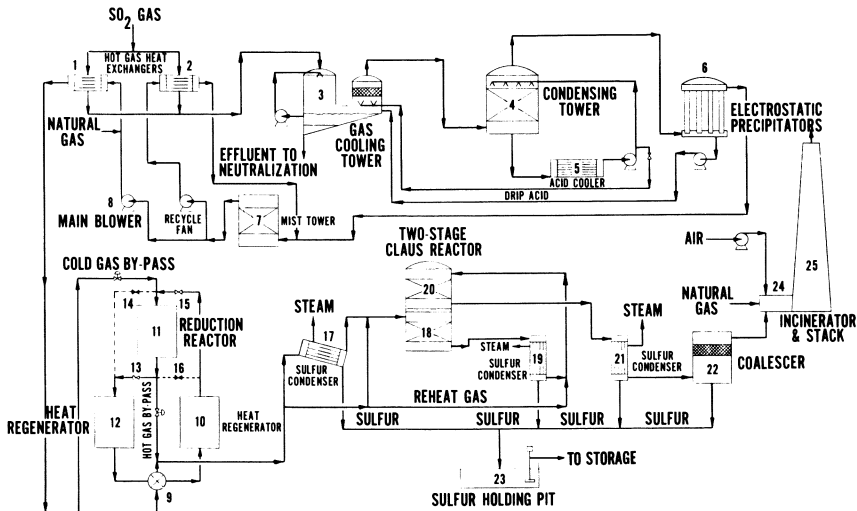


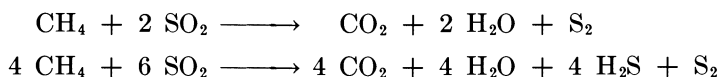
Figure 1. Allied Chemical sulfur dioxide reduction technology typical roaster gas application

tower while the gas is cooled and saturated by a recirculated weak sulfuric acid solution. The demister pad at the tower outlet is continuously sprayed with weak acid from the condensing tower. The underflow from the gas cooling tower is treated with lime to precipitate dissolved metallic impurities removed from the gas and to neutralize the acidity before being delivered to a waste pond where the solids are allowed to settle.

The process gas is further cooled in the condensing tower (4) by circulating weak acid which is cooled externally in impervious graphite heat exchangers (5). Entrained droplets of acid mist are removed from the gas in electrostatic precipitators (6). Drips from the precipitators are returned to the gas cooling tower.

The temperature of the clean gas is then raised above the dew point of sulfuric acid by admixing with a reheated stream of the same gas in the mist tower (7). This recycle gas stream is heated by circulation through the hot gas heat exchanger (2). The process gas is drawn through the wet purification system and then forced by a centrifugal blower (8) through the balance of the plant. Natural gas, which serves as the reducing agent, is introduced into the process gas stream at the blower discharge, and the mixture is passed through the hot gas heat exchanger (1) to raise its temperature above the dew point of sulfur before entering the reduction reactor system.

The principal function of the catalytic reduction system is to maximize use of the reductant while producing both sulfur and hydrogen sulfide, so the hydrogen sulfide/sulfur dioxide ratio in the gas stream leaving the system is essentially that required for the subsequent Claus reaction. Although the chemistry of the primary reaction system is extremely complex and includes reactions involving 11 different elements and compounds, it may be summarized in the following equations:



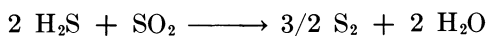
The preheated process and natural gas mixture enters the catalytic reduction system through a four-way flow reversing valve (9) and is further preheated as it flows upward through a packed-bed heat regenerator (10) before entering the reduction reactor (11).

Thermally stable catalysts developed by Allied Chemical for this facility cause rapid and efficient reaction of the natural gas with the sulfur dioxide to form hydrogen sulfide and elemental sulfur vapor while substantially eliminating the formation of undesirable side reaction products (5, 6). The temperature of the gases entering the reactor is held constant by continuously bypassing a varying quantity of cold process gas around the upflow heat regenerator. The heat that is generated in

reactor (11) by the exothermic reactions sustains the overall heat in the system. After leaving the reactor, the main gas flow passes down through a second heat regenerator (12), giving up its heat to the packing in that vessel before leaving the catalytic reduction system through flow reversing valve (9). A thermal balance is maintained in the system by passing a minor flow of the hot gases from the reactor (11), around the downflow regenerator and the flow reversing valve (9), and remixing it with the main stream before entering sulfur condenser (17).

The primary function of the heat regenerators (10) and (12), then, is to remove heat from the gases leaving the catalytic reactor (11) and to use this heat to raise the temperature of the incoming gases to the point where the sulfur dioxide–natural gas reaction will begin. The direction of flow through the two regenerators is periodically reversed to interchange their functions of heating and cooling the gases by using the flow reversing valve (9) and four water-cooled butterfly valves (13), (14), (15), and (16). The valve arrangement shown in the flow diagram is specially designed to maintain the gas flow through the catalytic reactor (11) in one direction only. All five valves are operated from a central control system which synchronizes their movement so that each flow reversal is completed in less than 1 sec.

The elemental sulfur that is formed in the primary reactor system is condensed in a horizontal shell-and-tube steaming condenser (17). This represents over 40% of the total recovered sulfur. The process gas stream then enters the first stage (18) of a two-stage Claus reactor system where the following exothermic reaction occurs:



After the first stage of Claus conversion, the gas is cooled in a vertical steaming condenser (19) to condense additional sulfur. Further conversion of hydrogen sulfide and sulfur dioxide to sulfur takes place in the second stage Claus reactor (20). This sulfur is condensed in a third steaming unit (21). A coalescer (22) containing a mesh pad then removes entrained liquid from the gas stream. Molten sulfur from the three condensers and the coalescer is collected in a sulfur holding pit (23) from which it is pumped to storage. Residual hydrogen sulfide in the gas from the process is oxidized to sulfur dioxide in the presence of excess air in an incinerator (24) before being exhausted to the atmosphere through a stack (25).

This reactor–heat regenerator system offers several important benefits. Temperature profiles inherently favor approach to chemical equilibrium and maximum use of the gaseous reducing agent over a wide range of operating rates. Yet, with the considerable heat capacity of the

packed beds, the system is not seriously upset by flow rate changes and minor variations in feed gas composition. At the same time, the reactor-heat regenerator design solves the engineering materials problems caused by the highly corrosive nature of the strongly reducing sulfurous gases. In fact, at the elevated temperatures involved, the use of metallic construction materials is impractical. Combining the regenerator function of reaction heat storage and use with the fixed bed single-stage reactor, then, results in a rugged and efficient design (7). This system is particularly advantageous for large process gas volumes such as those experienced in the Falconbridge facility.

Continuing Technology Development

In view of the considerable interest in sulfur dioxide reduction to sulfur both in this country and abroad, Allied Chemical extended the use of this technology to control sulfur dioxide emissions from other metallurgical operations as well as from fossil fuel combustion. The experience gained in design, construction, and operation of the large Canadian facility provided the perspective for continuing process research and parallel engineering development.

At the outset, two major goals were established to achieve broad applicability for sulfur dioxide reduction in emission control. The first goal was to develop process capability encompassing the widest practical range of inlet sulfur dioxide concentrations while the second was to develop process modifications so that various gaseous and liquid hydrocarbons could be used as reducing agents.

The first goal has been achieved, and the spectrum of feed gas sources to which the Allied Chemical sulfur dioxide reduction technology may now be applied is the principal subject of discussion in this paper. The effort to use reducing agents other than natural gas in these systems has also advanced through feasibility studies into the development stage, involving alternatives ranging from propane and butane through middle distillates such as No. 2 fuel oil. Allied Chemical now expects to offer a family of processes permitting sulfur dioxide reduction operations to be tailored to the specific requirements of individual locations and projects.

While the Canadian plant operation was documenting process performance with a 12-13% sulfur dioxide source, work was being done to establish the basis for designs of systems to process more concentrated feed streams, containing up to 100% sulfur dioxide (dry basis). Lower sulfur dioxide concentrations and the influence of oxygen in feed gases were also being studied so the lower limit boundary conditions for process applicability could be identified. This was realized through

detailed investigation of the kinetics of the complex reaction chemistry in this system. A comprehensive mathematical model of the system was subsequently developed which incorporated the unsteady state heat transfer functions in addition to chemical kinetics and thermodynamics.

Because of these efforts it is now possible to evaluate precisely a broad range of process alternatives and modifications, as well as to conduct dynamic simulations on models of particular interest. Present engineering design capability allows efficient process profiles to be established over a wide spectrum of feed gas compositions while optimizing major parameters, including reducing agent use, overall sulfur recovery, and major equipment duties. Operating considerations such as turndown and the influence of potential system upsets may also be evaluated.

Feed Gas Considerations

Most sulfur dioxide feed streams, and especially metallurgical sources, contain dust particles and other impurities such as arsenic and selenium oxides. In order to produce high quality sulfur, the gases must be cleaned as thoroughly as if sulfuric acid were to be produced. This can be reliably accomplished in a wet purification system similar to that used in the Falconbridge plant. Not only can the gases be freed of most contaminants, but the scrubbing treatment recovers any valuable mineral content which may have been carried by the entering gas.

Once the feed stream has been purified, the sulfur dioxide and oxygen dimensions must be defined. Depending upon its source, the sulfur dioxide may vary from a few tenths of 1% to 100% (dry basis), in combinations with oxygen from 0% up to the line shown on Figure 2. The dotted line represents the gas composition that results when 100% sulfur dioxide (dry basis) is diluted with air. The only gas compositions to which Allied Chemical sulfur dioxide reduction technology is not directly applicable are those in the shaded area at the lower left of this diagram. This lower boundary represents a practical limit which has been established by heat balance and thermodynamic considerations rather than by economic factors.

In the Allied process, both oxygen and sulfur dioxide in the feed gas react chemically with the reducing agent in identical volumetric proportions. However, the heat released in the reduction of sulfur dioxide is only a fraction of that liberated by the reaction of the reductant with oxygen. Consequently, the process design must not only obtain the optimum reaction product composition but also must control the temperatures throughout the system. Evaluation of the effects of varying both the oxygen and sulfur dioxide contents during operation is therefore important. Except for cases involving very weak sulfur dioxide-oxygen concentrations, the quantity of gas being treated is not a major factor because

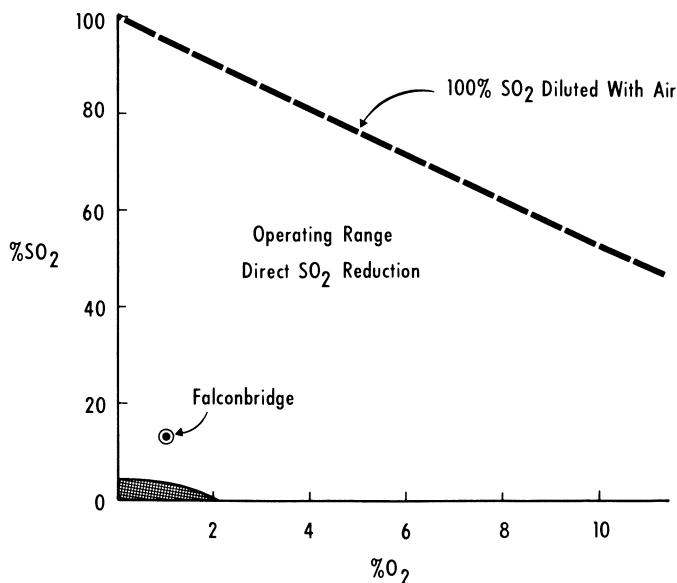


Figure 2. Allied Chemical sulfur dioxide reduction, gas compositions in volume % (dry basis)

the design and operation can be adjusted to achieve a workable heat balance for duties as small as 5–10 tons/day of sulfur in the feed.

The gas composition from the fluidized bed roasters at Falconbridge was a somewhat special circumstance in that the oxygen content was quite low, approximately 1%, and the sulfur dioxide concentration approached the theoretical maximum for pyrrhotite ore roasting. The Allied reactor–regenerator system was ideally suited to this gas composition.

Combination with Sulfur Dioxide Concentration

Since the proportion of reducing agent introduced should be regulated precisely to achieve the desired product gas composition, the sulfur dioxide and oxygen concentrations in the feed gas to the reduction unit should be fairly stable. Accordingly, the direct application of sulfur dioxide reduction to gases from the cyclic operation of the converters used in conventional copper smelting is not considered practical. In these cases, sulfur dioxide should be removed by a regenerable recovery system and subsequently released in concentrated, low oxygen form at a controlled rate.

Some sulfur dioxide concentrating systems can be designed to accept gases with fluctuating volumes and sulfur loadings. The sulfur dioxide is either physically or chemically bound in a solid or liquid medium in

these systems and is retained in inventory. The material is then thermally regenerated or steam stripped, and the sulfur dioxide is delivered to the final processing step at a constant rate. Only minor modifications of the Falconbridge process are then necessary to reduce such regenerated gas streams containing up to 100% sulfur dioxide (dry basis) to elemental sulfur.

The adaptability of this sulfur dioxide reduction technology to a feed gas containing 100% sulfur dioxide (dry basis) will be demonstrated at the D. H. Mitchell Station of the Northern Indiana Public Service Co. (NIPSCO) at Gary, Indiana (8). In this application the process will be combined with the Wellman-Lord sulfur dioxide recovery process to provide a complete flue gas desulfurization system for a 115-MW coal-fired boiler in a project jointly funded by NIPSCO and the Environmental Protection Agency.

As is the case in cyclic copper converter operations, substantial changes in sulfur loading are encountered in emissions from fossil fuel-fired boilers. Variations in gas volume, and hence in the sulfur loading, will be accommodated at NIPSCO by providing large storage capacity for the sodium sulfite-bisulfite scrubbing solution. The sulfur dioxide will be desorbed from the solution by heating, and a steady flow of sulfur dioxide gas will be delivered to the reduction unit.

Engineering, procurement, and construction of the entire facility at NIPSCO is the responsibility of Davy Powergas, Inc. Allied Chemical is providing the sulfur dioxide reduction process technology as well as

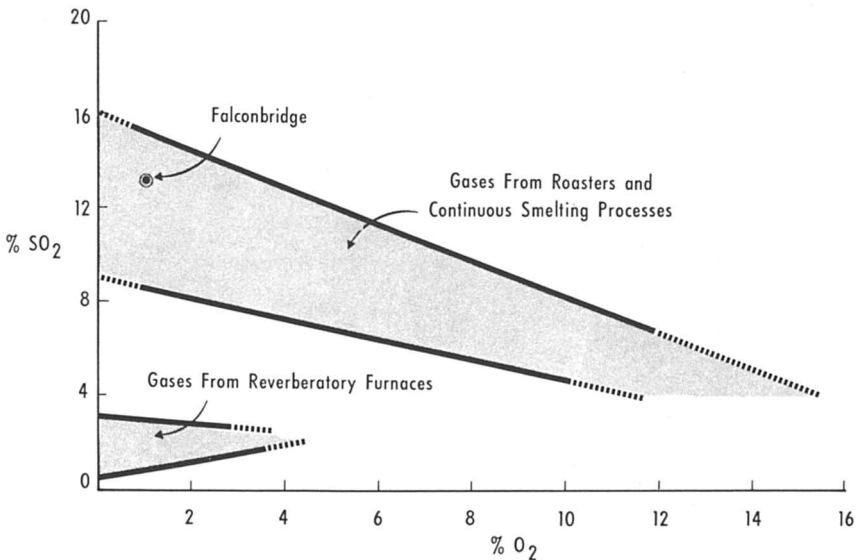


Figure 3. Typical compositions of gases from metallurgical operations

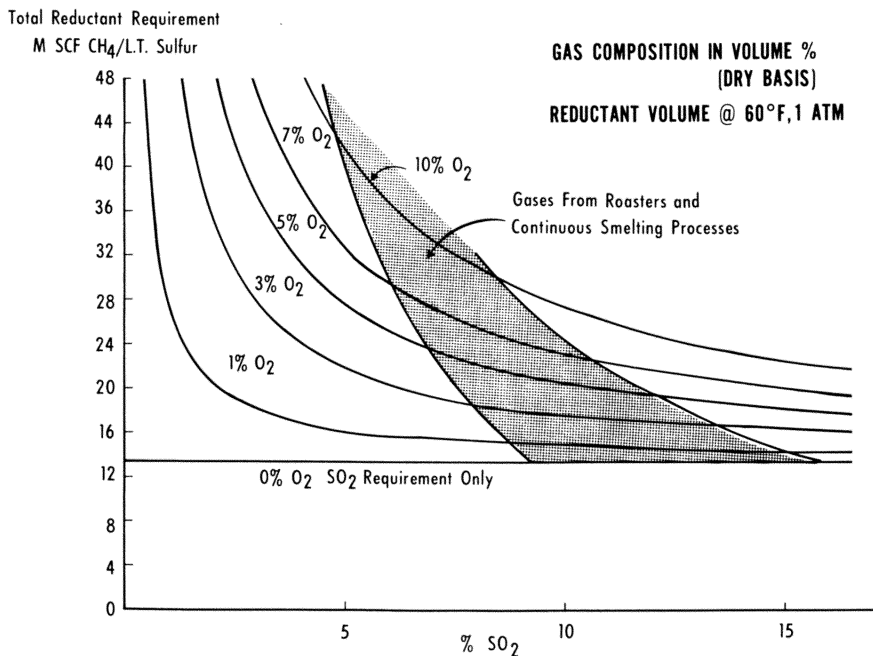


Figure 4. Gases from roasters and continuous smelting processes

technical and start-up services under contract with Davy Powergas. Then, under a separate agreement with NIPSCO, Allied will operate the entire flue gas desulfurization system and will market salable by-products on a continuing basis.

Metallurgical Applications

The selection of processes for controlling sulfur dioxide emissions from metallurgical sources is largely governed by the composition of the gases being treated. Typical gas compositions from non-ferrous metallurgical operations which have relatively constant sulfur dioxide and oxygen contents are shown in Figure 3. Allied Chemical sulfur dioxide reduction technology can be applied directly to metallurgical gases across the entire range of compositions represented by the wide band. The Allied technology is not directly applicable to gases from reverberatory furnace operations in which both the sulfur dioxide and oxygen contents are generally less than 3%. Because of the low sulfur dioxide concentration and large volume of gases from these sources, a concentrating system would be used to recover the sulfur dioxide for subsequent reduction.

Air dilution of the gas at the source should be restricted wherever possible, as this minimizes the volume of gas to be handled in the system

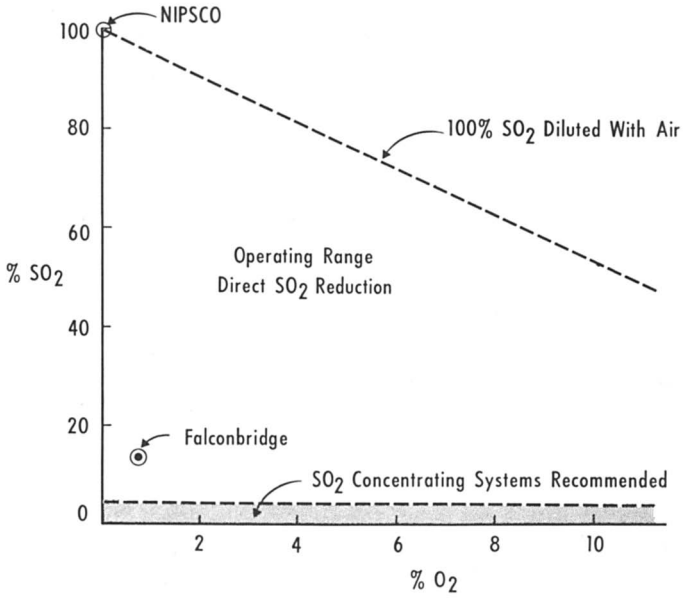


Figure 5. Composition of gases from sulfur dioxide concentrating systems (dry basis)

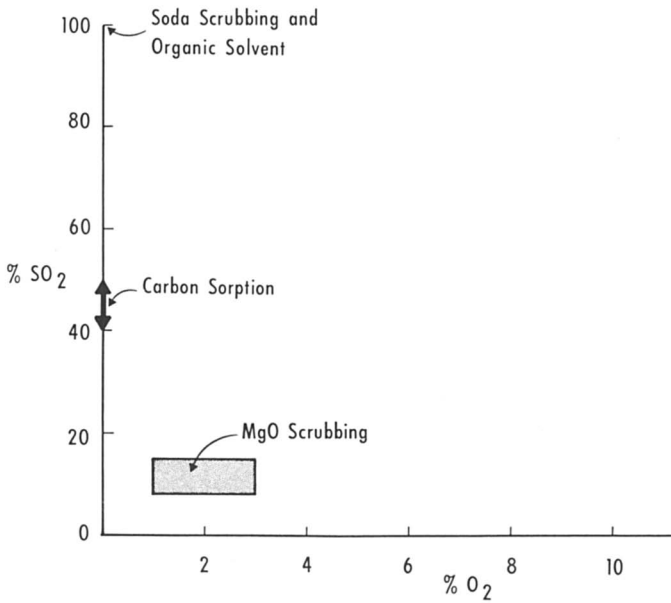


Figure 6. Gas compositions in emission control systems (dry basis)

and the quantity of reductant required as shown in Figure 4. The shaded area represents the range of compositions normally found in gases from roasters and continuous smelting processes.

There is obviously a cost penalty in terms of additional reducing agent consumption associated with the direct reduction of gases having higher oxygen contents. Although there probably will be situations in which it will be advantageous to accept a higher reducing agent consumption, the penalty must be weighed against the total costs which would be incurred if a sulfur dioxide preconcentration facility were to be used.

The composition of gases obtained from several types of sulfur dioxide recovery and concentrating systems is shown in Figure 5. One of the features of the Allied Chemical sulfur dioxide reduction system is that it is capable of processing the gases from these sulfur dioxide concentrating systems directly with only the reductant added. As a result, equipment size is minimized. By contrast, in manufacturing sulfuric acid, the gases from these concentrating systems typically would be diluted with air to give an oxygen/sulfur dioxide ratio of 1.3:1 to obtain satisfactory conversion of sulfur dioxide to sulfur trioxide. The resulting gas volumes are compared in Table I. In the soda scrubbing case (the system to be demonstrated at NIPSCO) the gas volume to the sulfur dioxide reduction unit is less than one quarter the volume to the acid plant.

Table I. Relative Process Gas Volumes^a

	<i>Total Gas Volume—M SCFM^b</i>		
	<i>From Recovery Unit^c</i>	<i>To Reduction Unit^d</i>	<i>To Acid Plant^e</i>
<i>Sulfur Dioxide Recovery System</i>			
Magnesium oxide scrubbing 12% SO ₂ , 1% O ₂	12.1	13.0	21.2
Carbon sorption 40% SO ₂ , 0% O ₂	3.6	4.4	12.7
Soda scrubbing or organic solvent 100% SO ₂	1.5	2.3	10.6

^a Basis 100 long tons/day sulfur equivalent in process gas.

^b Dry basis at 60°F. and 14.7 psig.

^c SO₂ volume 1.46 M SCFM (standard cubic ft./min).

^d Includes reductant as 100% CH₄.

^e Includes dilution air to give 1.3:1 O₂/SO₂ ratio.

In summary, Allied Chemical technology for reducing sulfur dioxide to elemental sulfur can be applied directly to a broad range of sulfur dioxide concentrations. As illustrated in Figure 6, the practical range for application of this technology extends from about 4% up to 100% (dry

basis) with oxygen contents up to the aforementioned economic break-point. In some instances, process considerations may justify direct sulfur dioxide reduction with higher oxygen contents in the feed gas and attendant higher reductant consumption. However, with sulfur dioxide contents of less than about 4%, use of a sulfur dioxide preconcentrating system with the sulfur dioxide reduction process applied directly to the product gas is recommended.

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Reduction of Sulfur Dioxide to Sulfur: The Elemental Sulfur Pilot Plant of ASARCO and Phelps Dodge Corp.

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The thermodynamic equilibria involved in reducing sulfur dioxide with fossil fuels were used to specify the primary reactor operating conditions of 350°C and 1 atm with a ratio of reformed gas to sulfur-bearing gas of 4.14:1. A pilot scale plant was built at ASARCO's El Paso smelter. During the initial phase of operation, two process problems were discovered: physical degradation of the catalyst pellets and overheating of the reactor, resulting in a major failure. A new primary reactor was designed and built using boiling media cooling with a new, stronger catalyst. After 90 days of operation with the new primary reactor on 12% sulfur dioxide feed, neither of these operating problems has occurred.

The elemental sulfur pilot plant financed by American Smelting and Refining Co. (ASARCO) and Phelps Dodge Corp. is located at ASARCO's El Paso, Tex., copper-lead smelter. Technology pioneered by both companies is used in this plant. The sulfur dioxide reduction process was developed by ASARCO while a process for reforming natural gas developed by Phelps Dodge provides the reducing gases.

Any large scale process for reducing sulfur dioxide to elemental sulfur will likely depend on a fossil fuel. Whether the fuel is used to reduce sulfur to such compounds as hydrogen sulfide or carbonyl sulfide which are then used as the reductant for sulfur dioxide or whether the fuel itself is the sulfur dioxide reductant, the overall thermochemistry is similar.

Thermochemistry of Sulfur Dioxide Reduction

The H-C-O-S System. Following the usual convention, the hydrogen-carbon-oxygen-sulfur system is represented as a tetrahedron with the four pure elements at the apexes as depicted by Figure 1. In the reduction of sulfur dioxide by fossil fuels, if we assume the fuel to be the sole

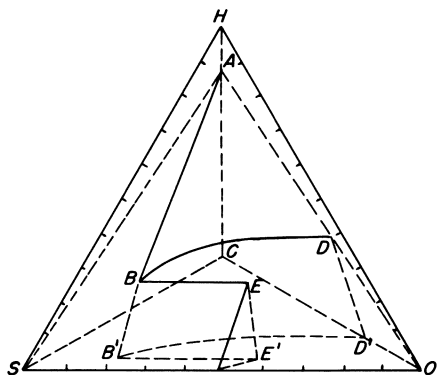


Figure 1. Hydrogen-carbon-oxygen-sulfur system

source of carbon and hydrogen, selection of a particular fossil fuel fixes the atomic ratio of hydrogen to carbon, thus limiting the region of interest in the H-C-O-S system to a plane. If methane, with an atomic ratio of hydrogen to carbon of 4.0, is the fossil fuel, then plane ASO defines the region of the H-C-O-S system within which all possible compositions must lie. When appropriate equilibria combinations consistent with significant constituents have been selected, *e.g.* SO₂, H₂S, COS, CS₂, SO₃, H₂, H₂O, CO, CO₂, S₂-S₈ and, where applicable, C(s) and S(l), and temperature and pressure have been specified, then carbon and sulfur saturation lines may be located. Carbon and sulfur saturation lines are symbolically illustrated in Figure 1 on plane ASO as are their projections onto the carbon-oxygen-sulfur ternary. This is not a simple vertical projection. Rather, the projection of any point on this plane lies at the intersection with the carbon-oxygen-sulfur ternary of a straight line connecting the hydrogen apex and the point being projected, *i.e.*, in Figure 1, point D' lies on the extension of a straight line connecting the hydrogen apex and point D. Using this technique, atomic stoichiometric relationships involving carbon, oxygen, and sulfur appearing in the projection are identical to those in the plane projected. To simplify the graphical illustrations, the plane of interest will be projected onto the C-O-S ternary throughout this discussion.

In Figure 2, regions of carbon, liquid sulfur, and homogeneous gas stability are plotted for the specified atomic ratio of hydrogen to carbon, 323°C (600°K), and 1 atm absolute pressure. In any practical process

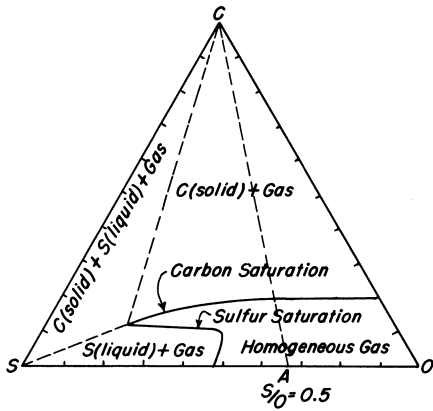


Figure 2. Regions of carbon, liquid sulfur, and homogeneous gas stability. $H/C = 4.0$, $S/O = 0.5$, $T = 323^\circ\text{C}$ (600°K), $P = 1.0\text{ atm}$.

for reducing sulfur dioxide to elemental sulfur, the region of carbon saturation is avoided. In this region not only would the yield of sulfur vapor be virtually zero, but carbon precipitation would foul the catalyst bed.

There are similar reasons for avoiding the sulfur-saturated region of the system, although there are equally valid reasons for intentional sulfur condensation on a catalyst, followed by a catalyst regeneration step, *e.g.*, to attain in a single catalytic stage sulfur yields otherwise only attainable in two or three stages. ASARCO chose to avoid sulfur condensation on the catalyst. There is, however, an additional constraint on the region of practical interest. Since we are concerned with sulfur dioxide reduction, we need only to examine the system chemistry of the homogeneous gas region lying along or to the right of Line AC of Figure 2, which denotes an atomic ratio of sulfur to oxygen of 0.5, *i.e.*, at an atomic ratio of sulfur to oxygen equal to or less than that for sulfur dioxide.

Proportioning of Reformed Gas and Sulfur Dioxide. We wish to determine the proper proportion of sulfur dioxide to reducer. Let us examine the variation in equilibrium composition and sulfur vapor yield along Line AC of Figure 2. These data are graphically shown in Figure 3,

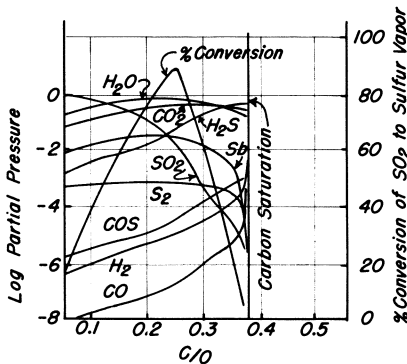
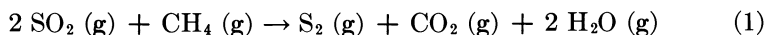


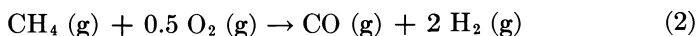
Figure 3. Gas phase composition. $H/C = 4.0$, $S/O = 0.5$, $T = 323^\circ\text{C}$ (600°K), $P = 1.0\text{ atm}$.

where gas phase composition is expressed in terms of log partial pressures. With fixed atomic ratios of hydrogen to carbon and sulfur to oxygen, Figure 3 illustrates the change in equilibrium gas phase composition with varying carbon-to-oxygen ratio, *e.g.*, as the proportioning of methane and pure sulfur dioxide is varied from fuel-lean to fuel-rich.

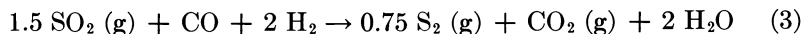
The curve of Figure 3 representing equilibrium percentage conversion of sulfur dioxide to sulfur vapor illustrates the importance of proportioning sulfur dioxide and reducing gas. With methane as the reductant, maximum sulfur vapor yield occurs at a system atomic ratio of carbon to oxygen of 0.25, consistent with the following simplified overall reaction:



In the ASARCO sulfur dioxide process, however, reformed natural gas is the reducer. If we assume natural gas to be comprised solely of methane, reformed natural gas formation in the process developed by Phelps Dodge Corp. may be expressed in terms of Reaction 2:



Sulfur dioxide reduction to elemental sulfur vapor may be expressed:

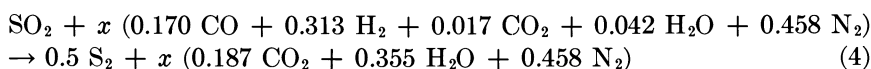


In Reaction 3 as in Reaction 1 the atomic ratio of carbon to oxygen is also 0.25. In theory, the maximum yield of sulfur vapor would depend on a temperature-dependent atomic ratio of carbon to oxygen. In other words, maximum yield of sulfur vapor depends on a carbon monoxide-to-carbon dioxide ratio (or a hydrogen-to-water ratio) which is in turn temperature dependent. While the absolute value of the carbon monoxide-to-carbon dioxide ratio corresponding to maximum conversion of sulfur dioxide to sulfur vapor changes with temperature, equilibrium partial pressures of carbon monoxide or hydrogen are essentially zero over a broad temperature range. Thus, in a practical sense, when methane or reformed methane is the reductant for sulfur dioxide, maximum equilibrium conversion of sulfur dioxide to sulfur vapor will occur at an atomic ratio of carbon to oxygen of 0.25 regardless of temperature in accordance with the simple stoichiometry of Reactions 1 and 3.

Natural gas of the southwestern United States contains, in addition to methane, several per cent ethane and lesser percentages of higher molecular weight hydrocarbons, up to and including pentane. The atomic ratio of hydrogen to carbon in this fuel is about 3.80. Reforming this

natural gas by the Phelps Dodge process typically produces a gas stream of the composition given in Table I.

The El Paso elemental sulfur pilot plant is designed to permit reduction of 12–100% sulfur dioxide in gas streams. In the reduction of pure sulfur dioxide, stoichiometric proportioning of reformed gas to sulfur dioxide may be defined by:



where x = moles of reformed gas/mole of sulfur dioxide. Solving for x , the stoichiometric proportioning of reductant to sulfur dioxide required

Table I. Typical Reformed Gas Composition

<i>Constituent</i>	<i>Volume %</i>
CO	17.0
H ₂	31.3
CO ₂	1.7
H ₂ O	4.2
N ₂	45.8

4.141 moles of reformed gas/mole of sulfur dioxide. Pilot plant process design for reducing pure sulfur dioxide therefore provides for blending of reformed gas and sulfur dioxide in the stoichiometric volume ratio of 4.141 to 1 and introduction of this mixed gas stream into the primary or first-stage catalytic reactor. This leads to a system composition defined by the following atomic ratios: H/C = 3.797, S/O = 0.331, C/O = 0.257.

Temperature and Pressure Specification. Since equilibrium conversion of sulfur dioxide to sulfur vapor increases with decreasing temperature, the reduction process was designed so that the primary reduction stage operates at the minimum temperature consistent with reaction kinetics which avoids sulfur condensation on the catalyst. Taking these factors into account, the primary catalytic reactor is operated at 350°C (623°K).

It was estimated that actual operating pressure at the primary reactor outlet would be 2.7 lb/sq in. gage, equivalent at the El Paso elevation to 1.04 atm absolute. Since sulfur dioxide reduction will entail a volume shrinkage caused primarily by formation of polyatomic sulfur vapor species, it is estimated, with the aid of Reaction 4, that the gas stream leaving the primary reactor will have a nitrogen content of 43.5%, equivalent to a nitrogen partial pressure of 0.45 atm. At the temperatures and pressures of interest, nitrogen may be considered an inert gas. In terms of gaseous species involved in equilibria within the H-C-O-S system, the sum of their partial pressures must be equal to the total pressure at the point in the reactor where equilibrium is approached less the par-

tial pressure of nitrogen—an estimated H-C-O-S system pressure in this case of 1.04 minus 0.45, or 0.59 atm.

Equilibrium Gas Phase Composition. Having defined optimum proportioning of reformed gas and sulfur dioxide and having specified

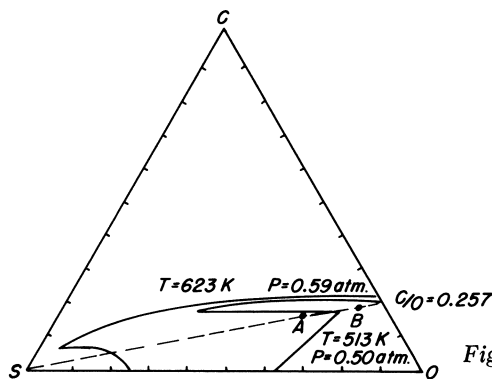


Figure 4. System composition. $H/C = 3.797$, $C/O = 0.257$.

temperature and pressure at 350°C (623°K) and 0.59 atm, respectively, the equilibrium gas phase composition may be calculated. The system composition, denoted as point A, together with carbon and sulfur saturation lines is depicted in Figure 4. At the specified primary reactor operating conditions the system composition is well inside the homogeneous gas region. Equilibrium gas phase composition at point A is given in Table II.

From the gas phase composition in Table II, it may be calculated that 79.4% sulfur dioxide is converted to sulfur vapor. Cooling this gas in the absence of a catalyst leads to no equilibrium shift other than that associated with sulfur vapor condensation; this has been borne out in the Claus process. By cooling a gas stream of the composition cited in Table II to 140°C (413 K), equilibrium sulfur condensation corresponds to 78.4% first-stage recovery of liquid sulfur.

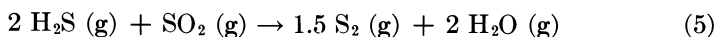
Table II. Equilibrium Composition of Gases Leaving First-Stage Reactor

Constituent ^a	Vol. %	Constituent	Vol. %
CO ₂	17.62	S ₂	0.09
H ₂ O	31.07	S ₃	0.01
H ₂ S	3.20	S ₄	0.05
SO ₂	1.59	S ₅	0.30
N ₂	43.64	S ₆	1.08
		S ₇	0.67
		S ₈	0.68

^a CO, H₂, COS, CS₂, and SO₃ are present in negligibly small concentrations.

After the condensation of sulfur vapor, most of the sulfur remaining in the gas phase is present as hydrogen sulfide and sulfur dioxide in the volume ratio of 2 to 1. With sulfur condensation, the atomic ratio of sulfur to oxygen in the gas phase is reduced while the other atomic ratios remain unchanged. Graphically, this equilibrium condensation of sulfur vapor, decreasing the gas phase ratio of sulfur to oxygen to 0.071, is represented in Figure 4 by the shift from point A to point B along the line having a constant atomic ratio of carbon to oxygen of 0.257.

With the gaseous sulfur-bearing species being predominantly hydrogen sulfide and sulfur dioxide, further recovery of elemental sulfur depends on the Claus reaction:



To avoid condensing sulfur vapor on the catalyst used in the secondary, or Claus-type reactor, gases leaving the primary sulfur condenser must be reheated. For the plant operating conditions under discussion, the gas stream is reheated to 205°C (478 K). As the Claus reaction is slightly exothermic, it is estimated that the temperature of the gas stream will rise, allowing for thermal losses, by about 35°C to 240°C (513 K) as equilibrium is approached. Allowing for the expected pressure drop as the process gas stream passes through the process train and for the change in relative volume of inert nitrogen as compared with the total volume of "active" gaseous species, we can estimate that H-C-O-S system pressure will be 0.50 atm. Sulfur and carbon saturation lines conforming to this pressure and the expected temperature of 240°C (513 K) are also shown in Figure 4. Point B, corresponding to system composition, lies to the right of the sulfur saturation line. Therefore, under equilibrium conditions, sulfur condensation on the secondary reactor catalyst is avoided. The theoretical equilibrium gas phase composition is listed in Table III.

Table III. Equilibrium Composition of Gases Leaving Second-Stage Reactor

<i>Constituent</i> ^a	<i>Vol. %</i>	<i>Constituent</i>	<i>Vol. %</i>
CO ₂	18.53	S ₅	0.01
H ₂ O	34.41	S ₆	0.18
H ₂ S	0.75	S ₇	0.11
SO ₂	0.37	S ₈	0.25
N ₂	45.39		

^a CO, H₂, COS, CS₂, S₂, S₃, and S₄ are present in negligibly small concentrations.

From the data of Tables II and III, it may be calculated that equilibrium conversion of hydrogen sulfide and sulfur dioxide to sulfur vapor in the secondary reactor is 78.0%. Cooling this gas stream to 140°C (413 K) will lead to a liquid sulfur recovery of 76.1% of the secondary reactor output. Overall recovery in the two stages, then, may be calculated to be 94.9%.

Overall recovery could be increased slightly by adding a third catalytic stage. However, it was not deemed necessary to use a third stage in the ASARCO-Phelps Dodge pilot plant because it represents technology well established in the Claus process.

Laboratory Development Program

The initial laboratory investigation of the process now being piloted at the ASARCO El Paso plant involved bench scale evaluations of 19 different primary sulfur dioxide reduction catalysts. Also, fixed-bed and fluid-bed catalysis were compared, and various construction materials were evaluated in the corrosive hydrogen sulfide and sulfur vapor atmosphere generated in gas phase reduction of sulfur dioxide.

Following completion of the bench scale test program, an engineering contractor conducted a study and prepared the preliminary design for a pilot plant having a nominal production capacity of 20 short tons of sulfur/day when treating pure sulfur dioxide. This study found that fixed-bed catalysis was more practical. The preliminary pilot plant design, therefore, provided for a fixed-bed primary reactor of the shell-and-tube type in which the catalyst would be in the tubes.

Based on this engineering study we concluded that further laboratory studies should be made more fully to define the primary reactor catalyst loadings required to approach equilibrium conversion of sulfur dioxide to sulfur vapor over the range of pilot plant operating conditions. The reactor used in this additional study duplicated as nearly as possible the geometry of the proposed pilot plant reactor. The laboratory reactor was fabricated of type 304 stainless steel pipe. An electrically heated molten lead bath maintained the desired operating temperature.

Gas streams for the experimental reactor contained nitrogen, hydrogen, carbon monoxide, sulfur dioxide, and in some cases oxygen, from cylinders, which were blended to synthesize a mixture of reformed natural gas and a sulfur dioxide-bearing gas stream of the desired composition. The composition of this head gas stream was continuously monitored by an on-line process chromatograph. The mixed gas stream was saturated with water vapor at a controlled temperature and pressure to provide a water vapor content consistent with that in actual plant operation.

Gas samples from the reactor were analyzed by mass spectroscopy and gas chromatography and conversions of sulfur dioxide to sulfur vapor were computed from the combined analytical data. In this large-scale test program, effects on catalyst loading of a number of variables were examined in detail. While the laboratory experimentation had been quite extensive, operation of a pilot plant was considered necessary to permit scale-up of the process to the 200–300 ton/day plants conceivably required in the future.

The Elemental Sulfur Pilot Plant

Operating Conditions of the Pilot Plant. Because of fuel costs a sulfur dioxide-bearing gas stream of relatively low oxygen content is necessary to permit practical application of the ASARCO sulfur dioxide reduction process. Additionally, for any given sulfur production rate, equipment size increases as sulfur dioxide concentration in the gas stream decreases. There is, therefore, some lower sulfur dioxide concentration where it becomes more economical to concentrate the sulfur dioxide before reduction. Preliminary capital and operating cost estimates indicated that this breaking point was in the range of 12–15% sulfur dioxide. For these reasons, the pilot plant was designed to treat gas streams containing 12–100% sulfur dioxide. We anticipated that the major operational effort would be directed first to treating a gas stream containing 12% sulfur dioxide. Such a gas stream is typical of that generated in flash smelting of copper concentrates or in the newer copper smelting processes presently under development. The second principal mode of operation will reduce pure sulfur dioxide, in response to the requirement for concentrating the sulfur dioxide in more dilute gas streams before reduction. Sulfur production capability in the latter case amounts to 20 short-tons/day. However, since plant design provides for handling essentially the same total process gas volume regardless of sulfur dioxide concentration in the head gas, sulfur production decreases to approximately 8.5 short-tons/day when treating a 12% sulfur dioxide-bearing gas stream.

As usual in the conventional copper or lead smelter, none of the El Paso smelter gas streams has a sulfur dioxide concentration as high as 12%. In the pilot plant, then, the 12% sulfur dioxide gas stream is generated by burning molten sulfur in a spray-type sulfur burner to produce a gas stream containing 18% sulfur dioxide. This hot gas stream, at 1350°C (1623 K), is cooled to about 360°C (633 K) in a waste heat boiler. When the pilot plant is operating with this 18% gas, process tail gases are recycled to dilute the 18% head gas stream to 12%. In an alternate mode of operation, liquid sulfur dioxide is vaporized to generate the pure gas.

The Phelps Dodge reforming process (1) uses catalytic partial combustion of natural gas with preheated air to produce a reformed gas stream having a total hydrogen plus carbon monoxide content of 48–50% by volume. The reformer is a refractory lined, vertical, cylindrical steel vessel packed with nickelized alumina pellets. Air, preheated to 430–480°C (703–753 K), together with natural gas at a volume ratio of 2.8–3.0 to 1, respectively, is introduced through a mixer in the top of the reformer. In passing through the catalyst bed, the gas stream approaches the equilibrium composition corresponding to the outlet temperature and pressure of 1000°C (1273 K) and 1.15 atm absolute. The reformed gas which is generated is free of carbon particles and contains only traces of unreacted hydrocarbons. A controlled portion of the hot reformed gas is diverted through a water-cooled shell-and-tube heat exchanger to maintain a reformed gas temperature of 420–460°C (693–733 K).

Reformed natural gas and gases from either the sulfur burner or the sulfur dioxide vaporizer are combined stoichiometrically and introduced into the primary catalytic reactor at 350°C (623 K). The reformed and sulfur burner gases are cooled to maintain the mixed stream at this temperature. The primary reactor is a vertical shell-and-tube heat exchanger with the tube filled with catalyst. Since sulfur dioxide reduction is highly exothermic, an organic heat transfer fluid is circulated through the shell side to control reactor temperature. Coolant leaving the primary reactor is split into two streams. One stream is circulated through a kettle-type heat exchanger where steam at 35 lb/sq in. gage is generated. The other stream passes through a shell-and-tube heat exchanger which reheats the process gas stream before it is introduced into the second catalytic reactor.

The gas stream leaves the primary reactor at approximately the inlet temperature and is essentially at equilibrium, which amounts to conversions of sulfur dioxide to sulfur vapor of approximately 69% when treating a 12% sulfur dioxide gas and about 80% when reducing pure sulfur dioxide.

Following the primary reactor, the ASARCO–Phelps Dodge pilot plant duplicates typical Claus process practice. Tail gases from the primary reactor are cooled in a horizontal shell-and-tube condenser to condense sulfur and are then reheated to approximately 205°C (478 K) and passed through a second catalytic stage. This is a fixed-bed reactor with no internal cooling. The only reaction involved in the second stage is a shift in the equilibrium between hydrogen sulfide and sulfur dioxide to yield additional sulfur vapor. The process gas stream from the secondary reactor passes through a secondary condenser to recover additional sulfur and, thence, to an incinerator where residual hydrogen sulfide and traces of sulfur vapor are burned and exhausted to the atmosphere.

Operational Problems of the Pilot Plant. Pilot plant operation began in late August 1971 and initially investigated treatment of a 12% sulfur dioxide gas stream. A number of minor start-up problems were resolved, and a relatively stable, around-the-clock operation was achieved by mid-September. Operation in this mode continued, with some interruptions, until late February 1972. During this period 91 days of operation were logged. Typically, sulfur recoveries averaged 88–92% as compared with a theoretical recovery of approximately 93%. Eleven days of downtime were attributed to curtailed industrial use of natural gas. Other than this, most of the downtime was caused by two problems.

The first problem involved generation of the 12% sulfur dioxide-bearing gas stream. Condensation of trace amounts of sulfur trioxide, generated in burning sulfur, caused severe corrosion of tubes and tube sheets in the waste heat boiler. While not typical of potential problems which might be encountered in commercial adaptation of the sulfur process, this corrosion problem did cause the plant to be shut down for almost a month while the boiler was repaired. Operating the boiler at a higher pressure, leading to a higher tube wall temperature, has largely eliminated sulfur trioxide corrosion.

The second major problem involved the catalyst used for the primary reactor. Specifically, decrepitation of catalyst pellets in the first few inches of the bed increased the pressure drop through the primary reactor. No loss of catalyst activity has been detected. An extensive laboratory investigation isolated the cause of physical failure and evaluated possible alternative solutions.

The pilot plant began operating with a mixture of reformed natural gas and vaporized sulfur dioxide in late March 1972. After operation in this mode for approximately 10 days, a second liquid flowing out of the primary sulfur condenser was noted, and the plant was immediately shut down. At that time the plant was producing sulfur at the maximum design throughput of 20 tons/day with 90–92% recovery as compared with a theoretical recovery of slightly over 94%. The second liquid proved to be the organic heat transfer fluid. Leaks were found in the primary reactor and the secondary reactor preheater. The leaks in the preheater were relatively minor, but the problem in the primary reactor involved a major failure.

Removal of the primary reactor heads revealed warpage over approximately one-half of the upper tube sheet and showed evidence of leakage at a number of points on the bottom tube sheet. Many tubes in the area of the upper tube sheet warpage were burned through while the space between these tubes was solidly blocked with carbon from thermal decomposition of the organic coolant. Review of the reactor design indicated that cooling of the reactor should have been more than

adequate if the coolant flowed uniformly to all parts of the reactor. The failure was attributed to a combination of the conditions discussed below.

Bypassing of the coolant through the annular space between tubes and baffles was caused by tight tube pitch, close baffle spacing, and small window area, and this robbed the far side of the reactor of coolant. Bypassing in this manner was the only way in which flow could have been maintained following heavy carbon deposition. It is likely that bypassing resulted in overheating more than half of the reactor, causing carbonization of the coolant and subsequent tube failure.

A vapor lock in the reactor could have prevented liquid phase cooling near the top of the reactor. Organic heat transfer fluids undergo some degradation with use, leading to the formation of more volatile compounds or to polymerization, forming higher boiling compounds. Throughout the pilot plant operation there was noticeable formation of "low boilers." While these were automatically vented from the system, there is some evidence that venting was not adequate.

After a thorough review of possible alternatives, we decided that boiling media heat removal was conceptually a better choice for our reaction system. The boiling heat transfer coefficient is several times greater than the liquid film coefficient, so it is advantageous to use the boiling media over as much of the reactor length as possible. An extensive laboratory scale test program generated heat transfer data to confirm that expected heat fluxes are low enough to prevent transition from nucleate to film boiling. This transition could cause vapor blanketing of the tubes and possible tube failure.

Based on the results of this program, a new primary reactor has been designed and installed at El Paso. This reactor produces 10 tons of sulfur/day when using pure sulfur dioxide feed and 7.8 tons/day on 12% sulfur dioxide feed gas.

Operation was resumed at El Paso on October 28, 1973, using a 12% sulfur dioxide feed gas. Only minor operational difficulties have been encountered to date with this feed. However, curtailed natural gas use forced shutdown of the plant on several occasions. The future availability of natural gas for industrial use could limit application of the ASARCO sulfur dioxide reduction process. It is probable that a suitable reducing gas can be generated using other fossil fuels, although this alternative has yet to be proved.

Based on the laboratory work discussed above, a somewhat different catalyst was specified for this pilot run. There is evidence that the rate of catalyst decrepitation has been decreased. The catalyst decrepitation problem will be conclusively resolved through longer term operation of the plant.

Costs of the Pilot Plant

The capital cost of the ASARCO-Phelps Dodge pilot plant was \$1,610,000. Another \$1,300,000 has been budgeted for operation. Many questions will be answered by the operation of this plant, including such cost-related questions as catalyst life for the differing modes of operation. In terms of capital cost, it is estimated that a plant capable of reducing pure sulfur dioxide gas to produce 200 tons of elemental sulfur/day can be constructed for approximately \$10,000,000. Allowing for the cost of connecting flues, the required highly efficient gas cleaning equipment, and a plant for absorbing and concentrating the sulfur dioxide, such as a plant using the ASARCO dimethylaniline process, it also has been estimated that the overall capital requirement for facilities capable of recovering 200 short-tons/day of elemental sulfur from copper converter gases would be about \$30,000,000. Direct operating cost of such a plant is estimated at \$30-35/short-ton of sulfur, depending on fuel costs. These estimates are based on 1972 construction and operating labor costs and must be viewed as budgetary estimates only, based on incomplete pilot plant evaluation of the process.

Literature Cited

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RECEIVED April 4, 1974. Certain process details and specific laboratory and pilot data have been omitted from this discussion of the ASARCO sulfur dioxide reduction process because of their proprietary nature.

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Sulfuric Acid Plants for Copper Converter Gas

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Conventional sulfuric acid plants have traditionally been used to recover sulfur dioxide from smelter gases, but these are inadequate to meet the proposed sulfur dioxide emission standards. Double absorption, which removes sulfur trioxide from the partially converted sulfur dioxide gas stream, reduces the sulfur dioxide emission to less than 500 ppm in the undiluted stack gas. Two double absorption plants using Lurgi technology have been operating with copper converter gas since early 1973. In spite of the wide and frequent variations in gas volume and sulfur dioxide concentration, these plants have consistently maintained sulfur dioxide emission levels well below 500 ppm. This paper presents data on the design and operating conditions for these plants.

The smelting of nonferrous metals, primarily copper, zinc, and lead, generally causes sulfur dioxide emissions varying from as much as 15% to less than 1% sulfur dioxide depending on the type of operation. Some sulfur dioxide is recovered as sulfuric acid. The nonferrous smelter industry—either in operation or under construction in 1974—has a total sulfuric acid production capacity of about 15,000 tons/day. About one third of this output comes from lead and zinc smelters which produce a reasonably steady gas stream containing 5–14% sulfur dioxide, depending on the type of roaster or sinter machine used. With a steady gas flow and sulfur dioxide concentration, designing a sulfuric acid plant to use this off-gas presents few problems except for cleaning the gas in the purification section of the plant.

However, this paper is primarily concerned with sulfuric acid production from copper smelters where most of the sulfur dioxide is in a gas stream which varies widely and frequently, both in gas volume and in sulfur dioxide concentration. This gas stream presents a real challenge

to the sulfuric acid plant designer, especially in view of the proposed Environmental Protection Agency (EPA) regulation which would limit sulfur dioxide emissions from the acid plant to an average of 650 ppm over a 6-hr period. In the conventional process which has been used for many years, the maximum conversion of sulfur dioxide to sulfur trioxide is 98%. This process will reduce the sulfur dioxide in a gas containing 8.0% sulfur dioxide to about 1800 ppm in the stack gas leaving the absorber. With a gas containing 4% sulfur dioxide, 98% conversion will reduce the stack gas to 850 ppm. Both of these concentrations are greater than the proposed EPA limitation of 650 ppm, and a different approach is required.

This has been accomplished in the double-catalysis process developed by Bayer and Lurgi. Davy Powergas, who is a Lurgi licensee for this process, built the only two plants of this type in the United States which use copper converter gas. They have kept sulfur dioxide emissions well below the guaranteed 500 ppm level.

In the conventional plant sulfur dioxide is converted to sulfur trioxide in a series of three or four catalyst beds with cooling between the beds to remove the heat of reaction. The overall conversion is limited by the equilibrium for the relative partial pressures of sulfur dioxide, sulfur trioxide, and oxygen and the temperature of the converter exit gas. This equilibrium is equivalent to about 98.5% conversion.

In the double-catalysis plant a major portion of the sulfur trioxide is removed from the gas in an intermediate absorption tower after the second stage of conversion. The balance of the gas, which is returned to the converter for the final two stages of conversion, is a very weak sulfur dioxide gas with a high oxygen-to-sulfur dioxide ratio. The equilibrium conditions for this gas leaving the converter are very close to 100% conversion of the total sulfur dioxide entering the converter. In steady state operation, which is not possible with copper converter gas, over 99.8% conversion of sulfur dioxide to sulfur trioxide is expected in double-catalysis plants.

Copper Smelter Operation

A brief description of a typical copper smelter operation will help in understanding the extremely variable nature of the sulfur dioxide gas stream to be processed. The copper concentrates delivered to the smelter are a mixture of copper and iron sulfides. In current practice these are processed in two or three steps to produce 99% blister copper. In some smelters the concentrates are first partially roasted, removing 20–50% of the sulfur. This produces a relatively strong, steady gas stream containing 4–14% sulfur dioxide, depending on the type of roaster used.

The partially roasted material, or green concentrates if no roasting step is included, is then charged to the reverberatory furnace. Here the charge is melted, and a matte containing 25–50% copper and 40–20% iron settles to the bottom while an iron slag floats to the top. Some of the sulfur in the charge is burned but additional fossil fuel firing is required to provide the necessary heat. If the charge has been roasted, an additional 10–30% of the sulfur will be burned. With green concentrate feed about 20–40% of the sulfur will be burned. The off-gas from the reverberatory furnace is a steady flow but it contains only $\frac{1}{2}$ –2½% sulfur dioxide.

The final step, a batch operation, takes place in the copper converters. Matte, withdrawn from the reverberatory furnace, is charged to the converter along with a siliceous fluxing material. Air is blown through the molten charge, and the iron sulfide is selectively oxidized to form iron oxide and sulfur dioxide gas. The iron oxide combines with the flux to form a slag. When slagging is essentially complete the air blowing is stopped and the slag is skimmed off. Additional matte and flux is charged to the converter, and the operation is repeated until a full converter charge is completed. This may require four to eight separate charges, depending on the composition of the matte. The individual slag blows may each last as long as 1 hr. No air is blown for about 15 min between charges while the slag is being skimmed and an additional charge is added. When the charge is complete and essentially all of the iron has been slagged, the final copper blow is started to burn the remaining copper sulfide. This copper blow may last for several hours before all the sulfur is removed and a 99% blister copper is obtained. The converter is then unloaded and made ready for the next charge. Figure 1 shows typical variations in sulfur dioxide concentrations in the converter gas during slag and copper blows for a plant with two converters operating.

Most smelters have at least three converters, and one or more converters should be on the operating cycle at all times to provide a reasonably constant gas flow. The operating time for one cycle may be from 6 to 12 hr, depending on the operation of the particular smelter and the type of concentrates being treated. The gas flow during the full converter cycle is intermittent because it is necessary to shut off the air blow during slag skimming and charging.

The sulfur dioxide concentration in the gas directly above the converter charge is close to theoretical—about 16% during slag blows and 21% during copper blows. The converter hoods, however, are not tight because the converter must be rotated for charging and skimming. From 100 to 300% air will leak in to prevent appreciable sulfur dioxide leakage into the working area around the converters. In a typical operation the

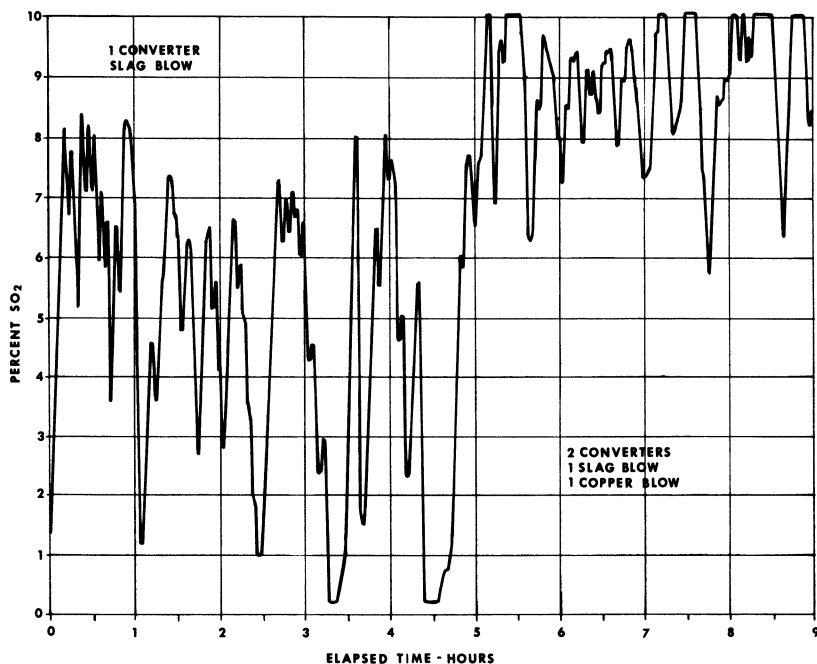


Figure 1. Variation of sulfur dioxide concentration in a typical copper converter gas

off-gas from the converter may average about 4% sulfur dioxide during the slag blows and 8% during the copper blow. This gas will contain 60–80% of the total sulfur contained in the concentrates if they are charged directly to the reverberatory furnace. If the concentrates are partially roasted before smelting only about 30–50% of the sulfur will be in the converter off-gas.

Plant Design Considerations

From the point of view of the sulfuric acid plant designer it would be advantageous if the smelter had a roaster generating a high strength sulfur dioxide gas for the base load. This would reduce the effect of the wide swings in the sulfur dioxide concentration of the converter gas. Unfortunately, most of the existing roasters produce a very weak sulfur dioxide gas, and the sulfuric acid plant must be designed to use only the converter gas.

For this example of acid plant design considerations, assume that a smelter has three copper converters and that the acid plant must be able to take all of the converter gas and maintain a sulfur dioxide level of less than 500 ppm in the acid plant stack gas. The maximum gas flow from

each converter is 30,000 standard cu ft/min (SCFM), and no more than two converters will be on the line at any time. The maximum sulfur dioxide concentration with the maximum gas flow will be 8%. The plant is to be autothermal when operating with as low as 4% sulfur dioxide. This means that no fuel firing will be required to keep the plant in thermal balance if the gas has at least 4% sulfur dioxide. For gas containing less than 4% sulfur dioxide, a fuel-fired indirect heater will be required.

To meet these conditions the acid plant must be designed to handle 60,000 SCFM of gas. When this gas contains the maximum of 8% sulfur dioxide the acid production rate is equivalent to 960 tons/day. Since this condition may persist for at least 1 hr, the catalyst loading and the acid coolers must be designed for this acid production rate.

Defining the minimum sulfur dioxide concentration for the plant establishes certain other design criteria. If only one converter is on the line with a slag blow producing 4% sulfur dioxide gas, the equivalent acid production rate is only 240 tons/day. This is still not the minimum operating rate since there will be periods, presumably short, when the sulfur dioxide concentration decreases to 1% or even zero. Some of the gas-to-gas heat exchangers must be sized to maintain the autothermal requirement with 60,000 SCFM of 4% sulfur dioxide. The gas-cooling facilities in the purification section of the plant must be able to reduce the water content of the gas sufficiently to permit the production of 93% sulfuric acid with 4% sulfur dioxide gas. This necessitates cooling the gas to about 85°F. Figure 2 shows the required gas temperature for various plant elevations and sulfur dioxide concentrations.

Another major consideration in the design of the plant is the nature and quantity of impurities in the gas stream delivered to the acid plant. No acid plant can operate satisfactorily with an inadequate gas purification section. The gas will normally be delivered to the acid plant at about 600°F after most of the dust has been removed in electrostatic precipitators. However, the gas may still contain dust, as well as sulfur trioxide, halogens, arsenic, and other metallic vapors.

Gas Purification

In the purification section of the acid plant the gas first enters a weak acid scrubber where its temperature is reduced to about 130°F by water evaporation. It is then cooled to about 85°F to reduce its water content to the required level. Finally, it is cleaned in electrostatic mist precipitators where the last traces of dust and the acid mist formed from the sulfur trioxide in the gas are removed. The type of equipment used in the purification section will vary somewhat with individual plant conditions and operator preferences.

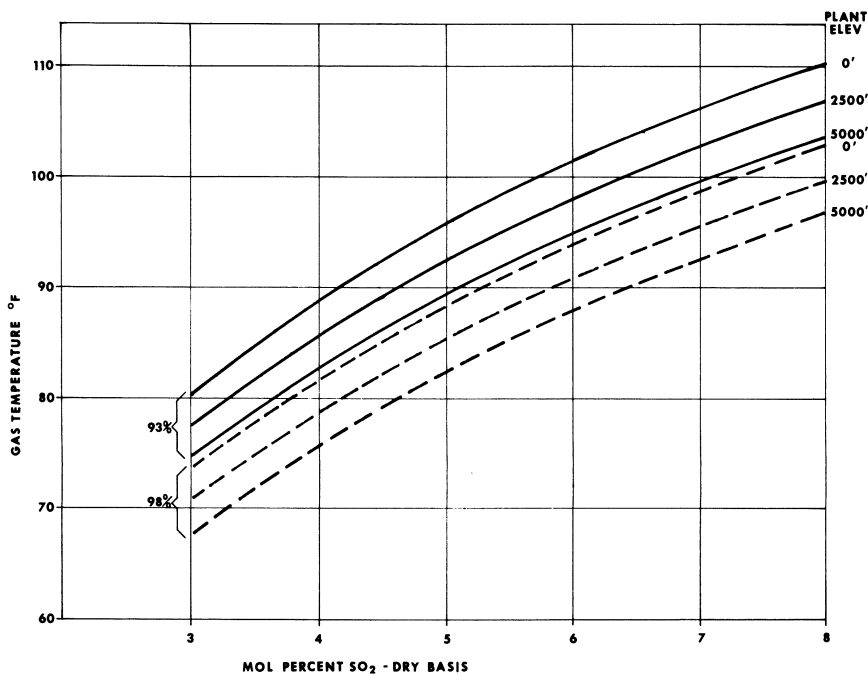


Figure 2. Gas cooling required to produce 93% or 98% sulfuric acid

GAS SCRUBBING AND COOLING. If the gas contains fluorine, two scrubbing towers in series may be required to remove the fluorine completely. This step is necessary primarily to protect the catalyst in the contact section of the acid plant. Excess scrubbing liquor from the second scrubber is transferred to the first scrubber, and the weak acid purge from the system is taken from the first scrubber.

Since fluorine will attack the usual acid-proof refractory materials, the first scrubber, which is subject to the highest fluorine content, is lined with carbon brick. The scrubber may be either a venturi-type or an open spray-type tower in which the gas is quenched to its saturation temperature. Weak acid is recirculated over this tower to remove as much of the dust and fluorine as possible, as well as to quench the gas.

In the second tower the gas must be cooled to meet the required water balance for acid production. This is usually a packed- or tray-type tower with liquor coolers in the recirculated weak acid stream. The temperature to which the gas must be cooled is determined by its sulfur dioxide content, the product acid strength desired, and the elevation of the plant above sea level. As shown in the chart, each of these factors has an important effect on the required temperature. An allowance has

been made in the calculation to permit the addition of some water to the strong acid system to provide more flexible control of acid strength.

If the fluorine or dust content of the gas is not excessive, a single packed- or tray-type tower with cooling of the recirculated liquor can be used for both gas scrubbing and cooling. Direct cooling of the gas with once-through cooling water is no longer considered practical for two reasons. First, the water will be contaminated with dust and the acid formed from the sulfur trioxide in the gas, making disposal a problem. Second, some of the sulfur dioxide will be absorbed in the water, and the amount of stripping air required to recover this and avoid a nuisance will dilute the main gas stream excessively.

Materials of construction are an important consideration in the gas scrubbing system because fluorine and chlorine may be present. The scrubbing liquor is usually less than 10% sulfuric acid below 135°F, and a stainless steel (such as 20 alloy) would be suitable for pumps, valves, and liquor coolers if halogens are not present. The alternatives are glass- or plastic-lined, graphite or higher alloys. The towers are usually a carbon steel shell with an impervious membrane and an acid brick lining, although plastic can be used in some areas.

ELECTROSTATIC MIST PRECIPITATORS. The gas leaving the scrubbers is essentially free of halogens and dust but it still contains acid mist. The amount of acid mist depends primarily on conditions in the smelter. In gas from copper converters, the sulfur trioxide content may vary from 2 to 10% of the total sulfur oxides. The amount of sulfur trioxide formed depends largely on the temperature and time the gas contacts the iron oxide in the dust and the scale on the carbon steel flues. The sulfur trioxide combines with the moisture in the gas to form sulfuric acid vapor. When the gas is cooled in the scrubbers, most of this vapor condenses as a finely divided acid mist, although some of it is absorbed in the scrubber liquor. Sulfuric acid mist, which is generally considered to be particles less than 5 μ , is very difficult to remove from a gas stream, so only a portion of the mist will be removed in the scrubber. If the remaining mist were allowed to enter the contact section of the acid plant it would corrode the carbon steel ducts and heat exchangers and the main blower. It must, therefore, be removed as completely as possible in the purification section of the plant. This is accomplished in the electrostatic mist precipitators.

These precipitators are usually made of sheet lead. They resemble a vertical tubular exchanger with high voltage discharge electrodes suspended in the center of each of the 10-in. diameter tubes. The gas, flowing upward through the tubes, is exposed to a corona discharge from the electrodes which drives the mist particles to the grounded tube walls. The collected acid runs down the tubes and is collected in the lower

header as 5–10% sulfuric acid. The acid, which is saturated with sulfur dioxide and which contains the last traces of dust from the gas, is usually returned to the scrubber circulating system.

The gas leaving the scrubbers may contain as much as 100 mg/SCF of sulfuric acid as acid mist, and two mist precipitators are usually installed in series to obtain 99% removal efficiency. This efficiency could be obtained in a single larger unit giving the same total residence time but this would be less reliable. The efficiency is a function of power input to the discharge electrodes, and this is limited by the voltage at which arcing occurs in the tubes. Entrained acid droplets in the gas stream will aggravate the arcing and require reduced input voltage which lowers the unit efficiency. With two units in series the voltage is reduced only on the first unit so that the overall efficiency is affected only slightly.

The impurities removed from the gas in the purification system must be purged from the system, and the purge is normally taken from the scrubbing tower. Makeup water is usually required to provide this purge because the gas entering the scrubber normally contains less water than the cooled saturated gas leaving the mist precipitators. The quantity of makeup water required is the total of the amount added to the gas stream and the amount required to maintain the acid and/or the dust concentration in the scrubber liquor below a selected limiting figure. The purge stream is saturated with sulfur dioxide and is discharged from the system

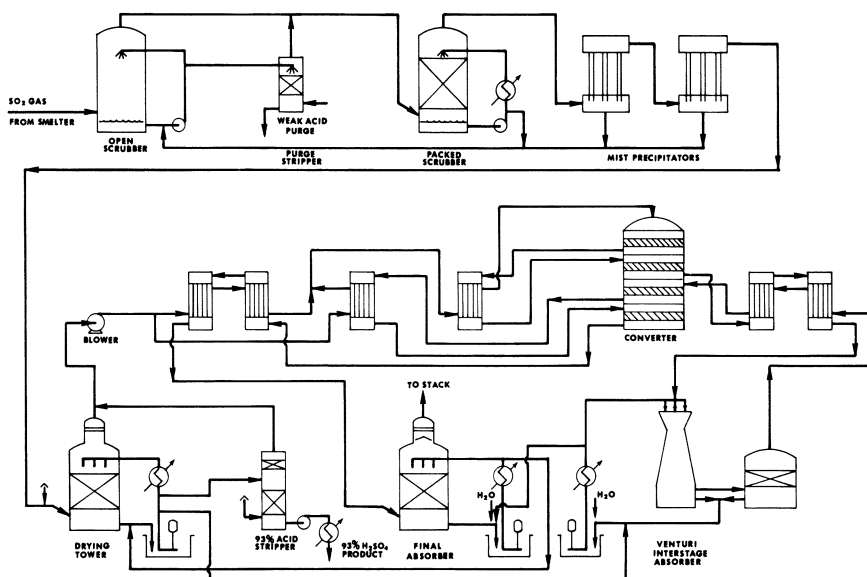


Figure 3. Flow diagram of a double-catalysis sulfuric acid plant

through a stripper where most of the sulfur dioxide is recovered in a small stream of stripping air which is added to the main gas stream.

The gas leaving the mist precipitators should contain only sulfur dioxide, oxygen, nitrogen, and water vapor, but there will be some traces of impurities which are not harmful to the contact section of the acid plant.

If the gas has not been adequately cleaned, the contact section of the plant will have continuing operating problems. Improper operation of the mist precipitators will permit acid mist to enter the contact section. This will result in corrosion and sulfate accumulation in the gas ducts, the blower, and the heat exchangers. The corrosion is particularly severe in the heat exchangers because the tube wall temperature, with hot sulfur trioxide gas in the tubes, exceeds 300°F. The sulfate accumulation on the duct walls is normally not a serious corrosion problem but it eventually breaks loose and is carried onto the catalyst beds in the converter. This sulfate, and also any dust that may pass through the purification section, will gradually blind the catalyst beds. This reduces the conversion efficiency and increases the pressure drop through the plant.

Contact Section

In the contact section of the plant, the saturated gas is first dried by contact with 93% acid and then the sulfur dioxide in the gas is oxidized to sulfur trioxide. The sulfur trioxide is absorbed in 98% acid where it combines with the free water present to produce additional sulfuric acid. Figure 3 is a typical flow diagram of a double-catalysis sulfuric acid plant operating with sulfur dioxide gas from copper converters.

To obtain essentially complete oxidation of sulfur dioxide to sulfur trioxide excess oxygen in the gas above the stoichiometric requirement is necessary. The volume of oxygen in the gas should at least be equivalent to that of the sulfur dioxide, and it is preferable to have a slightly higher ratio.

There are times during the operating cycle of the copper converter when the oxygen-to-sulfur dioxide ratio is lower than is desirable. During these periods dilution air must be mixed with the gas entering the drying tower of the contact section of the plant to increase its oxygen content.

The gas is dried by contact with recirculated 93% acid as the gas passes up through the packing in the drying tower. The acid absorbs the moisture from the gas and is heated by moisture condensation and by the resultant acid dilution. This heat is removed by pumping the acid through coolers before it is returned to the top of the tower.

Since dried gas is not corrosive, carbon steel ducts are used for the remainder of the plant. The gas leaves the drying tower at about 110°F, and after passing through an entrainment separator it goes to the main blower. The blower provides sufficient suction to draw the gas through the purification section and the drying tower and sufficient pressure to deliver it through the balance of the plant. The total pressure drop through a clean double-catalysis plant, including the purification system, is usually about 200 in. WG (7.25 psi), and an additional 25–30 in. WG is usually added for the design of the blower to allow for pressure buildup in the system.

Conversion. The gas leaves the blower at about 175°F and is heated in the shell side of a series of gas-to-gas shell and tube heat exchangers to the required converter inlet temperature of 820°F.

In the converter, four catalyst beds are arranged one above the other with division plates between the beds. The gas leaving each catalyst bed is cooled in the tube side of the shell and tube heat exchangers to the desired temperature before entering the next bed. The temperature rise in the catalyst beds will vary considerably with the wide variation in the sulfur dioxide content of the feed gas. The quantity of catalyst installed in each bed will be determined by the maximum sulfur dioxide flow, which is usually an 8% gas. Therefore the catalyst loading is greater than required for a weaker sulfur dioxide gas, and a higher conversion will be obtained on the first bed. This is enhanced by the lower temperature rise obtained with a weak sulfur dioxide gas for a given percentage conversion of sulfur dioxide to sulfur trioxide. For example, approximately 65% of an 8% sulfur dioxide gas will be converted to sulfur trioxide in the first bed with a temperature rise of 285°F. With a 4% sulfur dioxide gas about 85% will be converted with a temperature rise of only 190°F. The differences and temperature rises will be less on subsequent beds. The extent of conversion approaches equilibrium on each bed, and the gas must be cooled after each bed so that further conversion can be achieved in the next bed.

Absorption. In a typical double-catalysis plant, the gas leaving the second stage of conversion passes to the interstage absorption tower where the sulfur trioxide is absorbed from the gas. With an 8% sulfur dioxide gas more than 85% of the sulfur dioxide has been converted to sulfur trioxide at this point, and with a 4% gas over 95% has been converted. The gas leaving the converter must be cooled at least to 450°F but not below 300°F before entering the absorber. The heat available from this cooling is used to reheat the gas returning from the absorber to the third stage of conversion.

One of the major problems in designing a double-catalysis plant is to make it autothermal when operating with a weak sulfur dioxide gas. The

only heat available to the converter-heat exchanger system is the exothermic heat of reaction of oxidizing sulfur dioxide to sulfur trioxide and the heat of compression in the main gas blower. Some of the heat can be recovered from the gas going from the converter to the absorbers but this gas stream, with its sulfur trioxide content, should not be cooled below 300°F to avoid possible acid condensation in the heat exchanger.

In a conventional type plant with a single absorber it is practical to design the plant to be autothermal with a gas containing as little as 3% sulfur dioxide because heat is only lost when the gas goes to the absorber plus the normal heat lost to atmosphere. In the double-catalysis process, heat is lost from the gas stream going to each of the two absorbers. In the normal design of absorber, if the total gas stream leaves the interstage absorber at 170–180°F to be reheated to converter temperature it would be impossible for the plant to be autothermal with 4% sulfur dioxide gas.

A solution to this problem, developed and patented by Lurgi, uses a venturi-type interstage absorber. The acid and gas flows are co-current down through the vertical venturi so that the gas leaves the absorber at essentially the same temperature as the acid. With suitable adjustment of the acid circulating rate the gas exit temperature can be maintained at 250°F. This additional 70–80°F insures autothermal operation with 4% sulfur dioxide gas in a double-catalysis plant. Some additional heat advantage can be gained by bypassing a portion of the gas direct from the second to the third stage. This, however, increases the quantity of sulfur trioxide in the gas leaving the converter, thereby reducing the maximum conversion that can be achieved. Sulfur trioxide absorption in the interstage absorber is essentially complete, and very little passes to the final stages from this source. The absorber circulating acid is maintained at 98% sulfuric acid to obtain good absorption. The heat resulting from absorbing sulfur trioxide and cooling the gas is removed from the acid in coolers before the acid is returned to the absorbers.

The gas entering the third stage of the converter has a very low sulfur dioxide content with a high oxygen-to-sulfur dioxide ratio so that a high conversion is possible in the last two stages. Adequate facilities for cooling between these stages are important, so that the final converter exit temperature can be low to provide the best equilibrium conditions for maximum overall conversion. This cooling also provides a safety factor against upsets in operation of the first two beds which would require more than normal conversion in the last two beds with a higher temperature rise. The converter exit temperature is a controlling factor in the degree of conversion that can be achieved, and it should be maintained as low as possible, preferably below 800°F.

The gas leaving the final stage of the converter is cooled in heat exchangers before going to the final absorber. The heat recovered in

these exchangers and in those cooling the gas after the first and third stages of the converter is used to preheat the sulfur dioxide gas leaving the blower to the required converter inlet temperature.

In the final absorber, which is similar to the drying tower, the sulfur trioxide is absorbed from the gas. The remainder of the gas, with a sulfur dioxide content below 500 ppm, is vented to the atmosphere through a demister which removes acid mist.

Automatic Controls. A certain amount of automatic control of process operating conditions is necessary to cope with frequent large changes in sulfur dioxide content of the gas. A sulfur dioxide analyzer, indicating the sulfur dioxide content of the gas at the main blower, controls the admission of dilution air to the drying tower when the sulfur dioxide content of the feed gas exceeds 8%. A second analyzer records the sulfur dioxide content of the gas leaving the final absorber.

The temperature of the gas entering each of the first two catalyst beds is automatically controlled by adjusting the heat exchanger bypasses. The acid strength and levels in each of the three pump tanks serving the drying and absorption towers are controlled automatically by regulating the various cross transfers, adding water, and delivering the product acid to storage. These controls take care of the adjustments for wide changes in acid production, freeing the operator to make the minor changes which optimize the operation.

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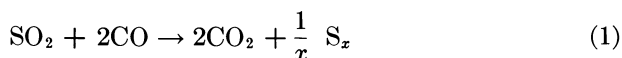
Dual-Catalyst Beds to Reduce Sulfur Dioxide to Elemental Sulfur in the Presence of Water Vapor

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Water vapor decreases the effectiveness of an iron–alumina bifunctional catalyst in reducing sulfur dioxide with carbon monoxide. This problem can be averted by enriching the iron content in the bifunctional catalyst. The water–gas–shift reaction between water vapor and carbon monoxide generates an equivalent quantity of hydrogen. A post-catalyst bed of pure alumina must be used because of the hydrogen sulfide which is generated in the reduction step with hydrogen as well as that which is produced from the hydrolytic decomposition of the carbonyl sulfide byproduct. By deliberately releasing some sulfur dioxide (equal to half of the hydrogen sulfide produced) from the first catalyst, both pollutants can be suppressed by a Claus reaction on a post-catalyst.

In the search for solutions to the problem of sulfur dioxide pollution, one of the techniques that has been considered by the Bureau of Mines is catalytic reduction with carbon monoxide.



x varies between 2 and 8

for $x = 2$: $\Delta F^\circ_{700} = -31.5$ kcal; $\Delta H^\circ_{700} = -48.9$ kcal

for $x = 8$: $\Delta F^\circ_{700} = -34.1$ kcal; $\Delta H^\circ_{700} = -61.3$ kcal

This method has several advantages: nitrogen oxides can be simultaneously reduced, carbon monoxide can be made available in the required

concentrations as a flue gas constituent from furnaces operating near or slightly over the stoichiometric ratio of fuel to air, and the main reaction product, sulfur, can be easily stored.

Single-bed catalysts had been used to produce sulfur from dry sulfur dioxide gases. Ryason (1, 2) used either Cu, Pd, Ag, Co, or Ni supported on alumina. Khalafalla and Haas (3) optimized the composition of iron–alumina catalysts to produce sulfur from dry gases containing sulfur dioxide and carbon monoxide. Querido and Short (4) demonstrated the feasibility of reducing sulfur dioxide by carbon monoxide on a copper–alumina catalyst at concentrations and temperatures typical of power plant stack gases.

Recently Okay and Short (5) reported that the sulfur dioxide reduction activity of the single-bed copper–alumina catalyst was reduced when water was added to an inlet gas containing 0.2% sulfur dioxide. Neither hydrogen nor hydrogen sulfide was detected in their experiments although thermodynamic calculations indicate that these gases could form at detectable concentrations.

The objective of this investigation was to examine the effect of water vapor on the reduction of sulfur dioxide with carbon monoxide on an iron–alumina bifunctional catalyst and to devise double-catalyst beds to cope with the deleterious effect of water. The catalyst temperature of the first bed in this double-bed system was varied to adjust the ratio of reactants entering the second bed in order to maximize the removal of sulfurous gases.

Experimental Apparatus and Procedure

The major portion of the experimental apparatus is described in previous publications (3, 6). A water injector pump was inserted into the preheating portion of the furnace. The exit gas lines and gas chromatograph were maintained above 100°C by heating tape to prevent water condensation.

A Fisher partitioner gas chromatograph was used to analyze for CO, CO₂, SCO, H₂S, and SO₂. The analyzers were calibrated with commercial gas mixtures. Helium, rather than nitrogen, was used as a diluent throughout this work not only because the heating and cooling periods are decreased by its high heat conductivity and low heat capacity but also because the nitrogen chromatographic peak interferes with that of carbon monoxide on columns of 13× molecular sieve and 15% Uncon on Teflon.

In a previous publication (7), it was shown that naturally occurring minerals or solid waste byproducts containing mainly alumina and iron catalyzed Reaction 1, sometimes as effectively as synthetic iron–alumina

Table I. Chemical and Physical

Catalyst	Chemical Analysis (%)				
	Al ₂ O ₃	FeO ₃	SiO ₂	CaO	Na ₂ O
Berbecé bauxite ^b	80.0	1.5	7.5	—	—
Red bauxite	53.1	9.4	2.5	0.5	—
Jamaican red mud	23.0	39.1	3.9	3.8	3.8
Surinam red mud	20.7	22.4	15.0	6.3	10.4

^a Surface areas of indurated samples were determined by the BET method.

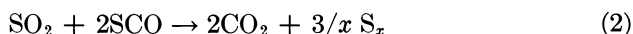
^b Average analysis.

mixtures. For practical reasons some of these solid wastes were used as catalysts in this investigation.

The samples were dried, pulverized to 100 mesh, briquetted into minus 16- plus 20-mesh pellets, and indurated at 600°C for 6 hr. The chemical and physical properties of these catalysts are given in Table I. The Berbecé bauxite, a product of British Guiana, was obtained from Milwhite Co., Inc., Houston, Tex. The Arkansas red bauxite was obtained from David New—Minerals, Providence, Utah. The Jamaican and Surinam red mud samples were supplied by the Federal Bureau of Mines Albany Metallurgy Research Center, Albany, Oreg.

In a typical experiment, an appropriate quantity of the dried catalyst was placed in a Vycor tube (1.2 cm diameter) on a perforated porcelain disk, heated in nitrogen to 600°C for 2 hr, reduced in hydrogen for 1 hr, and then cooled to operating temperature in helium. The gas mixture (1.1 atm, absolute) was metered through the catalyst bed at a nominal flow of 0.5 l. (STP)/min. The flow of the reactants through the catalyst was maintained for several hours until a steady-state gas analysis representative of catalytic reaction was obtained.

This preconditioning of the catalyst is necessary to separate the chemical reactions from the catalytic ones (7). In the first few minutes, the iron surface transforms to catalytically active pyrrhotite, as shown (7) by the gradual increase in carbon monoxide consumption and corresponding increase in carbon dioxide production. The initial gaseous sulfide by-products react with the iron in the catalyst to form iron sulfides. In a previous publication (8), it was shown that lattice sulfur is a more versatile and useful carbon monoxide-sulfurizing agent than molecular sulfur. The hypothesis tested was that metal sulfides with relatively weak metal-to-sulfur bonds are more effective in forming the active intermediate (9) carbonyl sulfide.



x varies between 2 and 8

for $x = 2$: $\Delta F^\circ_{700} = -14.2$ kcal; $\Delta H^\circ_{700} = -4.9$ kcal

for $x = 8$: $\Delta F^\circ_{700} = -21.7$ kcal; $\Delta H^\circ_{700} = -42.1$ kcal

Properties of the Catalysts

<i>Chemical Analysis (%)</i>					<i>Surface Area^a (m²/g)</i>
<i>K₂O</i>	<i>TiO₂</i>	<i>MgO</i>	<i>LOI</i>	<i>P₂O₅</i>	
—	2.5	—	2.5	—	230
0.03	—	0.03	26.4	—	100
—	6.4	0.21	16.2	0.4	12
—	10.3	0.05	11.3	—	8

Experiments were conducted at different carbon monoxide ratios, r , defined as

$$r = \frac{P_{\text{CO}} - y[P_{\text{O}_y}] - x[P_{\text{NO}_x}]}{2P_{\text{SO}_2}}$$

where P is the partial pressure of the subscript gaseous species, y can be 2 or 3 for oxygen, and x can be 1 or 2 for nitric oxide. In the present work, P_{O_y} and P_{NO_x} in the feed gas were always zero.

Results and Discussion

The effect of water vapor on the removal of sulfur dioxide with various iron-containing alumina catalysts was examined first. A gas consisting of 3% sulfur dioxide, 6% carbon monoxide, 0–25% water, and the balance helium was passed at a flow rate of 0.5 l. (STP)/min through a 2-g bed of Berbece bauxite at 475°C, and the exit gases were analyzed for sulfur dioxide. The decrease in sulfur dioxide removal when water was added is illustrated by curve *a* of Figure 1. Removing the water did not bring the catalyst back to its original activity (curve *a'*). The sequence of tests, shown by the arrows, indicates that as the water content was increased from 0 to 2.5%, the catalyst activity deteriorated. Moreover, when the water flow was stopped, the original activity was not restored. This indicates that water is held rather strongly on this catalyst and that its desorption is very slow. The same trend was observed with a 2-g catalyst of Arkansas red bauxite. However, the higher iron content increased the sulfur dioxide removal as shown in curves *b*, *b'*, and *b''* of Figure 1.

When an iron-rich catalyst such as Jamaican red mud (20 g at 380°C) was used in this test, it not only exhibited much higher levels of catalytic activity, but it was also only slightly affected by the presence of up to 25% water vapor in the inlet gas. This is demonstrated by curve *c* of Figure 1. Thus, in order to suppress the adverse effect of water vapor on the catalytic reduction of sulfur dioxide with carbon monoxide,

an iron-rich alumina catalyst is needed because the iron component can also catalyze the water-gas-shift reaction:

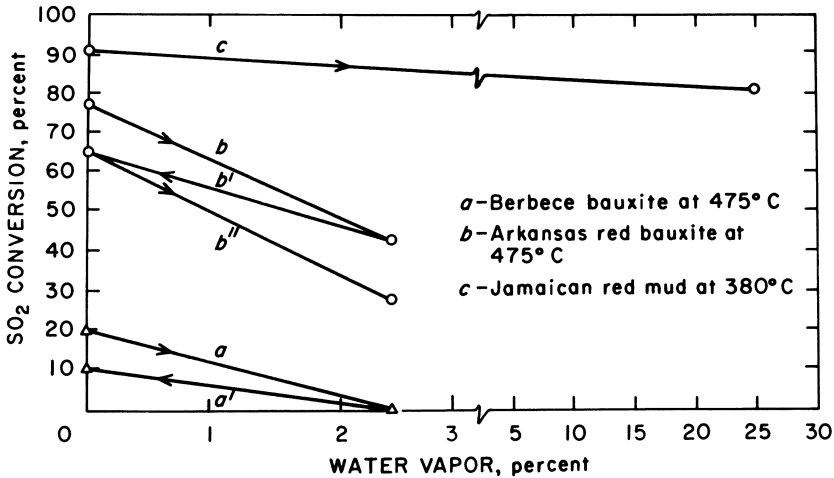
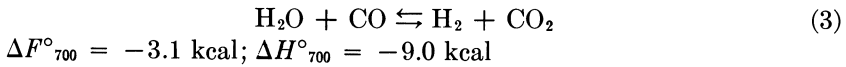
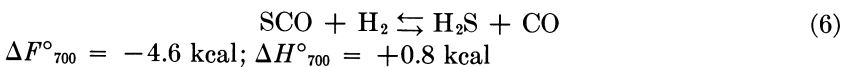
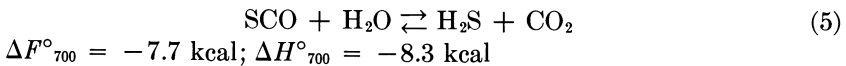
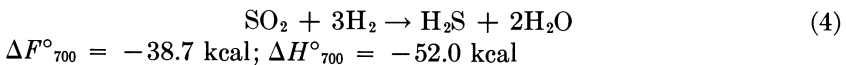


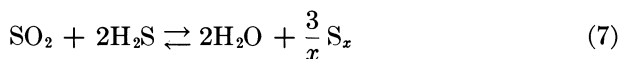
Figure 1. Effect of water vapor on sulfur dioxide conversion using various iron-containing alumina catalysts

Because hydrogen is also a reductant of sulfur dioxide, the decay in sulfur dioxide removal efficiency will decrease by increasing the iron content up to 27.4% of the catalyst.

However, the beneficial effect of iron is disturbed by the hydrogen sulfide which is produced according to Reactions 4, 5, and 6:



This gas is recognized by its offensive smell in the presence of large amounts of water vapor. Fortunately, hydrogen sulfide will react with sulfur dioxide according to the Claus reaction:



x varies between 2 and 8

for $x = 2$: $\Delta F^\circ_{700} = -4.4$ kcal; $\Delta H^\circ_{700} = +12.6$ kcal

for $x = 8$: $\Delta F^\circ_{700} = -11.8$ kcal; $\Delta H^\circ_{700} = -24.5$ kcal

to produce elemental sulfur and water vapor. An ideal removal system should convert 67% of the sulfur dioxide to hydrogen sulfide in a primary iron–alumina catalyst before the remaining sulfur dioxide will react with the newly formed hydrogen sulfide on a secondary Claus catalyst.

Single-Bed Isothermal Catalysts. Detailed analyses of exit gases from single-bed isothermal catalysts were determined with 2 g of red bauxite at 475°C. The inlet gas contained 3.4% sulfur dioxide, 5.9% carbon monoxide, and 90.7% helium. Figure 2 (Section A) shows that the sulfur dioxide analysis decreased from 3.4 to 0.8. In other words, about 76% of the sulfur dioxide was removed in the dry state at a carbon monoxide ratio, r , of 0.87. However, when 3% water vapor was added (Section B), the sulfur dioxide in the exhaust gas increased to 1.9%, illustrating the poisoning effect of water. When water vapor flow was stopped, the sulfur dioxide exhaust analyses decreased slowly (Section

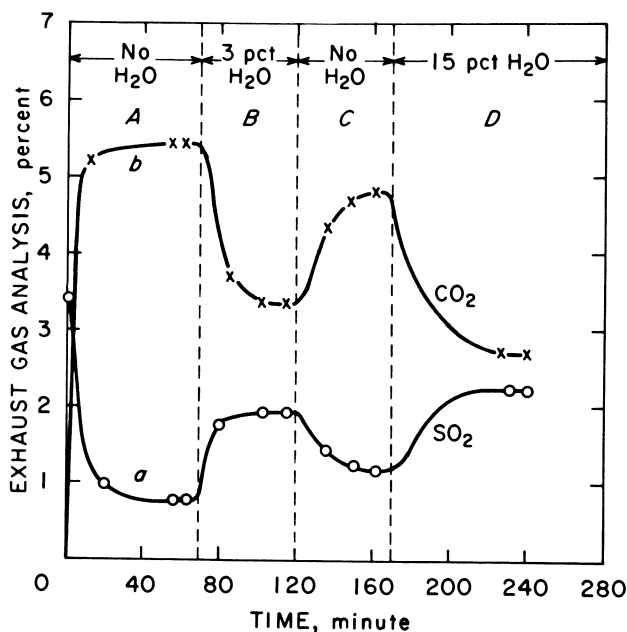


Figure 2. Effect of water vapor on the catalytic activity of red bauxite: a = sulfur dioxide, b = carbon dioxide

C) but did not return to the initial value (Section A) within 40 min. The addition of 15% water vapor (Section D) further decreased the sulfur dioxide removal efficiency. Curve *b* in Figure 2 depicts the analyses of carbon dioxide when the bauxite catalyst was subjected to the water treatment. The mirror image resemblance of curves *b* and *a* in Figure 2 suggests that the reaction stoichiometry is closely represented by Equation 1 and that the poisoning effect of water is essentially caused by its competition for chemisorption on the alumina Lewis acid sites with the sulfur precursor of the intermediate (9) reductant carbonyl sulfide.

The preceding test was repeated with 20 g of Jamaican red mud catalyst replacing the red bauxite at 420°C. The results in Figure 3 indicate that up to 20% water vapor slightly inhibited the sulfur dioxide conversion on this iron-rich catalyst. In absence of water, carbonyl sulfide was formed (curve *a*), but with water, hydrogen sulfide (curve *c*) was formed instead.

Thermodynamic equilibrium compositions were calculated by Okay and Short (5) for the sulfur dioxide reduction reactions in the reactor feed gases with and without water. Equilibrium was calculated by the technique of minimizing the free energy which uses a modified steepest

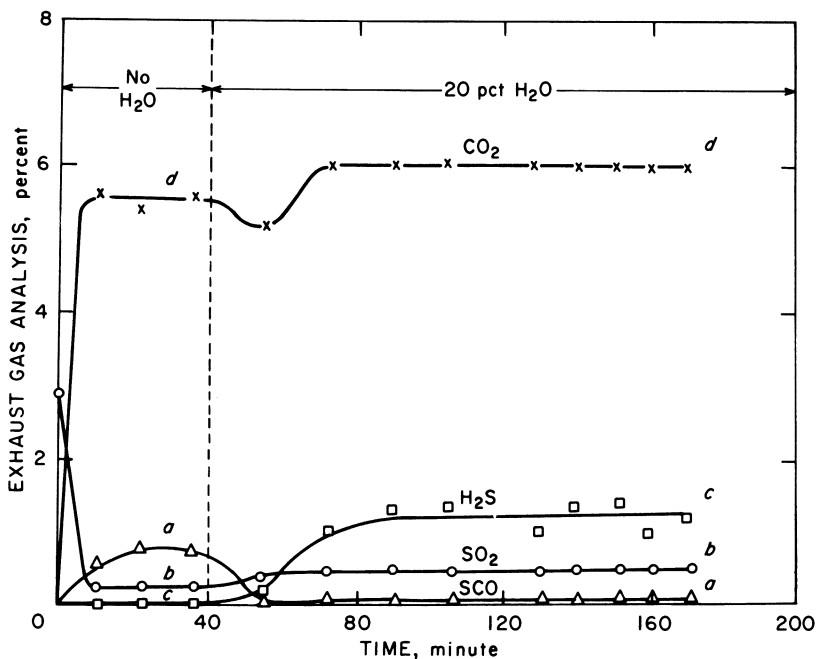


Figure 3. Effect of water vapor on the catalytic activity of Jamaican red mud: *a* = carbonyl sulfide, *b* = sulfur dioxide, *c* = hydrogen sulfide, *d* = carbon dioxide

descent search. They concluded that at a given temperature, higher carbon monoxide ratios are required in the presence of water to convert a certain percentage of the sulfur dioxide feed. They did not, however, detect hydrogen sulfide in their experiments. The thermodynamics of the system favor hydrogen sulfide production in the presence of water, whereas in the dry system carbonyl sulfide production is the only adverse reaction. Also, the water-gas-shift reaction is theoretically favored in the temperature range of 300–500°C, producing hydrogen sulfide.

A Fortran IV computer program developed by Redifer and Wilson (10) was used to predict thermodynamic equilibrium compositions for 400–700°K and 1 atm total pressure. The calculations are based on a procedure presented by Meissner, Kusik, and Dalzell (11) in which the set of simultaneous reactions is simplified to a set of series-consecutive reactions. Each reaction is carried out in turn on the reactant mixture as though a set of ideal batch equilibrium reactors were aligned in series in which the products from one equilibrium stage become reactants for the next reactor. After all the reactions have been completed, products from the last reactor are recycled to the first reactor, and the reaction sequence is repeated. Equilibrium of all components is complete when the product compositions at the end of two consecutive cycles are identical. The method compares favorably with the free energy minimization technique and is useful for changing conditions or input parameters.

Thermochemical data needed to calculate the equilibrium gas compositions were taken from the Janaf tables (12). The free energy equations for the sulfur vapor polymers—S₂, S₃, S₄, S₅, S₆, S₇, and S₈—were derived by Kellogg (13), based on second law correlations of their mass spectrometric data.

Figure 4 shows the variation with temperature of the equilibrium mole fractions for a few feed gas compositions. The curves in Sections A and B represent the equilibrium state for mixtures initially composed of 3.4% hydrogen sulfide and 5.9% carbon monoxide in the absence and presence of 15% water vapor, respectively. Helium made up the balance in each gas mixture. Species present at less than the micromolar fraction level were ignored. To conduct the same computer program on each gas mixture, an extremely low concentration of water vapor ($4.5 \times 10^{-5}\%$) was assumed in cases A and C of Figure 4. Sections C and D in this figure illustrate the effect of 7% water vapor for a sulfur dioxide-carbon monoxide mixture at the low concentration level. As expected, both hydrogen sulfide and hydrogen were present with the water vapor, and the concentrations of hydrogen sulfide and carbonyl sulfide increased with temperature up to 700°C.

The disparity between these results and those reported by Okay and Short (5) on a copper-alumina catalyst can best be explained in the

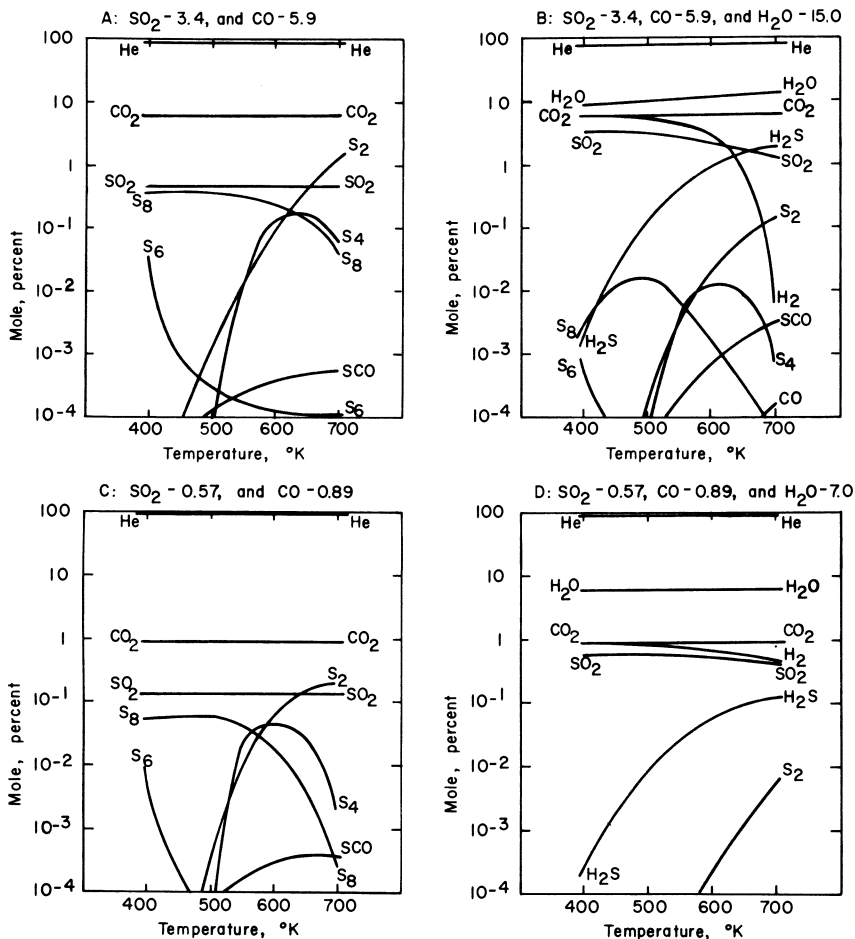


Figure 4. Effect of temperature on the equilibrium composition of sulfurous gas mixtures in the absence and presence of water vapor. The balance in each mixture was helium. Species present at less than 10^{-4} mole % were ignored.

light of the known (14) facts regarding the catalysis of the water-gas-shift reaction (Reaction 3) on iron and copper. In gases containing relatively large quantities of sulfur, iron sulfide is the best available catalyst for the water-gas-shift reaction (14). In general, iron oxide is a good commercial, high temperature shift catalyst. It is inexpensive, stable, and can withstand considerable quantities of impurities without being poisoned. However, relatively high temperatures, typically over 350°C , are required before the catalyst is sufficiently active for most commercial applications. Copper metal (14) is much more active than iron oxide and therefore has practical applications even below 200°C . Its high cost and

susceptibility to poisons are minor disadvantages, but they are outweighed by the high conversions that are obtained below 250°C. The copper low temperature-shift catalyst can be used only within a limited temperature range, above which activity is rapidly lost. These facts explain why Okay and Short (5) did not obtain hydrogen sulfide in the presence of water vapor on their copper–alumina catalyst between 450 and 500°C. They also indicate that hydrolytic decomposition of carbonyl sulfide according to Reaction 5 cannot play an important role. This agrees with a recent observation by Pearson (15) that the hydrolysis of carbonyl sulfide is inhibited by sulfur dioxide sorption on the catalyst surface.

Single-Bed, Nonisothermal Catalysts. In an attempt to circumvent the undesirable formation of hydrogen sulfide in the presence of water vapor, a nonisothermal reactor was constructed by placing 536 g of Jamaican red mud catalyst in a 2-cm diameter 96%–silica tube. The catalyst-filled tube was inserted into the bottom half of the furnace. This resulted in a 15-cm uniform temperature hot zone and a 25-cm zone with temperatures gradually decreasing to about 100°C at the lower reactor exit. The inlet gas consisted of 17% water vapor, 5.8% carbon monoxide, and 3.0% sulfur dioxide, and 74.2% helium. Figure 5 shows the dependence of the exhaust gas analysis on the hot-zone temperature of the Jamaican red mud catalyst. No sulfur dioxide was removed at hot-zone temperatures lower than 240°C. At 250°C, some sulfur dioxide was removed, and small quantities of hydrogen sulfide were formed. Above 300°C, more than 80% of the sulfur dioxide and virtually all of the carbon monoxide

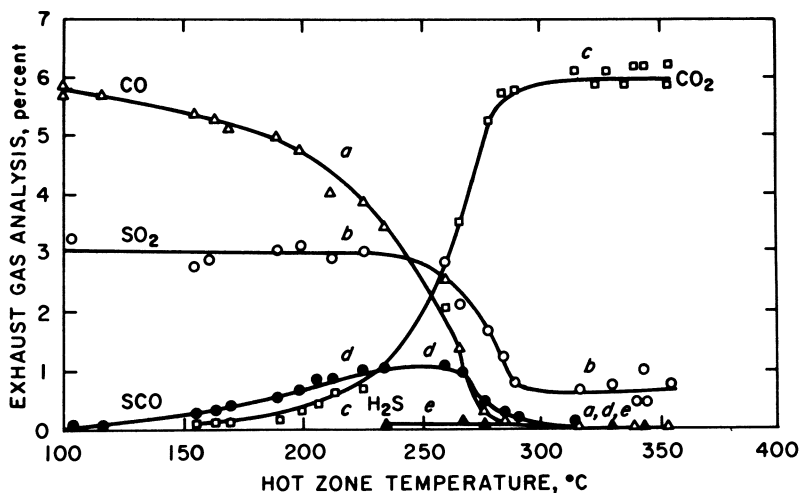


Figure 5. Effect of temperature of Jamaican red mud catalyst on exhaust gas analysis. Inlet gas: 3% sulfur dioxide, 5.8% carbon monoxide, and 17% water vapor in helium.

were removed, and no hydrogen sulfide or carbonyl sulfide was detected. The exhaust gas was mainly composed of carbon dioxide, water vapor, sulfur, and the unreacted sulfur dioxide which was the result of the slight insufficiency of carbon monoxide in the inlet gas. Reactions 1–6 probably occurred in the hot zone above 275°C, whereas Reaction 7 probably occurred down-stream from the hot zone. The hydrogen sulfide and sulfur dioxide concentrations (curves *b* and *e*, Figure 5) were considerably lower than those observed with an isothermal reactor at 420°C (Figure 3).

Double-Bed Catalysts. Because the temperature of the colder section in the nonisothermal catalyst bed could not be readily controlled, an apparatus was constructed that contained two separate furnaces, each containing 20 g of Surinam red mud. The temperature of the first bed was varied to determine the optimum operating conditions with an inlet gas of 0.57% sulfur dioxide, 0.89% carbon monoxide, and 3% water vapor in helium. The exhaust gas analyses from the first furnace are shown in Figure 6. These results indicate that the hydrogen sulfide and sulfur dioxide removal efficiency increases with temperature up to about 400°C. Beyond this temperature there is little improvement.

The optimum temperature of the second catalyst bed was determined with the first catalyst bed operating at 430°C but with 7% rather than 3% water vapor. The effect of the second reactor temperature on the sulfurous content of the final exhaust gases is shown in Figure 7, curves *a* and *b*. The results indicate that this second catalyst is more

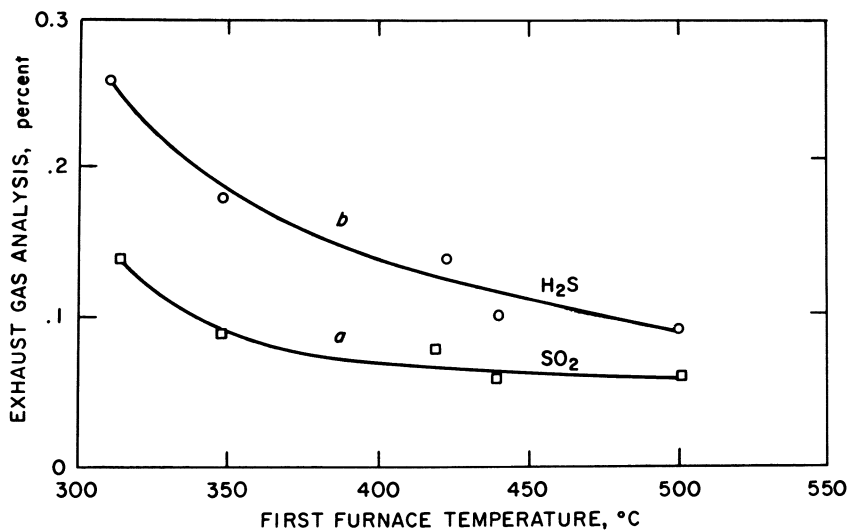


Figure 6. Effect of first furnace temperature on the exit gas composition. Inlet gas: 0.57% sulfur dioxide, 0.89% carbon monoxide, and 3% water vapor in helium.

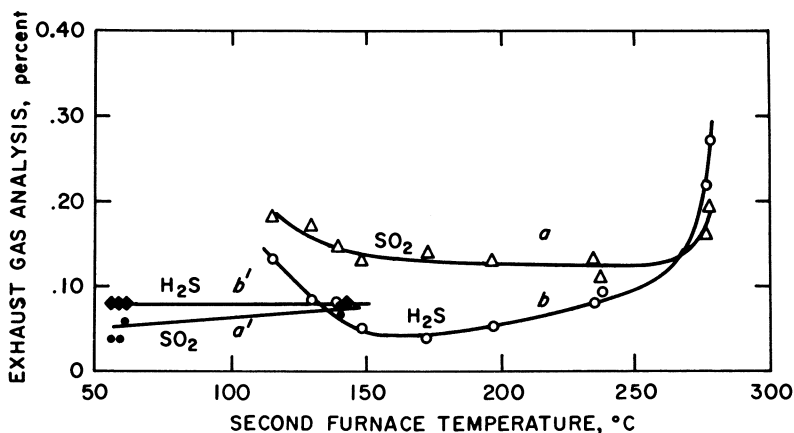


Figure 7. Effect of second catalyst temperature on the exit gas composition. *a, b* = Surinan red mud catalyst. Inlet gas to first catalyst: 0.57% sulfur dioxide, 0.89% carbon monoxide, and 7% water vapor in helium. *a', b'* = Berbece bauxite in second catalyst. Inlet gas to first catalyst: 0.44% sulfur dioxide, 0.80% carbon monoxide, and 20% water vapor in helium.

efficient between 150 and 250°C. Except for elemental sulfur, carbon dioxide, and water vapor, the final exhaust gas in this temperature range showed a flat minimum at 0.13% sulfur dioxide and 0.04% hydrogen sulfide. This corresponds to 70% conversion of sulfur dioxide (at $r = 0.86$) to elemental sulfur. With a single-bed catalyst at 430°C, Figure 6 predicts an exit gas containing 0.13% hydrogen sulfide and 0.08% sulfur dioxide in the presence of 3% water vapor. This corresponds to the removal of 63% of the sulfurous gases, *i.e.*, a decrease of 7 percentage points (or 10% on a relative basis) from the removal efficiency with a double-bed catalyst. The decrease in efficiency would probably have been greater if the single-catalyst bed tests (Figure 6) had been conducted in the presence of 7% water vapor.

Experience in catalysis (16) of the Claus Reaction 7 indicates that the activity of pure alumina is somewhat decreased by the presence of transition metals. Hence, an alumina catalyst with lower iron content should be more efficient than one with a high iron content. When the second catalyst (Surinam red mud containing 15.7% iron) in the preceding experiment was replaced with Berbece bauxite (1.1% iron) with the other experimental conditions remaining constant, the sulfur dioxide and hydrogen sulfide exhaust analyses in the range of 140–57°C were considerably lowered. This is illustrated by curves *a'* and *b'* of Figure 7. The inlet gas to the first catalyst in this test consisted of 0.44% sulfur dioxide, 0.80% carbon monoxide, and 20% water vapor in helium. In this low temperature range, Surinam red mud was not active enough to

drive the Claus reaction. Above 140°C, the difference between the red mud and bauxite catalyst activities decreases.

The effect of the second-catalyst temperature on the conversion efficiency of sulfur dioxide to elemental sulfur is shown in Figure 8.

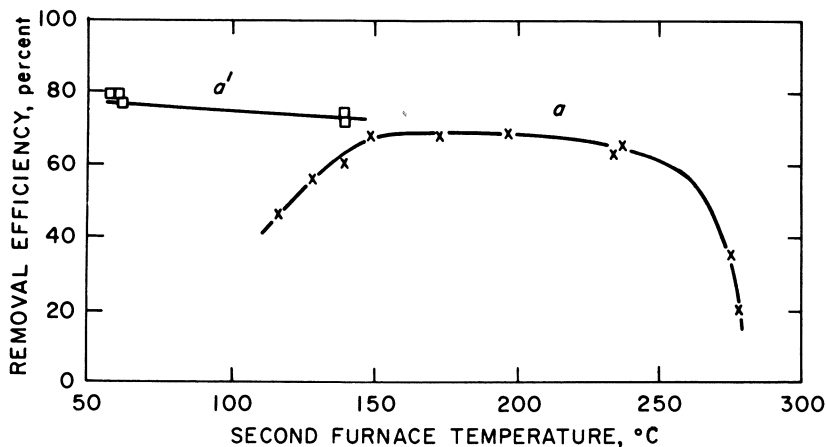


Figure 8. Effect of second catalyst temperature on the removal efficiency of sulfurous gases. *a* = Surinam red mud on second catalyst. Inlet gas to first catalyst: 0.57% sulfur dioxide, 0.89% carbon monoxide, and 7% water vapor in helium. *a'* = Berbece bauxite in second catalyst. Inlet gas to first catalyst: 0.44% sulfur dioxide, 0.80% carbon monoxide, and 20% water vapor in helium.

Curve *a* represents the data with Surinam red mud in the second catalyst and illustrates a decline in sulfur production efficiency with the second-catalyst temperature either above 250° or below 150°C.

Using Berbece bauxite at 58°C in the second bed, up to 79% (at $r = 0.91$) of the sulfurous gases were removed (curve *a'*, Figure 8). This is an improvement of more than 16 percentage points (or 25% on a relative basis) over the removal efficiency with a single Surinam red mud bed at 430°C (Figure 6). Unfortunately, the high efficiencies of the bauxite second bed below 120°C (melting point of sulfur) are of no practical value because the accumulation of solid sulfur at these temperatures would plug the reactor and necessitate frequent catalyst regenerations.

Additional tests with 20 g of Surinam red mud in the double-bed catalyst were conducted with sulfur dioxide-rich gases, simulating a smelter gas. The temperature of the first reactor was 475°C and that of the second was 230°C. The inlet gas into the first catalyst bed contained 3.15% sulfur dioxide, 5.97% carbon monoxide, and 3% water vapor in helium. After several hours, the exhaust gas analyses from the sec-

ond reactor indicated 0.13% sulfur dioxide and 0.26% hydrogen sulfide. With this dual-catalyst bed arrangement, 88% of the sulfur dioxide was converted to elemental sulfur. The results indicate that the second low-temperature catalyst offset the deleterious effect of water vapor on the catalytic reduction of sulfur dioxide.

Summary and Recommendations

Water vapor decreases the efficiency of catalytic reduction of sulfur dioxide with carbon monoxide. A two-stage catalytic reduction method was designed to solve this problem. The optimum temperature of the first reactor was about 430°C, whereas the second reactor (Claus) was most efficient below 250°C. However, the improved thermodynamic efficiency at lower temperatures is hampered by other mechanical considerations.

In practice, the Claus reactor should be operated above 120°C to avoid mechanical problems resulting from solid sulfur plugging the catalyst. Also, the viscosity of liquid sulfur exhibits a sharp peak at 190°C and exceeds 300 centipoise between 170 and 230°C. Therefore, unless the temperature of the second catalyst is carefully controlled between 120 and 170°C, it should be operated above 230°C, and preferably 250°C, to avoid catastrophic plugging of the catalyst. It may also be desirable to condense the sulfur produced from the first bed before entrance into the second bed and to cascade the second bed into different stages with intermittent sulfur collection devices between successive stages.

Acknowledgment

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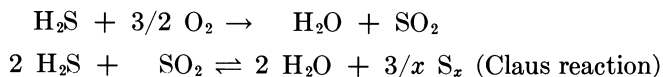
Effect of Basicity of the Catalyst on Claus Reaction

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The catalytic activities of acids and bases for Claus reaction were investigated by supporting these on Chromosorb-A (a relatively inactive gas chromatographic solid support) and other materials and obtaining the relative activities of these compounds for Claus reaction based on initial rates at 240°C. The experiments were carried out in a fixed-bed integral flow reactor using low partial pressures of reactants. Acidity did not enhance catalytic activity but the deposition of bases (1–8 wt %) induced a dramatic increase in the catalytic activity for Claus reaction. Attempts were made to measure the basicities of these catalysts and relate these to the observed catalytic activity for Claus reaction.

In 1972 Alberta produced 8×10^6 long-tons of elemental sulfur by sweetening sour gas (1), *i.e.*, a natural gas containing an appreciable amount of hydrogen sulfide. Hydrogen sulfide and other sulfur compounds are converted to sulfur by the well known modified Claus process using alumina-based catalysts. The basic chemical reactions are:



Bauxite catalysts (or alumina) are generally used in the Claus catalytic converters because of their high activity, durability, and low cost. Maximum equilibrium conversions are obtained at the lowest operating temperatures in the Claus catalytic converters. Theoretically, at this reactor temperature ($\sim 230^\circ\text{C}$), 99% equilibrium conversion is possible. However, because the Claus reaction is a complex equilibrium reaction, the temperature cannot be lowered too much as sulfur will condense on the

catalyst, and regeneration of the alumina-based catalyst poses serious problems because of sulfation—formation of aluminum sulfate, which is not a catalyst for Claus reaction. Further, at the lower temperature the conversion rates are low. On the other hand, carbonyl sulfide and carbon disulfide, which are produced during the high temperature oxidation of sour gas in the Claus furnace, only react with sulfur dioxide in the Claus reactor at fairly high temperatures. Consequently a compromise must be made on the operating temperature, and as a result, most of the Claus sulfur plants in Alberta operate at 95–97% efficiency, using three-stage catalytic converters with intervening sulfur removal. The unreacted sulfur compounds in the tail gas—carbon disulfide, hydrogen sulfide, sulfur dioxide, and carbonyl sulfide—are converted to sulfur dioxide by incineration and vented from stacks. Because of the stringent antipollution regulations which require reduced sulfur dioxide emissions and because of the high cost of equipment for tail gas cleanup, it is increasingly important to achieve maximum conversions in the Claus catalytic reactors.

During our investigation into the kinetics of Claus and related reactions (2), we became interested in determining those properties necessary for a good Claus catalyst. In exploratory studies of the effectiveness of acids, bases, sulfides, oxides, and salts as catalysts for the Claus reaction the basic oxides enhanced Claus activity the most. We continued to study the effect of catalyst basicity on Claus reaction, and the results are summarized in this report.

Experimental Procedures and Results

The reactants, hydrogen sulfide and sulfur dioxide, were diluted with helium, and then were passed over the catalyst which was contained in a $\frac{3}{8}$ in.-i.d. 316 stainless steel tube by a 100-mesh stainless steel screen. As shown in Figure 1, provision was made for analysis of reactant and product streams, for preheating the reactants before contacting the catalyst, and for condensing the product sulfur. Since the details of these operations are given in a previous publication (2), only brief descriptions will be provided here. The preheater was $5 \times \frac{3}{8}$ in. i.d. packed with stainless steel shavings and gave adequate preheating up to 60 ml helium/sec. The preheater and the reactor were heated by the same furnace which could easily be replaced by a Dewar cylinder of liquid nitrogen to permit measurement of nitrogen adsorption by the usual dynamic method (3), using a relative pressure $p/p_0 = 0.06$.

The sulfur condenser was a 16×1 in. i.d.-stainless steel tube and had baffles every inch to facilitate the critical sulfur condensation. With an unheated condenser, sulfur condensed at the condenser exit and into

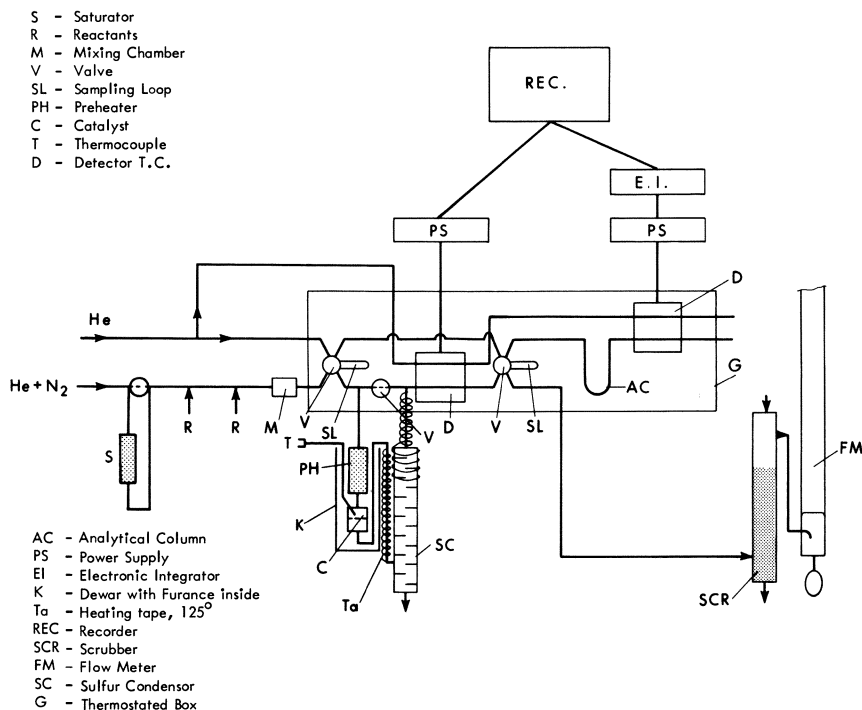


Figure 1. Diagram of flow reactor

the sampling section resulting in unreliable conversions. No attempt was made to keep the sulfur above the melting point in the condenser as this has been reported (4) to catalyze the Claus reaction. After extended experimentation we found that if the connecting tube from the reactor outlet and part of the condenser exit section were kept about 150°C (the temperature in the unheated section of the condenser was around 60°C), sulfur condensed satisfactorily. Periodically the condenser and other parts of the system had to be heated to remove the sulfur.

Nitrogen was introduced with the reactants as a marker. The analyses of the feed and product streams, carried out when the catalyst was bypassed, showed that no other part of the system was catalyzing the reaction, even when there was appreciable condensed sulfur in the condenser. The total pressure of the system was measured by a pressure transducer (Whittaker, model DM1) located ahead of the reactor.

As shown in Figure 1, there are two thermal conductivity detectors with Teflon-coated filaments and thermostated at 125°C. One is located immediately after the catalyst and measures retention volume and surface area. The second detector is located after the analytical column and analyzes feed and product samples. This detector output at maximum

sensitivity was fed to a Hewlett-Packard electronic integrator (No. 3370A) as well as to a conventional strip-chart recorder. The detector-integrator system was calibrated by injecting 2.0 ml samples of pure reactants at different pressures (measured by a digital manometer) ahead of the analytical column.

The apparatus was provided with 5.0 ml-sampling loops that both feed and product streams could be monitored. By operating a seven-port sampling valve, the separate gas chromatographic helium stream would sweep the contents of the sampling loop onto the analytical column of 8 ft \times $\frac{1}{8}$ in. Poropak Q followed by 2 ft Poropak T, maintained at 125°C. It provided good separations of nitrogen, hydrogen sulfide, water, and sulfur dioxide in about 5 min (Figure 2). After prolonged use the analytical column turned yellow although at 125°C, sulfur condensation is very unlikely. However, separate experiments showed that this did not interfere with the analysis efficiency. Adsorption measurements using frontal chromatography were studied in another apparatus, as described previously (2).

Materials. The chromatographic firebrick (Chromosorb-A) was manufactured by Johns-Manville. The material as received was slightly alkaline and had a measured surface area of 2.0 m²/g. It was washed, dried, and sieved to 20/30 mesh before use.

The cobalt-molybdate on gamma-alumina catalyst (Girdler G-35) was manufactured and kindly supplied by Chemetron Corp., Louisville, Ky. It was reported to have 3.5% CoO and 10.0% MoO₃. The catalyst, in $\frac{1}{8} \times \frac{1}{8}$ in. tablets, was crushed and sieved to 20/30 mesh granules for

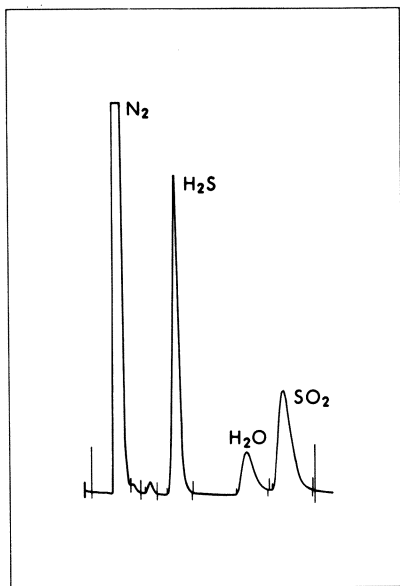


Figure 2. Chromatographic separation of N₂, H₂S, H₂O, and SO₂. Analytical column: 8 ft \times $\frac{1}{8}$ in. Poropak Q (50–80 mesh) followed by 2 ft \times $\frac{1}{8}$ in. Poropak T (50–80 mesh) operated at 125°C. Thermal conductivity detector: Teflon coated, 250 ma, thermostated at 125°C. He flow rate: 1.34 ml/sec.

kinetic studies. It had a measured surface area of 180 m²/g, using the one-point isotherm, compared with 192 m²/g by the BET method.

The porous alumina catalyst was supplied by B. I. Parsons, Department of Energy, Mines and Resources, Ottawa, Canada. It had a measured surface area of 220 m²/g (one-point isotherm), and a slurry of the material in distilled water had a pH of 10.0. The pore size varied between 1000 and 400Å, and the pore volume was 1.9 ml/g (5). The active alumina was manufactured by the Aluminum Co. of America, Portland, Ore.

Porasil (spherical porous silica beads) is a solid support manufactured for Waters Associates, Mass., by Pechiney-St. Gobain, France. The Porasil-F used in this study had a reported surface area of 4 m²/g and an average pore diameter greater than 1500Å. This material was slightly basic.

Bauxite (Poracel) is a commercial sulfur recovery catalyst manufactured and supplied by Philip Corp., Menlo Park, N.J. It was 90% Al₂O₃ with about 5% Fe₂O₃ and smaller amounts of TiO₂ and SiO₂ and had a reported surface area of 215 m²/g. However, a measured surface area of 142 m²/g was determined using the one-point isotherm. The catalyst samples used in this study were generally 20/30 mesh granules and were activated in flowing helium at the reaction temperature for 3 hr.

Reactants. H₂S and SO₂ were supplied by Matheson and had a purity of more than 99 mole %. Traces of CO₂ were present in both gases.

Pretreatment of Catalysts. **ACIDITY.** Dilute acids—hydrochloric, sulfuric, and phosphoric acids—were deposited by soaking Chromosorb-A in the dilute acid solution and decanting and drying the granules at 100°C. For the acid-loaded Chromosorb-A, no activity increase for Claus reaction was detected. The acid-loaded Chromosorb-A (~2%) at the end of the reaction was still acidic; a slurry of the catalyst in distilled water had a pH about 5.

BASICITY. Bases—sodium, potassium, and lithium hydroxides—were deposited by soaking the catalyst in the appropriate aqueous solution and drying the catalyst granules at 100°C. The exact loading was determined by leaching the adsorbate with hot distilled water for 72 hr at 70°C and titrating with 0.02*N* hydrochloric acid to pH 7. At base loadings up to 7%, the base could be leached from the catalyst, and the approximate original activity was restored. With higher base loadings (15–20%) the base reacted with the Chromosorb-A (new solid phases) and also decreased the surface area of alumina catalysts. However, these materials were not used in this study.

The effect of basicity on the following catalysts for Claus reaction was investigated: Chromosorb-A; cobalt–molybdate; activated alumina; bauxite; and Porasil. The base loadings were 1–6 wt %.

Rate Studies. Reaction rates, based on the disappearance of hydrogen sulfide, were determined only after steady-state conditions were established. This was indicated when successive analyses were within 0.5%, usually about 10 min from start-up. Several flow rates were used, with

conversions of 5–30% with an uncertainty of $\pm 2\%$. The initial rate was obtained by fitting the experimental data to the expression

$$x = C \tanh[D(W/F)]$$

where x is the fractional conversion of hydrogen sulfide, W/F in g, sec/mmole hydrogen sulfide, and C and D are constants.

The derivative of the above function with respect to W/F is:

$$\frac{dx}{d(W/F)} = (C)(D)(\text{Sech}^2[D(W/F)])$$

At $W/F = 0$, which is equal to the initial rate (r_o), the above derivative reduces to CD . The best values of C and D were obtained by a gradient search using a digital PDP-9 computer. Mezaki and Kittrell (6) have demonstrated that this expression is a convenient and relatively nondiscriminating way to extrapolate to zero conversion. The range of partial pressures (torr) of reactants used were hydrogen sulfide, 4–22, and sulfur dioxide, 2–22.

The initial rate $\left(\frac{\text{mmole of H}_2\text{S reacted}}{\text{sec} \cdot \text{g}}\right)$ was fitted to the expression

$$r_o = kp^a\text{H}_2\text{S} p^b\text{SO}_2.$$

For Chromosorb-A, kinetic measurements were made at three temperatures—434, 400, and 358°C—and for varying partial pressures of hydrogen sulfide and sulfur dioxide. An example of the data at a given temperature is given in Table I. Two levels of sodium hydroxide load-

Table I. Kinetic Data for Claus Reaction over Chromosorb-A at $434 \pm 2^\circ\text{C}^a$

$p_{\text{H}_2\text{S}}$ (torr)	p_{SO_2} (torr)	Fr. Conv. H_2S	W/F (g, sec/mmole H_2S)	r_o^b (computed)
4.00	2.00	0.105	46.0	0.0024
4.00	2.00	0.167	71.2	
4.00	2.00	0.184	85.0	
4.00	2.00	0.285	155.0	
22.03	2.02	0.066	8.0	0.0088
22.31	2.03	0.096	12.5	
22.52	2.04	0.138	24.0	
4.02	20.52	0.161	55.0	0.0029
4.04	20.51	0.257	97.5	
4.05	20.53	0.390	180.0	

^a H_2S order one and SO_2 order zero. At 390°C, the kinetic orders in H_2S and SO_2 (over Chromosorb-A) were one and zero, respectively. The accuracy of the kinetic orders is $\pm 10\%$.

^b mmoles H_2S reacted/sec.g.

Table II. Kinetic Data for Claus Reaction over Chromosorb-A Loaded with 5% Sodium Hydroxide at $242 \pm 2^\circ\text{C}^a$

$p_{\text{H}_2\text{S}}$	p_{SO_2}	x	W/F	r_o (computed)
4.00	2.00	0.166	47.8	
4.00	2.00	0.110	31.6	0.0039
4.00	2.00	0.240	11.0	
12.23	2.01	0.071	8.6	
12.21	2.03	0.168	32.4	0.0082
12.23	2.01	0.105	15.0	
4.04	10.15	0.185	33.9	
3.95	10.12	0.294	64.3	0.0054
4.01	10.22	0.410	106.3	

^a H_2S order, 0.7; SO_2 , 0.2.

ings—3.9 and 5.0% on Chromosorb-A—were studied. Measurements were made at five temperatures between 209 and 344°C for the 3.9% sodium hydroxide loading and at three temperatures between 200 and 290°C for the 5.0% loading. Table II gives the measurements at 242°C . The rate constants k (mmoles hydrogen sulfide reacted/sec, g, torr) determined for each set of measurements are summarized in Figure 3 as an Arrhenius plot.

Reaction Orders and Activation Energies. From the variation in initial rate with the partial pressure of reactants it was observed that the kinetic order with respect to sulfur dioxide was zero and that with respect

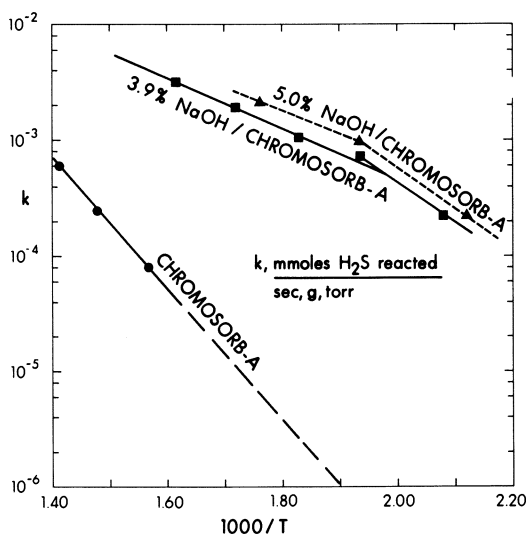


Figure 3. Arrhenius plot for Chromosorb-A with and without NaOH. 4.0 torr H_2S , 2.0 torr SO_2 . k , mmoles H_2S reacted/sec, g torr.

to hydrogen sulfide it was one for Claus reaction over the Chromosorb-A (Table I). However, on the 5.0% sodium hydroxide-loaded Chromosorb-A the kinetic orders with respect to hydrogen sulfide and sulfur dioxide were 0.7 and 0.2, respectively (Table II).

From the temperature coefficient of the rate constant, the activation energy for the Claus reaction over the Chromosorb-A was determined to be 25.0 kcal/mole and for the sodium hydroxide-loaded Chromosorb-A it was about 15 kcal/mole. The apparent change in the slope of the Arrhenius plot might indicate some transition in the controlling mechanism. Over the cobalt-molybdena catalyst, the Claus reaction appeared to be diffusion-controlled with an activation energy of 5.5 kcal/mole (2).

Reversibility of Sodium Hydroxide Loading. The analytical method for determining the degree of base loading assumes that the base is totally extractable when the impregnated and activated catalyst is leached with hot water. An experiment was performed on the extracted catalyst to check its activity. At 300°C, and a W/F of 260, the fractional conversion of hydrogen sulfide was 0.208 as compared with the expected 0.200, demonstrating almost complete reversibility of sodium hydroxide loading. However, after the catalyst had been used for 6 hr, the amount of extractable base decreased by about 40%.

Degree of Sodium Hydroxide Loading vs. Claus Reactivity. Samples of Chromosorb-A with loadings of 0.5, 1.0, 3.9, 7.2, and 10.5 wt % sodium hydroxide were prepared. The Claus reaction was carried out at $309 \pm 2^\circ\text{C}$, using 4.0 torr hydrogen sulfide and 2.0 torr sulfur dioxide and a W/F of 29–31. Any variation in the partial pressure of reactants on the observed conversion was adjusted on the basis that the kinetic orders with respect to hydrogen sulfide and sulfur dioxide were one and zero, respectively. The results are reported as rates against sodium hydroxide loading in Figure 4. As the sodium hydroxide loading was increased, the rate went through a maximum. The rate decline at higher sodium hydroxide loadings could be caused by the decreased surface area. The one-point isotherm method used to measure the surface area was not sensitive

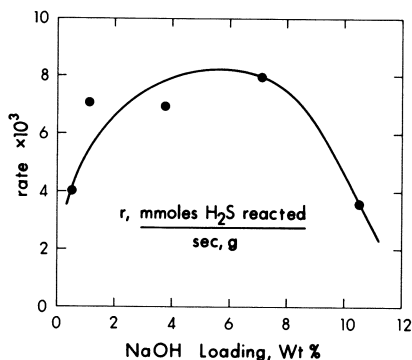


Figure 4. Effect of NaOH loading on Chromosorb-A vs. Claus reaction rate. 309°C, W/F 29–31. 4.0 torr H_2S , 2.0 torr SO_2 . Rate, mmoles H_2S reacted/sec, g.

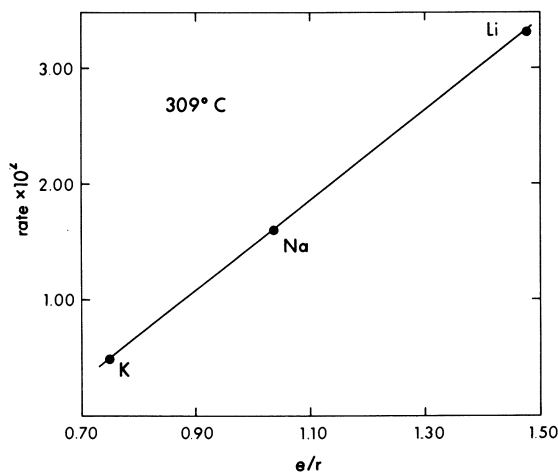


Figure 5. Polarizing power of Na^+ , Li^+ , and K^+ on Claus reaction. 4.0 torr H_2S , 2.0 torr SO_2 , 309°C. Constant He flow rate of 1.44 mmole/sec.

enough to detect such a surface area loss of Chromosorb-A (2 m²/g). On cobalt–molybdate, as the sodium hydroxide loading was increased, losses in catalytic activity and surface area were noted.

Effect of the Cation (of Group 1A). Samples of Chromosorb-A were prepared containing 1.8, 3.3, and 1.2% sodium, potassium, and lithium hydroxides, respectively. The catalysts were activated and experiments carried out at a constant helium flow rate of 1.44 mmole/sec. The results are summarized in Figure 5 where the rate/mmole base is plotted against e/r , which is the polarizing power of the cation. The results indicate a strong correlation between catalyst activity and the polarizing power of the cation.

Comparison of the Effect of Sodium Hydroxide on Different Catalysts for Claus Reaction. Table III compares a number of industrially important Claus catalysts and Chromosorb-A. The effect of sodium hydroxide loading (3.9%) on Chromosorb-A is also indicated. In Table IV the effect of sodium hydroxide on these catalysts is presented. It is evident that the sodium hydroxide-loaded Chromosorb-A is 15–30 times more active per unit surface area than commercial catalysts and that the effect of sodium hydroxide on the alumina-based catalysts is not very significant, compared with Chromosorb-A.

CHROMOSORB-A. Figure 3 shows that at about 240°C the rate constant for the sodium hydroxide-loaded Chromosorb-A (3.9%) is about 10³ times higher than the original sample.

COBALT–MOLYBDATE ON γ -ALUMINA. A sample of cobalt–molybdate was prepared containing 3.9% sodium hydroxide. At 309 ± 2°C, the ini-

Table III. Comparison of Different Catalysts for Claus Reaction at $240 \pm 2^\circ\text{C}$ ^a

<i>Catalyst</i>	<i>Surface Area</i> (m ² /g)	<i>Initial Rate</i> $\times 10^3$ (g)	<i>Relative Initial Rate</i> (g)	<i>Relative Initial Rate</i> (m ²)
Activated alumina ^b	140	5.2	2,100	30
Bauxite ^b	140	5.6	2,300	30
Porous alumina	180	40.0	16,000	150
Cobalt-molybdate on γ -alumina	220	14.4	6,000	60
Porasil	4	1.5	600	300
Chromosorb-A	2	0.0024 (extra- polated)	1	1
Chromosorb-A with 3.9% NaOH	2	4.0	1,000	1,000

^a 4.0 torr H₂S and 2.0 torr SO₂.

^b Initial rate adjusted to 240°C using an activation energy of 7.5 kcal/mole (21).

tial rate for this catalyst was 30% higher than the original sample (Figure 6).

BAUXITE. At 292°C the initial rate was 0.0166. With 2.2% sodium hydroxide loading the initial rate was 0.020, an increase of about 20%. More than 90% of the base could be leached out, and the surface area was unchanged. At 5% sodium hydroxide loading, there was considerable activity loss for the Claus reaction and a decrease in surface area to 70 m²/g.

ACTIVATED ALUMINA. At 295°C, the initial rate for this sample was 1.72×10^{-2} . At 2.8% sodium hydroxide loading, the initial rate was 2.32×10^{-2} , about 30% increase.

PORASIL. At 240°C, for the Porasil sample containing 2.1% sodium hydroxide, the initial rate had increased by a factor of two (Table IV).

Determination of Catalyst Basicity. Catalyst basicity was determined by making a suspension of about 0.50 g of the catalyst in 25.0 ml

Table IV. Effect of Base (Sodium Hydroxide)

<i>Catalyst</i>	<i>Surface Area</i> (m ² /g)	<i>Reaction Temp.</i> (°C)	<i>Initial Rate, mmoles H₂S Reacted</i> /sec, g (extrapolated)
Chromosorb-A	2	240	2.40×10^{-6}
Cobalt-molybdate on γ -alumina	220	309	1.91×10^{-2}
Bauxite	140	292	1.66×10^{-2}
Porasil (silica beads)	4	242	1.52×10^{-3}
Activated alumina	140	295	1.72×10^{-2}

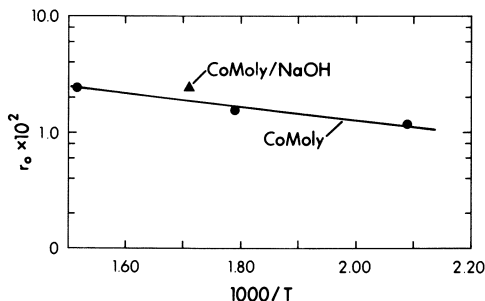


Figure 6. Effect of 3.9% NaOH on cobalt-molybdate on Claus reaction. Initial rate, 4.0 torr H_2S , 2.0 torr SO_2 . ● = cobalt-molybdate catalyst; ▲ = cobalt-molybdate catalyst with 3.9% NaOH.

benzene and adding 1.0 ml indicator solution, 0.128 g bromothymol blue in 100.0 ml benzene. If the catalyst possessed basic sites, the yellow dye reacted with the base by electron transfer to yield the green color of the conjugate base. The suspension was then titrated against 0.01*N* benzoic acid in benzene until the green color of the granules disappeared. The details of the method are given in the paper by Tanabe and Yamaguchi (7). Catalyst basicities are given in Table V as mmole/g. For the 250°C-activated catalysts the green color developed quickly with porous alumina and Chromosorb-A containing base. With bauxite, the color development was very slow. Sometimes the color was bluish-green.

Samples of porous alumina, activated alumina, bauxite, and Chromosorb-A with 3.9% sodium hydroxide were all heated in dry helium to 500°C for 3 hr, and the basic sites were determined on aliquots. Only Chromosorb-A with 3.9% sodium hydroxide on it showed any basicity (0.27 mmole/g). All of the samples were then exposed to water vapor at room temperature (24 torr) for 1 hr, and the titration was repeated. Interestingly, all samples except Chromosorb-A showed basicity. Prob-

on Catalysts for Claus Reaction

NaOH Loading (wt %)	Initial Rate for Base-loaded Catalyst	Relative Increase in Initial Rate
3.9	2.39×10^{-3}	1000
3.9	2.53×10^{-2}	0.31
2.2	2.05×10^{-2}	0.24
2.1	4.51×10^{-3}	2.0
2.8	2.32×10^{-2}	0.35

ably for the alumina-based samples, basic sites are produced when water is added. It is not clear why the Chromosorb-A with sodium hydroxide on it failed to respond to the basicity test until it was activated.

Basicities determined by the benzoic acid titration (Table V) did not appear to be quantitative as the green color reappeared periodically

Table V. Determination of Basicity (mmole/g) by Benzoic Acid Titration

Catalyst	Basicity Following Activation by:		
	250°C in Flowing He for 3 hrs	500°C in Flowing He for 3 hrs	500°C in Flowing He Followed by Exposure to Water Vapor (24 torr) at Room Temp. for 1 hr
Activated alumina	^a	^a	0.57 ^b
Porous alumina	0.14	^a	0.64
Bauxite	0.02	^a	0.12
Chromosorb with 3.9% NaOH	0.06	0.27	^a

^a Did not turn green.

^b The green color reappeared after 15 min.

on standing, and with Chromosorb-A containing sodium hydroxide, the end point was not always sharp. This method could not be used with cobalt-molybdate because of the intense blue color of the granules. Chromosorb-A containing 1.0 mmole sodium hydroxide/g appeared to have only 0.27 mmole/g basic sites as determined by benzoic acid titration. However, for porous alumina containing 0.7 mmole sodium hydroxide/g, a value of 0.64 mmole/g was determined by benzoic acid method. The low value reported for Chromosorb-A may be associated with the difficulty of determining the end point. The variation in initial rates on porous alumina, bauxite, and Chromosorb-A with 3.9% sodium hydroxide is compared to the basicity change of the catalyst in Table VI.

Adsorption of Sulfur Dioxide and Hydrogen Sulfide on Chromosorb-A. The frontal chromatography apparatus was similar to that used previously (2). On the Chromosorb-A, 4 torr hydrogen sulfide adsorption at 250°C amounted to 0.020 mmole/g, corresponding to a surface coverage of about 6%. The gas chromatographic breakthrough was not sharp. The hydrogen sulfide adsorption on Chromosorb-A containing 3.9% sodium hydroxide was 0.093 mmole/g, a four-fold increase (28% coverage). On both catalysts the irreversible adsorption of hydrogen sulfide was about 20% of the totals given above.

The sulfur dioxide adsorption on the other hand showed sharp breakthrough for both catalysts. For the 3.9% sodium hydroxide on Chromo-

sorb-A, 2 torr sulfur dioxide adsorption at 250°C was equivalent to 0.020 mmole/g, corresponding to about 6% coverage based on total surface. This was almost twice (0.012 mmole/g) the value for Chromosorb-A. The irreversible adsorption of sulfur dioxide was about 20% in both cases.

Discussion

The significant observations from this study are:

1. Acidity of the catalyst did not affect the rate of Claus reaction over Chromosorb-A.

2. Addition of small amounts of base to a very inactive catalyst (Chromosorb-A) increased its activity to the same order of magnitude as commercial catalysts while base addition to the latter catalysts had little effect.

3. The activation energy for Claus reaction over the 3.9, or 5.0% sodium hydroxide-loaded Chromosorb-A was about 15 kcal/mole.

4. The activity of the base-loaded Chromosorb-A for Claus reaction was $K^+ < Na^+ < Li^+$.

A facile explanation of the failure of acidity to enhance activity of any of the catalysts while base enhances the activity of a poor catalyst without affecting the active ones is that the Claus active catalysts owe their activity to basic sites. In general, alumina shows strong surface acidity when activated at 450°C in vacuum, and intensive investigation has shown this to happen in Lewis acid sites (8). There is also evidence that basic sites occur on alumina. Schwab and Kral (9) obtained evidence for basic sites by boron trifluoride adsorption on alumina, and Yamadaya *et al.* (10) reported up to 0.4 mmole/g of basic sites on alumina from benzoic acid titrations. Pines and Manassen (11) obtained indirect evidence of such sites from studies of the dehydration of primary alcohols.

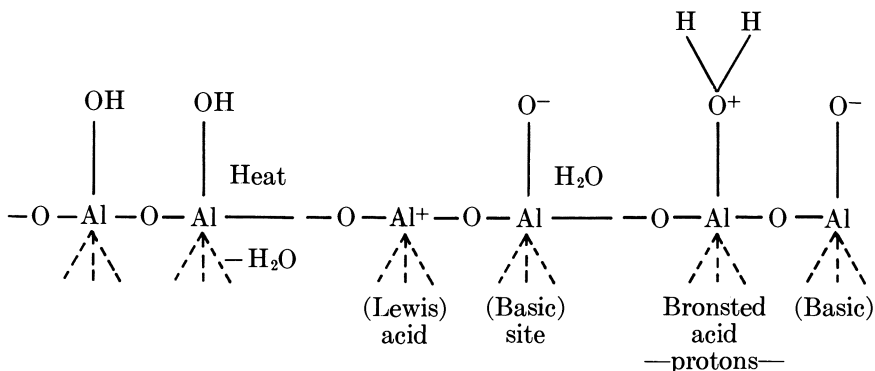
Table VI. Comparison of Catalyst Basicity and Catalytic Activity for Claus Reaction

<i>Catalyst</i>	<i>Basicity^a</i> (mmole/m ²)	<i>Relative</i> <i>Basicity</i>	<i>r_o/m²,</i> <i>240°C</i> (× 10 ³)	<i>Relative</i> <i>Initial</i> <i>Rate</i>
Porous alumina	0.0007	7	0.22	5
Bauxite	0.0001	1	0.04	1
Chromosorb-A 3.9% NaOH	0.030	300	2.0	50

^a 250°C activation.

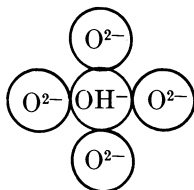
The review of active alumina by Lippens and Steggerda (12) and the monograph by Tanabe (13) may be consulted for further details. It appears reasonable therefore to conclude that Claus reaction is catalyzed by basic sites on the catalysts.

The nature of acidic and basic sites on alumina can be represented as follows (14):



The Lewis acid is a positively charged aluminum ion, and the basic site is a negatively charged oxygen ion, O^{2-} .

Peri (15, 16) has proposed a structure for the surface of alumina heated to 800°C in which five different types of OH^- were identified by IR spectra, and each site has a different local charge density. Type A with four O^{2-} ions as neighbors was the most basic, and the OH^- isolated from O^{2-} neighbors was the most acidic.



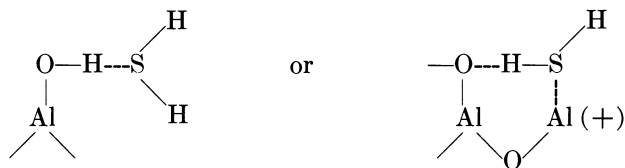
Peri (17) in his report on the ammonia adsorption on alumina suggested that the reaction



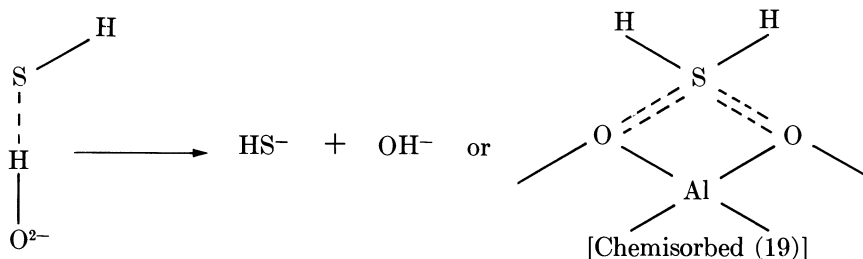
occurred on the O^{2-} basic site.

It is evident therefore that on alumina different kinds of catalytically active sites are present depending upon the preparation and pretreatment. On a partially dehydrated alumina, the surface contains O^{2-} ions, and Al^{3+} (Lewis acid) ions are present in the plane immediately below the 100 plane. It is suggested that these O^{2-} (basic sites) are catalytically active for Claus reaction.

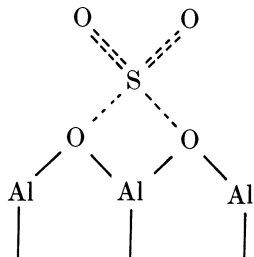
Adsorption of Hydrogen Sulfide. IR studies of hydrogen sulfide adsorption on alumina suggest that (18, 19) hydrogen bonding produces the following structure:



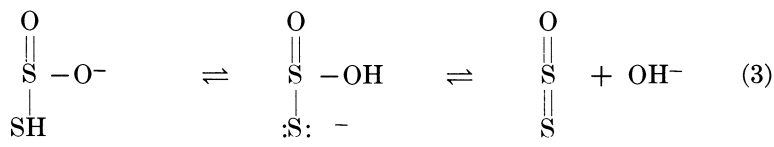
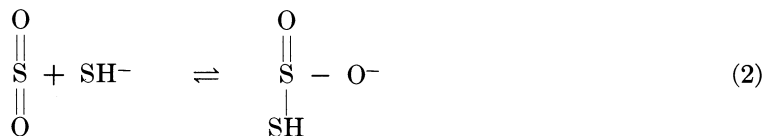
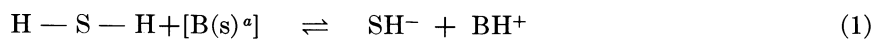
Irreversible adsorption of hydrogen sulfide has been reported (2, 20). It is proposed that hydrogen sulfide adsorption could also take place via O^{2-} sites:

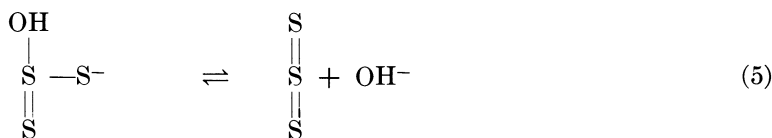
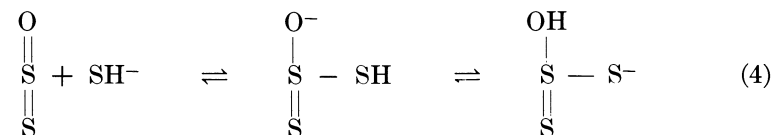


Sulfur Dioxide Adsorption. This may take place on basic sites, and considerable irreversible adsorption has been reported (2, 18). Further,



the adsorption of hydrogen sulfide and sulfur dioxide may take place on adjacent sites, and the mechanism for Claus reaction catalyzed by a base may be:





^a [B(s)*]-basic site on surface of the catalyst.

The increased rate of Claus reaction over the basic catalyst could be a result of more effective use of the available surface for reaction.

The zero-order dependence in sulfur dioxide for Claus reaction on Chromosorb-A indicates that under the reaction conditions the catalytically active sites are saturated with adsorbed sulfur dioxide. The first-order dependence in hydrogen sulfide suggests that the reaction of hydrogen sulfide with the adsorbed sulfur dioxide is rate controlling. For the Chromosorb-A containing 5.0% sodium hydroxide, the kinetic orders were 0.7 and 0.2 in hydrogen sulfide and sulfur dioxide, respectively. There is no simple explanation for the fractional orders on the base-loaded Chromosorb-A although different mechanisms could be potentially responsible. Kinetic orders of 0.8 and 0.5 in hydrogen sulfide and sulfur dioxide were reported by Dalla Lana *et al.* (21) for Claus reaction over a bauxite catalyst.

Even though the relative basicities of the catalysts determined by benzoic acid were not quantitative, examination of Table VI reveals that, at least for the three catalysts examined, there is a correlation between catalyst basicity and activity. The failure of active alumina-based catalysts to respond significantly to the base additions indicates that these untreated catalysts approached their maximum basicity under the reaction conditions. This explanation agrees with the observations of Liu (22).

Sulfur dioxide adsorption at 250°C (2 torr sulfur dioxide) on Chromosorb-A containing 3.9% sodium hydroxide amounted to 0.02 mmole/g compared with 0.06 mmole/g basic sites by benzoic acid titration. This suggests that sulfur dioxide is adsorbed on the basic sites. The sulfur dioxide adsorption corresponded to 6% coverage of the total surface of the catalyst.

The effect of the polarizing power of the cation on the Claus activity (Figure 5) could result from the fact that the basic sites (O^{2-}) associated with Li^+ are more effective in dissociative adsorption of hydrogen sulfide than those associated with Na^+ or K^+ .

The porous alumina used in this study is very active for Claus reaction. On the basis of initial rate/g it was about three times more active

than cobalt–molybdate and about seven times more active than bauxite or activated alumina. The large pore openings, $\sim 1000\text{\AA}$ allow reactants and products to diffuse in and out of the pores with ease, and the increased area, $220\text{ m}^2/\text{g}$ (compared with $140\text{--}190\text{ m}^2/\text{g}$ for other alumina catalysts) enables it to be more active. Further, the increased basicity of this catalyst (2.8% sodium hydroxide by hydrochloric acid titration in aqueous slurry and 0.64 mmole/g basic sites by benzoic acid, Table V) would enhance its Claus reactivity. Leaching of the base from this catalyst was a slow process. Experiments with the leached porous alumina showed fairly high activity.

In the commercial Claus reactors the alumina-based catalysts may have intrinsic basic sites to initiate Claus reaction. As water is produced during the reaction or introduced by the feed, more basic sites could be generated as observed in the basicity determinations in this study.

Acknowledgments

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Beavon Sulfur Removal Process for Claus Plant Tail Gas

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The Beavon sulfur removal process for the cleanup of Claus plant tail gas is a two-step process in which the sulfur contaminants are first catalytically hydrolyzed and/or hydrogenated to hydrogen sulfide and the hydrogen sulfide is then converted to elemental sulfur and recovered in a Stretford process unit. Commercial plants reduce the concentration of sulfur compounds as hydrogen sulfide in the tail gas from 1–3 vol % to less than 100 ppm. The treated gas contains less than 1 ppm hydrogen sulfide. The chemistry, design criteria, operating experience, and economics of the process are discussed.

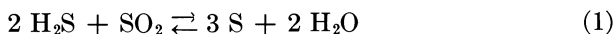
Claus plants are used in petroleum refineries and elsewhere to partially oxidize hydrogen sulfide to elemental sulfur using air as the oxidant. The efficiency of such plants is limited, and a nitrogen-rich tail gas is produced which contains water, carbon dioxide, and smaller amounts of other substances including sulfur compounds. Typically, about 3–10% of the entering sulfur is produced with the tail gas as carbonyl sulfide, methyl mercaptan, carbon disulfide, hydrogen sulfide, sulfur dioxide, and elemental sulfur as vapor or entrained droplets. Disposal of the incinerated tail gas has in the past been an air pollution problem because it contains about 10,000–20,000 ppm sulfur dioxide.

A number of commercial plants are now using the Beavon sulfur removal process to convert the sulfur content of Claus tail gas first to hydrogen sulfide and finally to elemental sulfur. These plants reduce the sulfur content of the tail gas from about 1–3% to less than 100 ppm of which less than 1 ppm is present as hydrogen sulfide. The foregoing con-

centrations are calculated as the sulfur dioxide equivalent on a volume basis. The processed tail gas can be directly discharged to the atmosphere without environmental problems.

Chemistry of the Claus Process

In a Claus plant about one-third of the hydrogen sulfide is combusted to sulfur dioxide, and the balance reacts according to Reaction 1; thermally at high temperatures and catalytically at lower temperatures (1, 2):

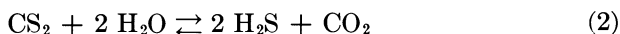


The catalytic reaction proceeds stagewise with interstage removal of the sulfur to shift the equilibrium. Interstage removal of water to shift the equilibrium even further is impractical because of plugging problems (3) with solid sulfur.

During the combustion of the hydrogen sulfide some of the sulfur reacts with hydrocarbons normally present to form carbon disulfide and methyl mercaptan. Carbonyl sulfide is also formed either by the partial hydrolysis of carbon disulfide and/or by the reaction of carbon dioxide and hydrogen sulfide. Some hydrogen and carbon monoxide are also formed in the Claus combustion step.

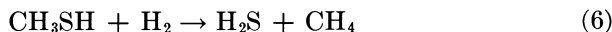
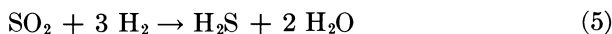
Chemistry of the Catalytic Reactor

The heart of the Beavon process is a catalytic reactor which converts essentially all of the sulfur in the tail gas to hydrogen sulfide either by hydrogenation or hydrolysis. Hydrolysis reactions are typified by Reactions 2 and 3:

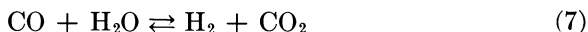


Residual carbonyl sulfide and carbon disulfide typically total about 25 ppm calculated as sulfur dioxide.

Hydrogenation reactions are typified by Reactions 4, 5, and 6:



While carbon disulfide and carbonyl sulfide can also be converted to hydrogen sulfide by hydrogenation, both are predominantly converted by hydrolysis. The supply of hydrogen is supplemented by the carbon monoxide content of the reactor feed gas which undergoes Reaction 7, the water-gas shift reaction:



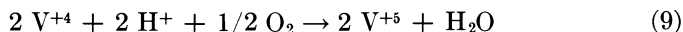
Chemistry of the Stretford Process

The hydrogen sulfide-containing stream from the catalytic step can be processed several ways to recover the sulfur content. The initial commercial development uses the Stretford process (4-10) to convert the hydrogen sulfide to elemental sulfur by a wet chemistry process developed by T. Nicklin and others at North West Gas of Stretford, England. The Stretford process has been accepted widely for treating coke oven gas and received the Queen's Award for industrial developments.

In this process the gas is first contacted in an absorber where hydrogen sulfide is absorbed into an alkaline solution and eventually converted to sulfur by Reaction 8 where V^{+5} is present as sodium metavanadate.



The reduced V^{+4} is later oxidized by air blowing in the presence of the disodium salt of anthraquinone, 2,7-disulfonic acid (ADA). The overall oxidation is represented by Reaction 9:



Sulfur formed in Reaction 8 is recovered by flotation during the air blowing in Reaction 9.

Some of the hydrogen sulfide feed undergoes side reactions and is converted to sodium thiosulfate and sodium sulfate. However, 98% or more of the incoming hydrogen sulfide feed is normally converted to elemental sulfur.

Plant Design

Pilot Plant. The Beavon sulfur removal process was studied in a pilot plant where the scale-up factor was 100 and 200 for the first two commercial units. General process operability was established at this stage.

Commercial Design. The design for a commercial plant is shown schematically in Figure 1. Reducing gas is generated by partial oxidation

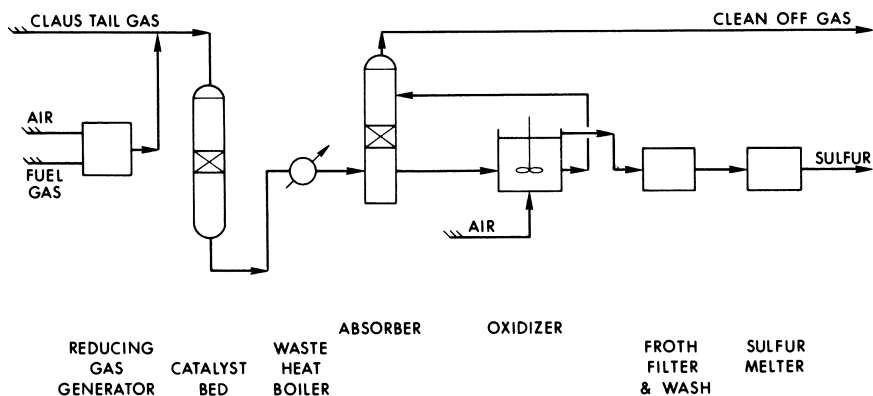


Figure 1. Flow diagram of the Beavon sulfur removal process

of a fuel gas and then mixed with the feed tail gas as a source of hydrogen and carbon monoxide. The hot reducing gas also preheats the tail gas. The mixed gases flow to the catalytic step after which the bulk of the water may be removed, and the gas stream is passed to the Stretford absorber. In the Stretford process, elemental sulfur recovered as a froth in the oxidizer is filtered, washed, and passed to a melter to separate molten sulfur and the entrained water.

Special Design Considerations. The initial plants consisted of two Claus/Beavon strings so that when one string was shut down the other could process the hydrogen sulfide load from the entire refinery without pollution. Some plants now under consideration will have only a single string with sparing of some items of equipment, *e.g.*, pumps, to provide sufficient reliability.

Hydrolysis, hydrogenation, and the shift reaction take place concurrently at moderate temperatures and atmospheric pressure over an extruded cobalt molybdate catalyst which is sulfided. Space velocities are about 2000 cu ft of tail gas plus reducing gas/hr/cu ft of catalyst. Because of the excessive heat released when sufficient air contacts these catalysts, extraneous air must be excluded from the catalyst at all times, especially during start-up and shutdown.

For maximum conversion of sulfur compounds it is desirable to operate as close to chemical equilibrium as possible. Both the pilot plant and commercial plants attained a fairly close approach to equilibrium with respect to the conversion of sulfur compounds. The many competing reactions throughout the reactor together with a close approach to equilibrium complicates process analysis.

Several things were done at the pilot plant stage to minimize reactor scale-up problems. The catalyst particle size in the pilot plant was the same as that now used in commercial plants. Catalyst bed depths in the pilot and commercial units were similar in order to have similar mass

velocities through both beds. Because of the large gas volumes and low pressure drop requirements, the catalyst bed is relatively shallow. This design requires proper gas distribution at the reactor inlet to prevent channeling. The pilot plant operated exclusively on a commercial Claus plant tail gas in order to include the effects of any and all unknown tail gas constituents in the process evaluation. Finally, the pilot plant was operated for over 3 months to make certain that the catalyst did not deteriorate rapidly with use. As of mid-January 1974, Union's two commercial units had each operated for 6 months without observable catalyst deactivation. The ultimate catalyst life is expected to be more than a year.

Unfortunately, upsets in an oil refinery Claus unit are routine because of frequent sudden changes in feed composition and flow. The Beavon unit provides excess hydrogen in the catalytic section to hydrogenate sulfur dioxide surges. The resulting hydrogen sulfide surges as well as those from the Claus unit are handled in the Stretford unit by providing a suitable excess of chemicals in the Stretford solution. Because the hydrogenation reactions are exothermic, sulfur dioxide surges, for example, will increase the temperature rise across the catalyst bed. The design tolerates surges without damaging the catalyst.

A waste-heat boiler may be installed on the reactor outlet gas line if the installation is large enough to generate steam economically. Steam may be generated at any pressure up to about 200 psig.

Water buildup must be prevented in the Stretford liquor. Water enters the Stretford unit with the feed gas and is also a reaction product in the Stretford process. Additional water enters with the filter wash. An evaporative cooler evaporates excess water and controls temperature.

The absorber is a simple splash-deck tower. Because the back pressure of hydrogen sulfide over Stretford solution is negligible, the absorber can be sized to reduce the inlet hydrogen sulfide concentration by a factor of 100,000. Commercial absorbers have met this design criterion.

In practice the oxidation of Stretford solution by Reaction 9 is kinetically limited so that a substantial improvement in performance can be obtained by staging the process. It is estimated that the overall residence time in the oxidizer can be decreased by as much as 50% when three oxidizer stages are used in place of a single stage. Commercially, a three-stage oxidizer is used in which power-driven stirrers churn air into small bubbles. An analysis of commercial oxidizer performance indicates that mass transfer is not a significant factor. Hence the bubble size is suitably small.

Operating Experience

At the present time seven units are operating and about fifteen more are in various stages of engineering and construction. By the time of this

publication, the total operating time logged will be about 36 unit-months. To date the hydrogen sulfide content of the treated tail gas has exceeded 1 ppm only during severe upsets. The aggregate time of these upsets is probably less than half a day. The treated tail gas purity has at all times exceeded the most rigid regulations by a wide margin.

Operating Problems. During the startups of the first two plants there was some difficulty with solution overloading, mainly because of upsets in the Claus units and in spite of the fact that these plants are designed with generous over-capacity. The frequency of these upsets quickly decreased as personnel learned to maintain proper operating ratios in the Claus units. For example, a 5% deficiency in the amount of air in the Claus unit can double the load on the Beavon plant.

The froth filter was the most troublesome single piece of mechanical equipment. Troubles diminished greatly as the operators became familiar with this new type of equipment. Methods to eliminate the filter have now been developed and will be tested on a commercial scale.

Construction Materials. Carbon steel is used for most of the plants; in some areas it is protected against rusting by a coal tar epoxy coating. The water outlet line of the sulfur melter is stainless steel. No notable corrosion has occurred.

Table I. Beavon Sulfur Removal Process Operating Costs^a

<i>Commodity</i>	<i>Unit Cost</i>	<i>Consumption Rate</i>	<i>Daily Cost (\$)</i>
Power	0.725¢/kw-hr	300 kw	52
Fuel gas	\$1.00/MM Btu	125 MM Btu	125
Soft water	20¢/M gal	12 M gal/day	2
Catalyst replacement ^b	—	—	8
Chemicals	—	—	140
Total costs			327
Less credit for 50 psig steam	\$1.00/M lb	2,500 lb/hr	60
Less credit for incinerator fuel	\$1.00/MM Btu	250 MM Btu	250
Net cost			17

^a Basis: 100 long-ton/day Claus Unit.

^b Assumed catalyst life is 3 yrs.

Economics. The capital investment for a Beavon plant to process tail gas from a 100-long-ton/day Claus unit is about \$1,250,000. Operating costs for a unit of this size are given in Table I. The fuel and steam required by the process is less than one-fourth of that required for simple incineration. Should fuel gas cost increase to \$2/MM Btu as has been forecast, the energy savings would make the operation profitable.

Conclusions

The Beavon sulfur removal process is now a reliable, established method for cleaning up Claus plant tail gas well beyond any proposed regulations. As with any new process, work is currently directed toward reducing capital and operating costs. The capital investment has already been reduced by about 20% over the original design. A further cost reduction now seems possible, thereby increasing the application possibilities of this process.

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RECEIVED April 4, 1974. The process is patented in the U.S. (#3,752,877, D. K. Beavon, Aug. 14, 1973) and Canada (#916,898, D. K. Beavon, Dec. 19, 1972), and patents are being sought in other countries. The process is licensed by the Union Oil Co. of California and is designed by the Ralph M. Parsons Co.

Sulfur Recovery in Oil Refineries Using IFP Processes

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The IFP-1500 process converts mixed hydrogen sulfide/sulfur dioxide streams to sulfur and water by a liquid-phase Claus reaction using a proprietary catalyst. The exit gas from the reactor contains 1000–2000 ppm sulfur dioxide after incineration. Plant investment and operating costs are both relatively low, and there is no problem with corrosion. The IFP-150 process takes sulfur dioxide streams down to 150–250 ppm sulfur dioxide by ammonia scrubbing and reaction with hydrogen sulfide-containing gas in a scheme similar to the IFP-1500. Nineteen IFP-1500 plants and four IFP-150 are now operating or under construction. A scheme is shown for converting all solid, liquid, and gaseous sulfur wastes in a refinery to water and sulfur, reducing sulfur dioxide concentration to 150–250 ppm.

When control of sulfur emission became an urgent concern of refineries and other plants operating on hydrocarbon feeds, a host of processes were developed on paper (1). The past 2 yrs have seen a shakedown and thinning of these processes. Of the more than 60 originally proposed, only about half a dozen have been developed commercially. This paper concerns itself with two of those commercially proved processes developed by the French Petroleum Institute (2, 3); one for taking emissions down to about 1500 ppm sulfur dioxide after incineration and the other for reducing sulfur dioxide to one tenth that level. At this time 19 IFP-1500 plants are licensed as are four of the IFP-150 plants.

The IFP-1500 Process

Process Description. The IFP-1500 process is best used to clean up Claus unit tail gas. The technology involved is essentially an extension of the Claus reaction itself but carried out in the liquid phase as shown in Figure 1. The tail gas at Claus unit exit pressure is injected into

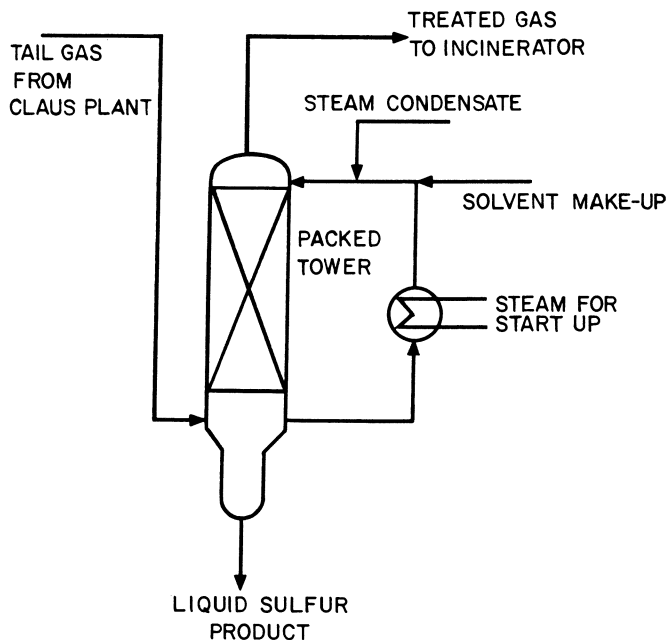


Figure 1. IFP Claus tail gas clean-up process

the bottom of a packed tower which provides high contact area between gaseous and liquid phases. The tower is sized to maintain pressure drop within acceptable limits, avoiding the need for a blower. A low vapor pressure polyethylene glycol solvent which contains a proprietary carboxylic acid salt catalyst in solution circulates countercurrent to the gas. The catalyst forms a complex with hydrogen sulfide and sulfur dioxide which in turn reacts with more of the gases to regenerate the catalyst and form elemental sulfur. The reaction is exothermic, and the heat is removed by injecting and vaporizing steam condensate. Temperature is maintained about 250–270°F, sufficient to keep the sulfur molten but not high enough to cause much loss of sulfur or glycol overhead. The sulfur accumulates in the boot of the tower and is drawn off continuously through a seal leg. Purity of the product sulfur is very good as shown in Table I. Overheads from the tower are sent to the

Table I. Typical Analysis of Sulfur from IFP-1500 Claus Tail Gas Clean-up Plants

	<i>Design</i>	<i>Actual^a</i>
Purity (% S)	99.7	99.96
Hydrocarbon (ppm)	100	100
Ash (ppm)	200	130
Color	yellow	bright yellow

^a From IFP unit serving a 270 long tons/day (LT/D) Claus plant.

same incinerator used to incinerate Claus tail gases were the IFP unit absent. Since there is no water buildup in the IFP process, corrosion is no problem. The whole unit is fabricated from carbon steel.

Sulfur Dioxide and Hydrogen Sulfide Concentration and Ratio. Design conversion of IFP-1500 units depends on concentration of hydrogen sulfide and sulfur dioxide in the Claus plant tail gas and on the amount of packing in the IFP tower. Figure 2 shows curves for plants with two different amounts of packing. For a given IFP-1500 plant, conversion varies with the concentration of hydrogen sulfide in the feed. This is responsible for the balancing effect which IFP-1500 units exert to a certain extent on Claus plant operation: as the Claus catalyst be-

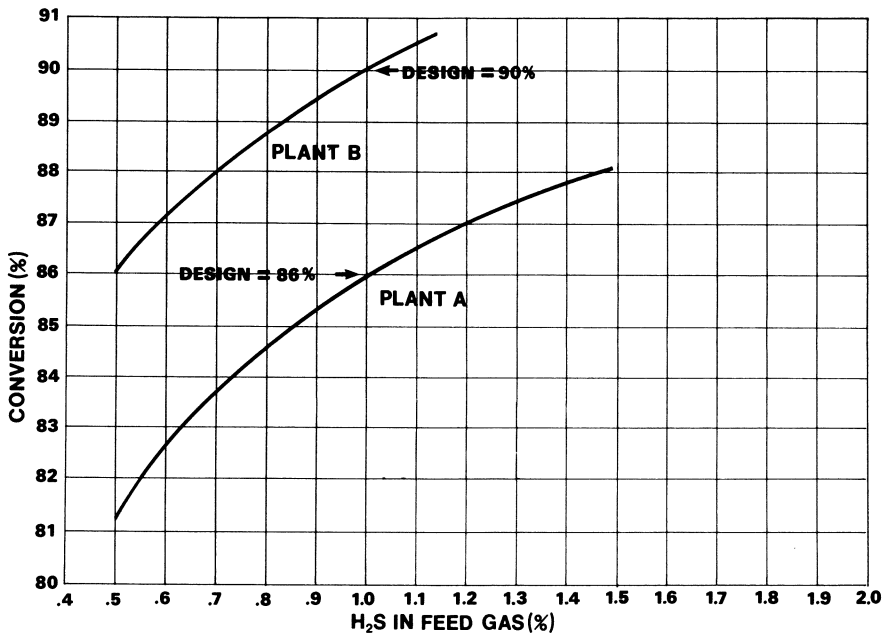


Figure 2. Conversion vs. hydrogen sulfide concentration in feed gas. $H_2S:SO_2 = 2:1$.

comes spent, the tail gas contains increasingly higher concentrations of hydrogen sulfide which in turn increases conversions in the IFP-1500 unit.

Figure 3 shows actual pen traces from the stack sulfur dioxide monitor of a recently commissioned IFP-1500 unit. Sulfur dioxide at the

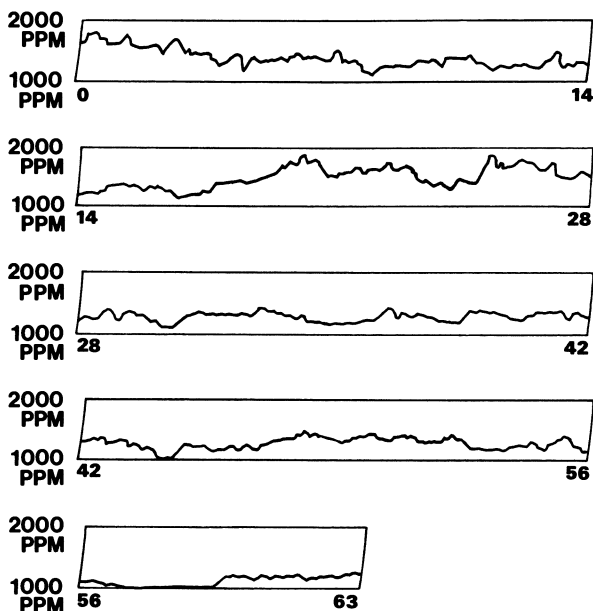


Figure 3. Stack sulfur dioxide concentration

stack mouth reached as low as 1000 ppm using only a conventional non-bauxite catalyst in the two stage Claus unit. Figure 4 is a composite of readings made during the start-up of the same plant, showing that sulfur dioxide emissions were brought as low as 800 ppm. Extrapolating these results to 100% conversion shows that about 400 ppm sulfur dioxide are left. This corresponds to equilibrium sulfur and to carbonyl sulfide and carbon disulfide generated in the Claus unit. These compounds do not react in the IFP-1500 process. To keep them at a minimum one can run the first reactor of the Claus plant somewhat hotter than usual and use a number of commercially available catalysts (4, 5).

The ratio of hydrogen sulfide to sulfur dioxide is especially important at high conversions. Figure 5 shows actual traces for sulfur dioxide, hydrogen sulfide, and the hydrogen sulfide/sulfur dioxide ratio for the feed to an IFP-1500 plant with a design conversion of 90%. Figure 6 shows the effect of varying the ratio on conversion for a plant of 93% design conversion. The design ratio here is about 2.2. A ratio that is too high or too low cuts conversions sharply. One that is too low also reduces

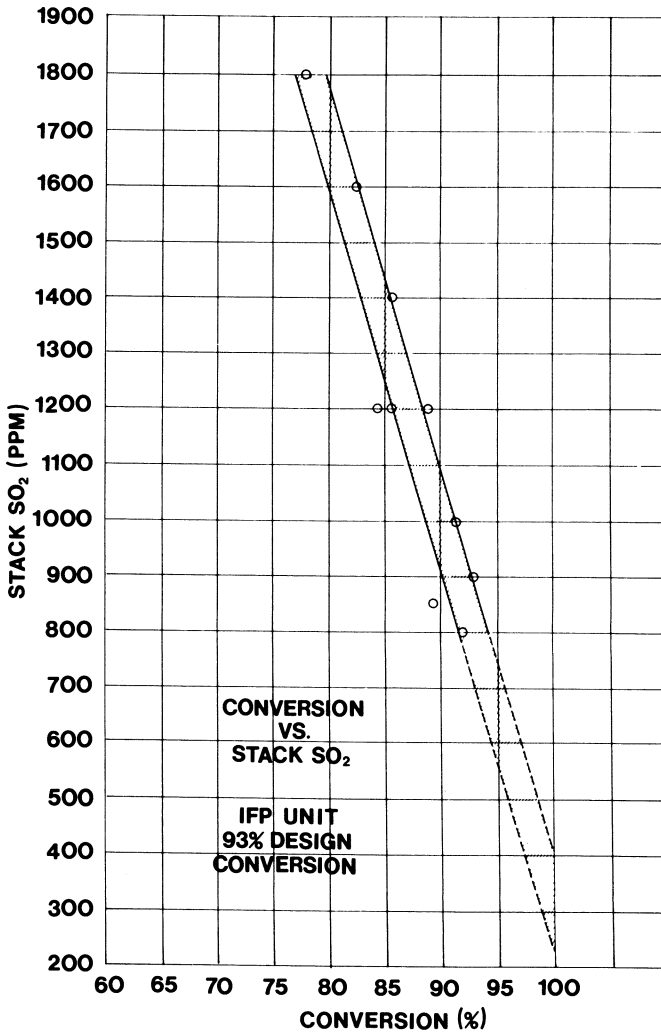


Figure 4. Conversion vs. stack sulfur dioxide concentration for an IFP unit with 93% design conversion

the quality of the product sulfur. Careful control of the Claus unit to maintain proper ratio not only optimizes conversion in the IFP-1500 unit, but also in the Claus plant itself.

Operating Factors. An advantage of the IFP-1500 process is its insensitivity to changes in gas flow rates. When the first industrial scale unit was started up in Japan, it operated on flows as low as 30% of design without adverse effect. Another advantage of the IFP-1500 process is that stream factor is long, generally in the range of 2 yrs. After

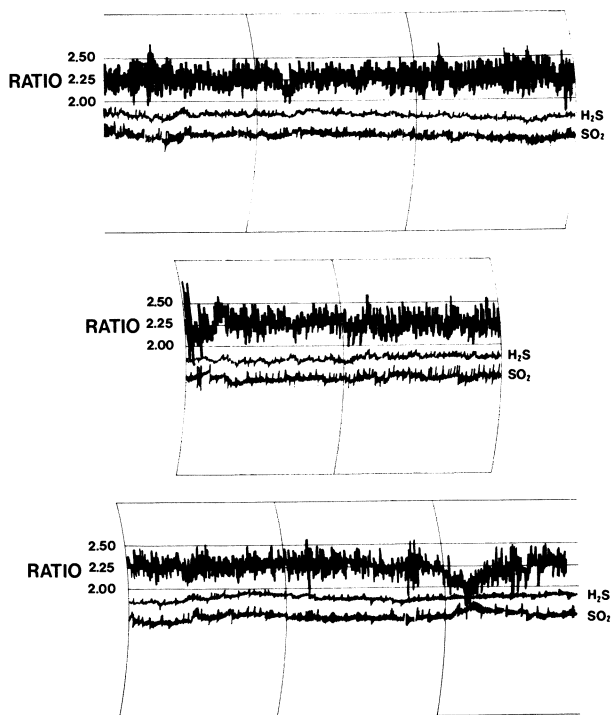


Figure 5. H_2S/SO_2 in feed to IFP unit

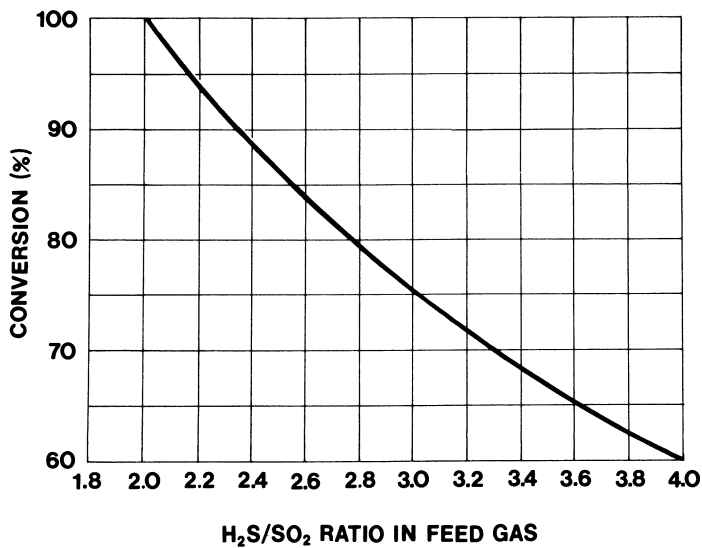


Figure 6. Conversion vs. H_2S/SO_2 ratio in feed gas for IFP unit with 93% design conversion

about 24 months a shutdown is needed to wash away catalyst which has been converted to sulfates and deposited on the packing in the tower. A simple wash with water is used. There is no extraordinary maintenance required, and there is no labor needed since the Claus plant operator himself runs the IFP-1500 unit.

Table II. Feed Specifications for a Two-stage 100 LT/D Claus Plant at 95 % Conversion

	<i>Lb-mol/hr</i>
H ₂ S	8.5
SO ₂	4.2
S ₁	1.9
COS + CS ₂	0.3
Balance	879.4
Total	894.0

Economics. Table II gives specifications for feed from a two-stage 100 LT/D Claus plant with 95% conversion. Table III shows the overall Claus + IFP-1500 conversions possible for plants treating tail gas from that Claus unit, with IFP-1500 plants of varying design conversion: 90%, 80%, 70%, and 60%. Table IV gives investment and operating costs for these IFP units.

It is interesting to examine the economics of the IFP-1500 process from another point of view. Starting with a fixed amount of money available for IFP plant investment, one can determine how many catalytic stages should be installed in a Claus plant to reach various sulfur dioxide emission levels. Table V shows typical analyses for tail gas from the first, second, and third converters of a 100 LT/D Claus plant. Table VI shows conversions possible in an IFP-1500 unit after treating

Table III. Overall Recovery as a Function of IFP Unit Design Conversion^a

	<i>Feed</i>	<u>% IFP Design Conversion, H₂S + SO₂</u>			
		<i>90</i>	<i>80</i>	<i>70</i>	<i>60</i>
Total free and combined S (lb-mol/hr)	14.9	1.7	2.9	4.2	5.5
Overall Claus + IFP recovery (%)	—	99.4	99.0	98.6	98.1

^a Total feed = 894.0 lb-mol/hr

each of these three effluent gas streams, expressed as percent IFP conversion and ppm sulfur dioxide going to the incinerator. These figures are based on spending half a million dollars on the IFP-1500 unit in each case. Where regulations specify 1500–2000 ppm (6), a Claus plant may

Table IV. Investment and Operating Costs

	% IFP Design Recovery ($H_2S + SO_2$)			
	90	80	70	60
Overall recovery Claus + IFP (%)	99.4	99.0	98.6	98.1
Battery limits investment (\$000) ^a	510	330	280	240
Solvent and catalyst consumption (\$/hr)	1.67	1.65	1.57	1.54
Utilities				
Condensate (lb/hr)	370	320	280	250
Power (KWHr/hr)	21	17	16	15

^a Erected project cost including engineering, royalties, process data book, and solvent inventory (January 1973)

Table V. Analyses of Tail Gas 100 LT/D Claus Plant

<i>Analysis (mol %)</i>	<i>Converter No. 1</i>	<i>Converter No. 2</i>	<i>Converter No. 3</i>
H ₂ S	1.48	0.59	0.34
SO ₂	0.74	0.29	0.17
S	1.26	0.14	0.13
H ₂ O	28.58	29.96	30.25
COS	.02	.02	.02
CS ₂	.01	.01	.01
Balance	67.91	68.99	69.08
Flow rate (lb-mol/hr)	1025.27	1009.13	1007.77

Table VI. Conversions Possible with Fixed \$500,000 Investment in IFP Unit for a 100 LT/D Claus Plant^a

	<i>Treating Tail Gas After</i>		
	<i>Converter No. 1</i>	<i>Converter No. 2</i>	<i>Converter No. 3</i>
IFP unit conversion, H ₂ S + SO ₂ (%)	90	86	85
Sulfur compounds to the incinerator (as ppm SO ₂)	3000	2000	1700
Solvent and catalyst consumption (\$/hr)	1.67	1.66	1.65
Utilities			
Condensate (lb/hr)	400	180	100
Power (KWHr/hr)	25	25	25

^a Battery limits investment including solvent inventory, 1973 basis

only need two stages. This was actually the case where an IFP-1500 unit was installed to clean up tail gas from a large two-stage Claus plant.

The IFP-150 Process

The IFP-150 process is basically a variation of the IFP-1500 process for handling sulfur dioxide streams. In it, the IFP-1500 process is coupled

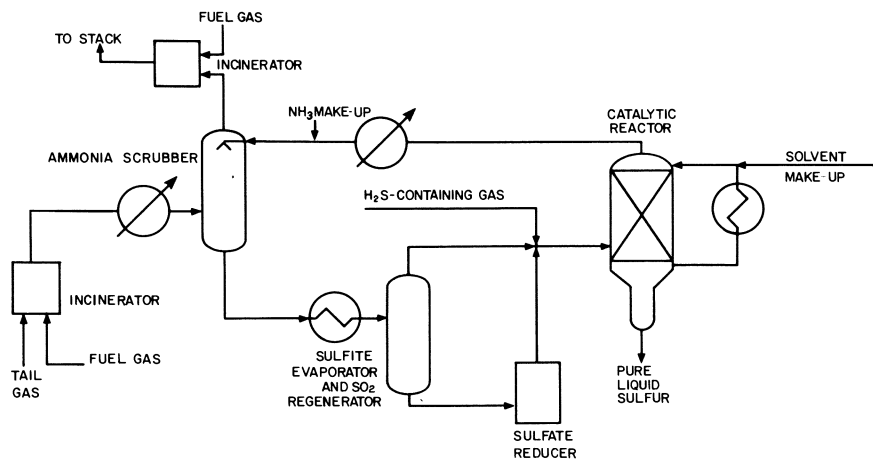


Figure 7. Flow diagram of the IFP-150 process

to an ammonia scrubbing section. Where refinery sulfur dioxide levels must be below 200 ppm at the stack mouth, scrubbers can be set up at many points to clean flue gases and various acid and sour streams. The effluents from the scrubbers are then piped to a central IFP-150 reaction section where sulfur-containing compounds are converted to elemental sulfur and aqueous ammonia is recycled to the several scrubbing sections. There is intermediate storage at several points in the refinery so that various units can operate at their optimum rates independent of the operation rate of the IFP-150 reaction section.

Process Description. Figure 7 shows the flow scheme. The tail gas is scrubbed with aqueous ammonia, reducing the sulfur dioxide concentration to 150–250 ppm. The cleaned gas is heated and vented to the stack. The brine, containing mostly ammonium sulfites, is heated in a forced-circulation evaporator where sulfites are decomposed to ammonia and sulfur dioxide. These are taken off overhead with water at about 300°F. Bottoms from the evaporator contain thermostable sulfates and thiosulfates which are reduced according to a proprietary IFP process using submerged combustion technology to avoid corrosion and solve heat transfer problems. The reaction is endothermic and uses reducing

gases produced by burning fuel gas in a deficiency of air. In the reduction, sulfates and thiosulfates are converted to ammonia, sulfur dioxide, and water which are mixed with the overhead stream from the evaporator.

Acid gas or other hydrogen sulfide-rich gas and the blended sulfur dioxide-ammonia streams are fed to the IFP-150 reactor at rates sufficient to maintain a 2:1 ratio of hydrogen sulfide : sulfur dioxide. In the reactor the hydrogen sulfide and sulfur dioxide dissolve in a high boiling point glycol to form elemental sulfur and water. The reaction liquor is maintained slightly above the melting point of sulfur, as in the IFP-1500 process, with liquid sulfur accumulating in the boot of the tower and being drawn off to storage through a seal leg.

The reactor tower operates in a flooded condition, with gases bubbling up through the solution. Perforated trays are used to improve contact. Solvent circulating countercurrent to the gases is taken from the bottom of the tower, pumped through a steam generator and back to the tower. The heat of reaction is thus removed, with steam leaving the generator at twice atmospheric pressure. Overheads from the tower are cooled, and aqueous ammonia is condensed and recycled back to the

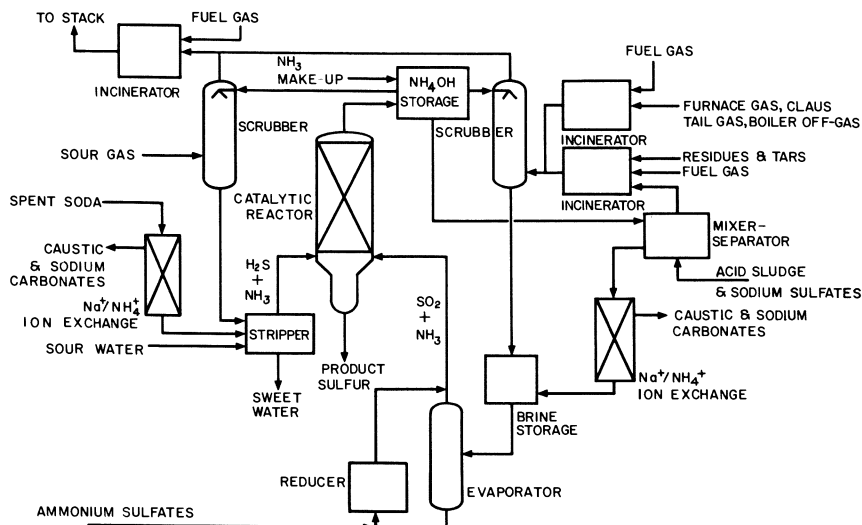


Figure 8. Total sulfur recovery using IFP-150 process in a refinery

scrubber. Some non-condensables containing inert gases, traces of sulfur vapor, and hydrogen sulfide are incinerated and recycled to the ammonia scrubber.

Figure 8 shows how the IFP-150 process can be integrated into an overall scheme for recovering sulfur from all gaseous, liquid, and solid sulfur-bearing refinery wastes.

**Table VII. Typical Performance and Economics of a
200 LT/D Claus Plant**

1787 lb-mol/hr to incinerator	
29.25 lb-mol/hr S compounds (as SO ₂)	
250 ppm SO ₂ in treated gas	
Investment	
Scrubbing (\$)	400,000
Sulfur conversion (\$)	600,000
Solvent inventory (\$)	40,000
Utilities	
Power (KWHr/hr)	190
Circulating cooling water (USGPM)	1400
Process water (USGPM)	3
MP steam (lb/hr)	5500
Chemicals	
LPG (lb/hr)	220
NH ₃ (lb/hr)	4
Solvent (\$/yr)	4000

Economics. Table VII gives economics for the IFP-150 process applied to Claus unit gaseous effluent.

Industrial References

Nineteen full scale IFP-1500 units have been licensed to clean up tail gas from Claus plants: five in the U.S., one in Canada, nine in Japan, three in Russia, and one in Belgium. The Claus units recover from 45 to 800 LT/D of sulfur. They produce 4.3–68.7 MMSCFD of tail gas with hydrogen sulfide concentrations ranging from 3.0% (single stage) to 0.9% (three stages). Thirteen units are already in operation.

Four IFP-150 units are under construction or already operating in Japan and France.

This paper was originally presented in January, 1974. At the time of acceptance for publication, September 1974, 24 IFP-1500 plants were in operation or under construction.

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RECEIVED June 11, 1974. Confidentiality agreements prevent disclosure of any other operating temperatures and pressures used in the IFP-1500 or IFP-150 processes.

The Shell Claus Offgas Treating (SCOT) Process

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The Shell Claus Offgas Treating (SCOT) Process won instant acceptance by the oil refining industry when it was announced in September 1972, and today it is the preferred method of meeting the most stringent emission regulations. Its functions are familiar to refinery operators, economical carbon steel is used throughout, and there are no waste discharges except the vent gas containing less than 500 ppm hydrogen sulfide (250 ppm sulfur dioxide after incineration) and a clean water condensate. This paper describes the SCOT Process and discusses the operating experience of the first commercial plants placed on stream. Two small skid-mounted units were designed and placed in operation in California within 8½ mos of contract award.

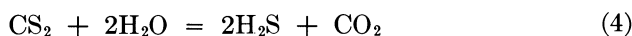
Specified recovery efficiency of sulfur recovery units (SRU) used to be based on economic considerations. Any increase in SRU efficiency which added to its cost had to increase profits based upon the sales value of the additional sulfur recovered. Sulfur recovery units were based on the classic Claus process which was, and still is, the cheapest way to recover over 90% of the sulfur in hydrogen sulfide-bearing streams. Most were very simple one or two catalytic stage plants. As the problem of reducing sulfur emissions has become more urgent, the complexity and cost of SRU's has risen, partially because of such routine sophisticated modifications as closed loop control of acid gas/air ratio, three or more catalytic reactor stages, high pressure steam reheat, ammonia and hydrogen cyanide handling capability, etc. Such plants are approaching the theoretical limits of sulfur recovery for the Claus process.

Following the National Environmental Policy Act of 1969, the drive of federal, state, and local regulations toward zero sulfur emissions has

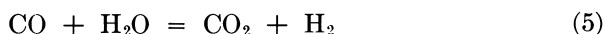
caused manufacturing and engineering-construction industries to develop numerous processes to capture the residual sulfur in Claus tail gas. As applied specifically to SRU offgas, a few of these processes have been successfully commercialized, namely the Wellman-Lord, IFP, and Parsons-Beavon processes. The most recent to join this parade of successful commercial processes is the Shell Claus Tail Gas Offgas Treating (SCOT) Process. It is licensed in the U.S. by Shell Development Co., by Shell Nihon Gijutsu in Japan and the Far East, and in all other countries by Shell Internationale Research Maatschappij.

Process Description and Chemistry

The following process description is from or derived from a paper presented by Naber, Wesslingh and Groenendaal of SIRM (1, 2, 3). The SCOT process may be divided into two sections—reduction—quench and amine. The reduction step converts essentially all sulfur values in Claus offgas to hydrogen sulfide. The elemental sulfur and sulfur dioxide are hydrogenated, and the carbonyl sulfide and carbon disulfide are hydrolyzed to hydrogen sulfide according to the following main reactions:



Normally, Claus SRU tail gas contains more than enough hydrogen and carbon monoxide to reduce the sulfur and sulfur dioxide, but an outside source of hydrogen or hydrogen-rich gas must be provided in case of an upset in the SRU which would cause the sulfur dioxide content to rise above normal. Carbon monoxide is as good as hydrogen for reduction by the following shift reaction:



The amine section absorbs most of the hydrogen sulfide from the gas while coabsorbing as little carbon dioxide as possible. These acid gases are recycled to the inlet of the Claus unit and become part of its feed. Because the solvent selects hydrogen sulfide and rejects most of the carbon dioxide, the size of the Claus SRU is increased by only 5–6% because of recycling inert carbon dioxide.

As shown on the process flow sheet, Figure 1, reducing gas is added to the SRU offgas, and the temperature is raised to the required reactor inlet temperature in a fired heater. Alternatively, if a source of reducing

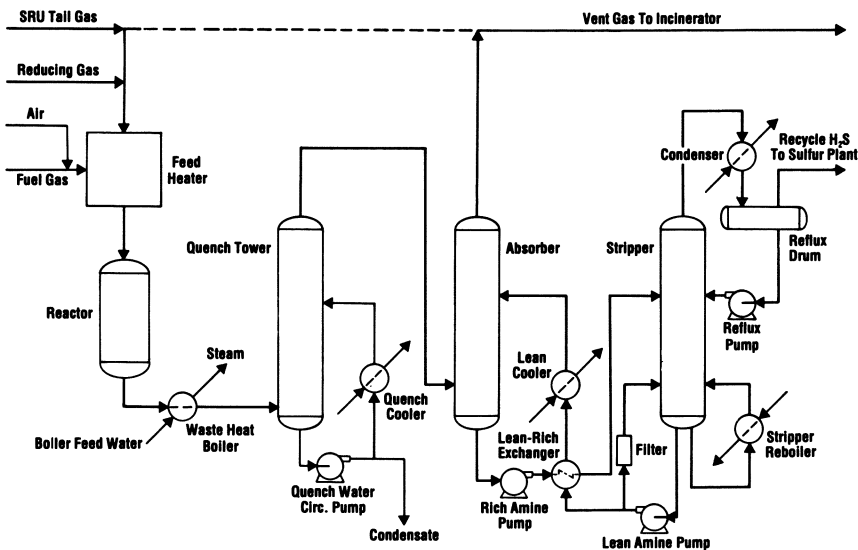


Figure 1. SCOT process flow diagram

gas is not available, a rich gas burner may be used which burns natural gas with substoichiometric air to yield both the needed hydrogen and carbon monoxide as well as reactor preheat.

Preheated gas enters the reactor containing a bed of cobalt-molybdenum catalyst where sulfur and its compounds are converted to hydrogen sulfide at about 300°C. Heat is recovered from the hot reactor effluent by generating steam in a waste heat boiler which provides about one third of the steam required for the subsequent SCOT stripper while partially cooling the reactants.

The gas is cooled to near ambient temperature by direct contact with water in a packed quench tower. The circulating quench water may be cooled by cooling water or by an air cooler with cooling water trim. The substantial quantity of water vapor contained in normal sulfur recovery unit tail gas is largely condensed in the quench tower, and the condensate is continuously withdrawn to maintain a constant level in the quench tower bottom. This condensate is in contact with the hydrogen sulfide in the gas stream and consequently must be stripped before discharging to the sewer. If the main plant has a sour water stripper, this water may be piped to that tower, or if not, a small sour water stripper may be added to this stream as an integral part of the SCOT plant itself. Hydrogen sulfide is returned either to the SCOT system or to the sour water strippers so that only clean water is discharged from the plant.

The cooled gas from the top of the quench tower enters the SCOT absorber where the hydrogen sulfide is absorbed selectively by an

alkanol-amine solution. The system is designed so that all but the small amount of hydrogen sulfide allowed by antipollution regulations is removed from the gas stream while only about 20–30% of the carbon dioxide is co-absorbed by the amine solution. The overhead gas from the absorber containing the designed amount of hydrogen sulfide, usually about 200–500 ppm, is sent to an incinerator where residual sulfur compounds are oxidized to sulfur dioxide before discharge through a stack to the atmosphere. The rich amine from the bottom of the SCOT absorber is pumped through a lean-rich exchanger to be heated while cooling the lean amine solution and is fed to the SCOT stripper. Heat input to the SCOT stripper through its reboiler generates water vapor to strip out the carbon dioxide and hydrogen sulfide which then go overhead with the water vapor, passing through a condenser where the water is condensed for reflux to the stripper. The uncondensed gases containing nearly all of the hydrogen sulfide and 20–30% of the carbon dioxide are then returned to the Claus unit where they join the main acid gas feed. The hot, regenerated amine solution is pumped from the bottom of the stripper through the lean-rich exchanger and a water-cooled lean amine cooler to the top of the absorber.

Table I. SCOT Operating Requirements for 100 LT/D SRU

Electric power (KW)	34
Steam (50 psig) (lbs/hr)	6,400
Boiler feed water (GPM)	6.4
Fuel gas (million Btu/hr)	2.9
Cooling water (GPM)	1,200
Catalyst, based 3-yr life (\$/yr)	10,000
Alkanolamine (\$/yr)	2,000
Capital costs	\$1,400,000

The amine section appears conventional but where the usual monoethanolamine (MEA) and diethanolamine (DEA) sweetening processes approach the equilibrium solubility of carbon dioxide and hydrogen sulfide, the selectivity for absorbing hydrogen sulfide and rejecting carbon dioxide is attained by the difference in reaction rates of the gases with the amine (usually diisopropanolamine, DIPA). The aim is to absorb nearly all the hydrogen sulfide before the carbon dioxide has had time to react with the amine. The absorption takes place at near atmospheric pressure. This differs from the conventional amine plant which usually operates at a considerably higher pressure. Unlike the sulfur oxide processes, this process is generally non-corrosive and carbon steel is used throughout except in the few cases where alloy is required because of conditions.

The SCOT Process is competitive with other processes for reducing sulfur dioxide levels to the 200–500 ppm range. Table I shows capital and operating costs for a typical unit to serve a 100 long ton/day (LT/D) SRU operating at 94% recovery efficiency per pass.

SCOT Process Development

The SCOT process was first made public in September 1972, at a technical meeting in Japan by Shell Internationale Research Maatschappij (SIRM). Shell had proved the effectiveness and life of the catalyst in the reduction step in bench-scale work at their Amsterdam laboratory and a semi-commercial demonstration on Claus SRU tail gas at Shell's Gerdorf, Germany refinery. Confidence in the effectiveness and selectivity of the amine absorption step was based on Shell's extensive use of the ADIP process in worldwide applications bolstered by laboratory bench-scale testing.

Commercial Plants

On the strength of the SIRM work, Douglas Oil Co. (a subsidiary of Continental Oil Co.) and Champlin Petroleum Co. bought the SCOT process for their refineries in California to meet the very strict Los Angeles APCD Code (4, 5). Both of these plants were assembled, complete with piping, instrumentation, insulation, and electrical wiring, on skids in the Dallas, Texas shops of Ford, Bacon and Davis and shipped by truck to the plant sites. Towers shipped directly to the jobsite by their vendors were placed, along with the skids, on prepared foundations in 1 day. Both units were started up the last week of June 1973, less than 9 months from contract award. Figure 2 shows the Champlin Petroleum SCOT Unit.

These two plants represent not only the first commercial application of the process anywhere, but also the first time the hydrogenation–quench section and the amine section had been operated as an intergrated whole. Even Shell's pilot plant and demonstration unit had not brought the separate sections together. While these California plants were small units added onto existing 9 and 15 LT/D SRU's respectively, they did provide the opportunity to discover and remedy the inevitable problems in a new process. Much was learned which increased the confidence in the design of much larger plants which were following on.

At an early date, Shell Canada Ltd. decided to install the SCOT process at their Waterton, Alberta gas processing plant. This plant, designed in the Netherlands, will treat the tail gas from a SRU capacity of 2,100 LT/D. Because the total sulfur emission allowable from a single

facility in Alberta is well above the capability of the SCOT process, this unit will treat only about two thirds of the total SRU capacity of the Waterton plant. The remaining one third of the SRU tail gas may be incinerated along with the SCOT tail gas and discharged to the air without exceeding the allowable emission rate.

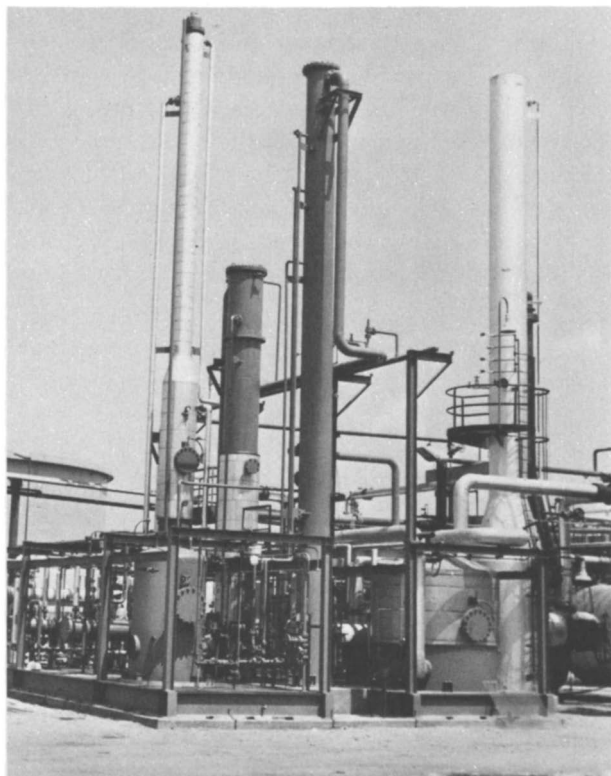
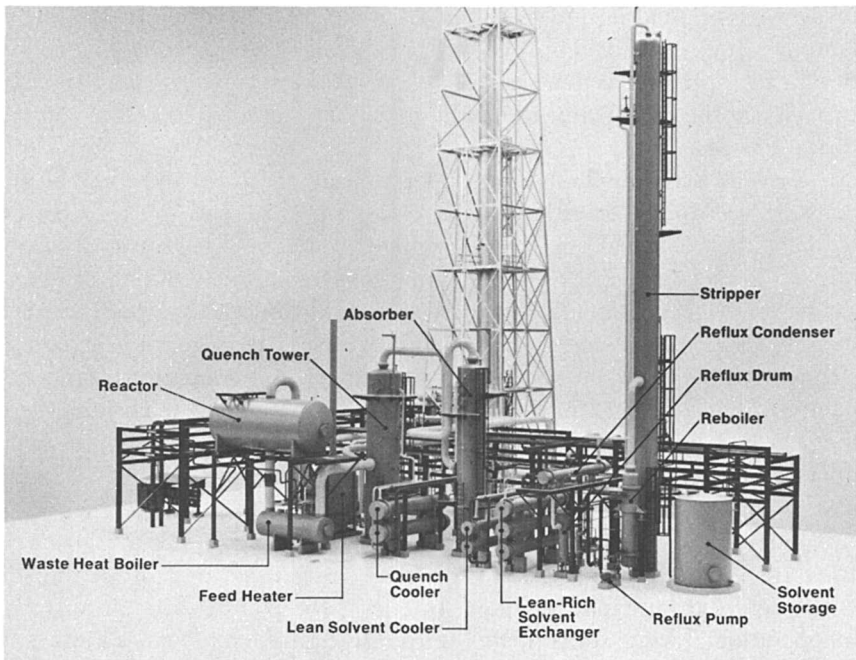


Figure 2. SCOT unit in 15 LT/D SRU of Champlin Petroleum Co., Wilmington, Calif.

In quick succession, a number of SCOT units were ordered in areas where the antipollution code requires very low emission levels. These were on new SRU's specifically designed to integrate the Claus SRU's with SCOT plants. They were BP Oil at Marcus Hook, Pa.; Marathon Oil at Detroit, Mich.; Standard Oil Co. (Ohio) at Lima, Ohio; Southwestern Oil and Refining Co. at Corpus Christi, Tex.; and Texaco Inc. at Port Arthur, Tex. At this writing, thirteen SCOT units are under contract in the U.S. and Canada, as detailed in Table II. Figure 3 is a model of a 160 LT/D SCOT unit under construction.

Table II. SCOT Units—U.S. and Canada

<i>Process User</i>	<i>Location</i>	<i>SRU (LT/D)</i>	<i>Startup</i>
Champlin Petroleum	Wilmington, Calif.	15	June 1973
Douglas Oil	Paramount, Calif.	8.8	June 1973
Murphy Oil	Meraux, La.	40	mid 1974
U.S. Steel	Clairton, Pa.	130	late 1974
B P Oil	Marcus Hook, Pa.	160	late 1974
Sun Oil	Duncan, Okla.	28	early 1975
Marathon Oil	Detroit, Mich.	80	early 1975
Shell Oil	Houston, Tex.	325	early 1975
Shell Canada	Waterton, Alta.	2100	early 1975
Southwestern Oil & Refining	Corpus Christi, Tex.	125	early 1975
Texaco Inc.	Port Arthur, Tex.	235	late 1975
Shell Oil	Norco, La.	40	late 1975

*Figure 3. Model of SCOT unit under construction in 160 LT/D SRU*

In Japan, virtually all SRU's are in high population density areas. Consequently, the SCOT process has been quickly adopted there. Seventeen SCOT units are slated to be built in Japan at this time.

Commercial Plants Startup and Operation Problems

While there were few mechanical problems during startup of the two California plants because of the conventional equipment, some process problems delayed full compliance with Los Angeles APCD Regulations.

Understated Sulfur Load Design. This problem is mentioned first because it had an important bearing on meeting guaranteed performance, even if there had been no other problems. This unit must consistently remove the last bit of sulfur from a stream that is subject to rather wide fluctuations caused by routine changes or upsets in preceding processes. This is especially true in refineries where multiple amine units and variations in refinery feedstocks can cause wide swings in both rate and composition of the acid gas feeding the SRU. Upsets in amine units can cause upsets in the SRU operation, and the SRU may be subject to upsets of its own if adequate instrumentation is not provided.

Both the California plants were added to existing SRU's. The sulfur content of the off-gases were at times well above that stated by the owners for original design of the SCOT units. The solution to this problem was simply to add improved SRU controls in old existing plants and design for optimum control in new plants and/or provide enough excess capacity in the SCOT unit to handle maximum anticipated sulfur content of the tail gas.

Solvent Stripper Design. In operation at greater-than-design sulfur loads, it was found that the solvent circulation rate had to be increased to meet the specifications for residual hydrogen sulfide in the absorber offgas. To accomplish this, the stripper was replaced with one of larger diameter to accommodate the increased liquid and vapor traffic in the tower. Incidental to the upgrading of stripper capacity were increased steam to reboiler, increased reflux condenser, and increased pump capacity. These changes have been accomplished at the Champlin Petroleum SCOT unit, and it has been operating smoothly with minimal operator attention and bettering its guaranteed performance by a wide margin since October 1973.

Sulfur Dioxide Breakthrough. Normally, enough sulfur dioxide is converted to hydrogen sulfide in the SCOT reactor so that sulfur dioxide is not detected in reactor effluent. In one of the plants, through mistakes in operation during startup, the sulfur dioxide content was allowed to rise to the point where the quench water became acidic, and sulfur dioxide was carried over into the SCOT absorber where it formed a compound with DIPA that was not regenerable at stripper conditions. As a result, the carbon steel quench water pump and the carbon steel quench water pipes where turbulence was high were rapidly corroded and the hydrogen sulfide absorbing capacity of the amine solution was lost.

While the consequences of sulfur dioxide breakthrough are serious, it is easy to prevent using the following procedures and precautions:

1. If initial catalyst sulfiding is to be done with sulfur dioxide-containing SRU tail gas, the reactor effluent must be isolated, bypassing the quench system.

2. There must always be an excess of hydrogen to guard against surges in sulfur dioxide content of SRU tail gas.

3. Protection against contamination of the amine by small amounts of sulfur dioxide is provided by the reaction of sulfur dioxide with hydrogen sulfide to form sulfur in low temperature Claus reaction in the water phase. The quench water itself provides very sensitive early warning of potential trouble from sulfur dioxide breakthrough, and proper instrumentation can sound an alarm and/or divert the SRU tail gas to the incinerator until the breakthrough is corrected. These indicators are color, pH, and turbidity, in order of increasing situation severity. With proper instrumentation the amine should never be contaminated.

The possibility of sulfur dioxide contamination of the DIPA has been considered so remote and the rate of DIPA degradation is so low that none of the plants now being designed and constructed have DIPA reclaiming facilities, as is common practice in MEA and DEA amine units. Since November 1973, none of the startup problems have recurred in the Champlin Unit, and the plant has operated well below the sulfur emission levels guaranteed by Shell and required by APCD regulations.

Performance Testing and Compliance

The performance of the Champlin SCOT unit has been tested by the Los Angeles APCD emission source test team. They found that the emission level was considerably below the statutory limits of 500 ppm sulfur dioxide. The plant has also been subject to a lengthy test by the mobile laboratory of the EPA with similar findings. Performance tests made by Shell Development Co. proved that the Champlin Plant met and exceeded its guarantee level of 500 ppm hydrogen sulfide in absorber offgas and that the selectivity of the solvent for hydrogen sulfide exceeded expectations.

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Commercialization of Lime–Limestone Flue Gas Scrubbing Technology

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Research-Cottrell has demonstrated the commercial availability of limestone flue gas desulfurization on a 115 MW installation. Certain chemistry and process considerations were taken into account in designing and operating these systems. Methods have been developed to minimize the occurrence of potential problems.

Since the first large sulfur dioxide control system was installed at the Battersea plant in London, it has taken almost 50 yrs for calcium-based scrubbing technology to become commercially acceptable. In 1926, the 125 MW coal-fired Battersea power plant was equipped with a spray packed tower and final alkaline wash section which removed more than 90% of the sulfur dioxide and particulate (1). Thames River water provided most of the alkali for absorption, and about 20% was made up from lime addition. The process operated in an open-loop manner, returning spent reagent to the Thames.

Subsequent programs to prevent water and air pollution supported by Imperial Chemicals Industries Ltd., British Power Authority consultants, and Howden Construction Co. led to the development of a closed-loop, lime-based, sulfur dioxide removal system. These types of systems were installed in 1935 at the Swainsea and in 1937 at the Fulham power plants. They operated successfully until World War II when they were shutdown because the vapor plumes provided aerial guidance to the Luftwaffe.

For the next 20 yrs no full-scale development work was performed in this area. In fact, during the mid-sixties, there were several steps backward when initial U.S. sulfur dioxide control systems started up and failed. For example, in the boiler injection of limestone followed by wet scrubbing, problems resulted from boiler and preheater pluggage rather than flue gas scrubbing.

Current Industry Status

During the last 3 yrs more progress has been made in calcium scrubbing technology than during the preceding quarter of a century. Presently 2500 MW of calcium-based scrubbers are operating with another 7600 MW under construction (2). Many of the initially installed units experienced difficulties, but the newer installations have performed better as the pollution control industry has gained confidence and experience.

EPA and pollution industry-supported development programs have confirmed many of the process constraints established during the original Howden-ICI projects (3). This is not to say that we have made a full circle and have learned no more than was available 25 yrs ago. However, if our initial development programs had been based on prior research results, we would probably be further ahead today. The major improvements in current processes result from the application of modern technology and operating techniques to extend system reliability.

Research-Cottrell's Status

In the mid-1960's Research-Cottrell entered the sulfur dioxide control field as an expert in particulate collection but as a novice in gaseous removal. Initial investigations used a flooded disc scrubber (FDS), which is essentially a high energy venturi requiring 8-10 in. w.c. pressure drop for 40-60% sulfur dioxide removal. Installing a series of FDS's to improve absorption efficiency required excessive pressure losses. Therefore, Research-Cottrell began investigations of the FDS in combination with a packed tower to increase sulfur dioxide removal at moderate pressure drops.

The pilot plant studies started in 1966 and have continued ever since. Pilot units have been installed at the Tidd Station of American Electric Power, the Cholla Station of Arizona Public Service, the Big Brown Station of Texas Utilities, and Research-Cottrell's Finderne Research facility. Development studies have been supported by EPA, by joint efforts with utilities, and by this company (4, 5, 6).

As a direct result of this pilot effort, a wetted film packing was found which exhibits excellent sulfur dioxide absorption with an exceptionally low pressure drop. This packing has outstanding mass transfer characteristics and high specific surface area. The packing developed by Munters Corp. is a key element in the limestone-based sulfur dioxide removal system.

Last October Research-Cottrell started up its first gas cleaning system, a 115 MW limestone wet scrubbing system at Arizona Public Service's Cholla plant. In this unit particulate and sulfur dioxide are

removed by a FDS-packed tower arrangement. Because of the results obtained at this commercial facility and from the pilot units, the Arizona Public Service awarded an additional contract for gas cleaning equipment on a new 250 MW boiler. In addition, the company is engineering 1900 MW of sulfur dioxide removal equipment for several major southwestern utilities.

Research-Cottrell realized that the industrial and utility markets required different types of sulfur dioxide removal equipment. Therefore, it contracted with Ab Bahco Ventilation of Sweden to market their sulfur dioxide removal technology in the U.S. and Canada. Bahco technology is particularly applicable to industrial boiler and process applications (7, 8, 9). The first U.S. Bahco installation will handle seven stoker-type boilers at the Rickenbacker Air Force Base in Columbus, Ohio.

Comparison of Lime-Limestone Wet Scrubbing with Other Systems

Since the utility industry represents the major market for sulfur dioxide control systems, it was necessary to develop a simple system which would not require a lot of attention, be inexpensive to operate, have moderate capital requirements, and not take effort away from their power producing function. Calcium-based scrubbing processes meet all of these requirements. In addition, the calcium reagents are inexpensive and form relatively insoluble reaction products which can be disposed of in sanitary landfills and slurry ponds.

The disadvantage of calcium-based technology is the low salt solubility which necessitates the use of very large absorbing surface areas, high liquid flow rates, and good pH control to prevent scaling and plugging. Most recent technological advances are in the areas of calcium salt scale prevention and controlled crystallization.

Soluble-based systems have better absorption capabilities and limited scaling and plugging problems. However they have problems associated with soluble salt disposal and higher reagent costs. The waste disposal problems have limited their application.

By-product processes have the advantages of soluble-based systems but have problems associated with more complex operation, increased capital and operating costs, and the need to develop by-product markets. Therefore, Research-Cottrell initially chose to develop calcium-based scrubbing technology to best meet the existing needs of its customers.

System Description

Figure 1 illustrates the components of a typical calcium-based sulfur dioxide scrubbing system. Flue gases enter a quenching section where

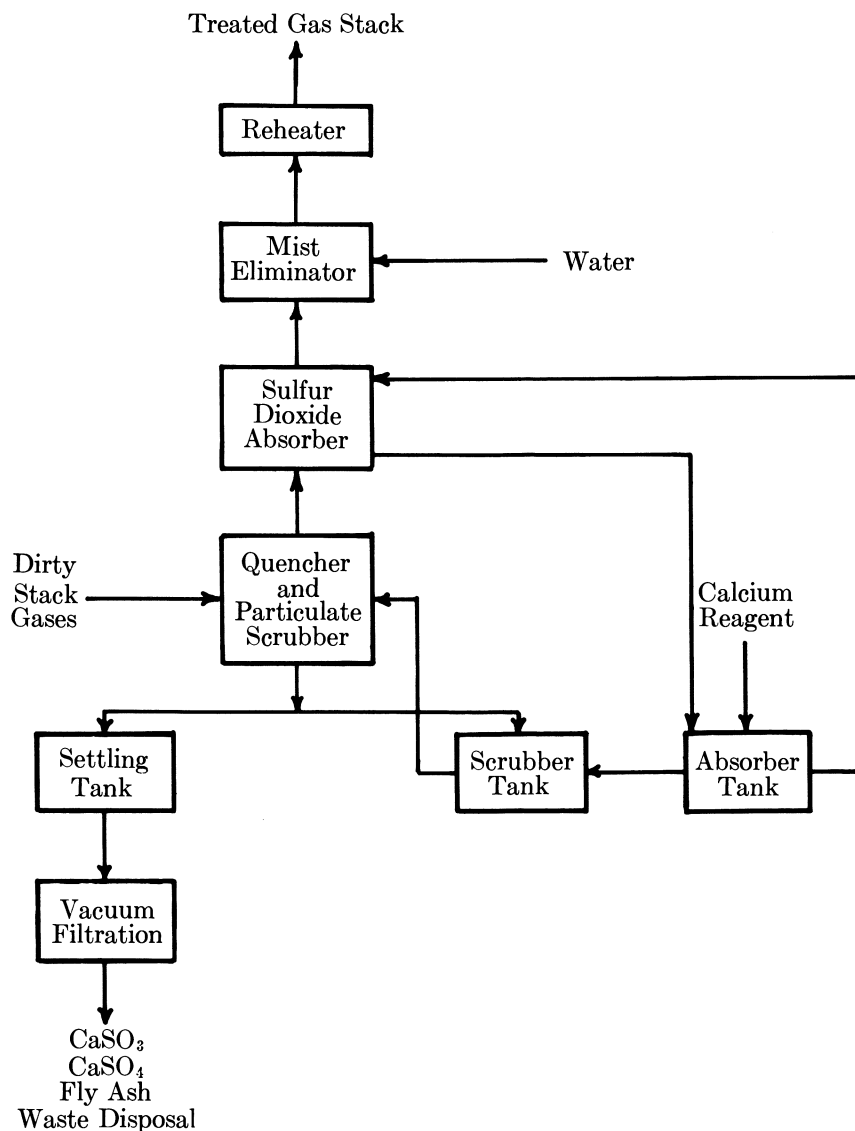


Figure 1. Typical calcium-based sulfur dioxide scrubbing system

the gas is cooled and particulate and some sulfur dioxide removal takes place. The quenched gas then enters the absorption section where the remaining sulfur dioxide is removed. Finally a mist eliminator removes water and reagent droplets. The cleaned gas is reheated and returned to the stack.

Calcium reagent is added to the absorber tank and pumped to the sulfur dioxide absorber. Most of the spent reagent is returned to the absorber tank, and part is provided as reagent make-up to the quencher system. The spent quencher reagent, containing particulate and reaction salts, is removed from the process as a sludge blow down. Make-up water, to compensate for evaporation losses and sludge blow down, is added primarily as mist eliminator wash.

Using this general approach, several sulfur dioxide removal systems have been developed. Figure 2 illustrates the Cholla sulfur dioxide removal system where a moderate energy scrubber is used for particulate removal, gas quenching, and incidental sulfur dioxide removal. The packed tower is the major sulfur dioxide absorption device. Make-up reagent is supplied to the packed tower, and the FDS receives spent reagent from the packed-tower system. Thus reagent flow is countercurrent to gas flow for maximum utilization.

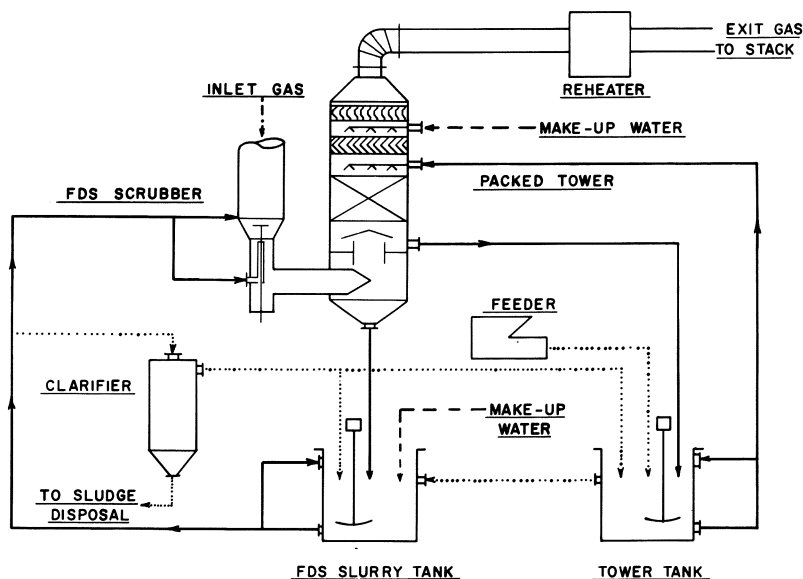


Figure 2. Process flow diagram

Research-Cottrell is also supplying a gas cleaning system using an electrostatic precipitator for dry particulate collection followed by a multi-stage gas liquid contactor for sulfur dioxide removal. The first stage is a cyclonic quencher for gas saturation and moderate sulfur dioxide absorption followed by a spray and packed-tower section where the major sulfur dioxide absorption takes place. Again the reagent is applied countercurrent to the gas flow.

Process Chemistry

The chemistry involved in lime-limestone scrubbing is very complex because of the limited solubility of the numerous reagents and reaction products. The major components are:

Reagent: Ca, Mg, CO₃, OH

Flue gas: SO₂, SO₃, CO₂, O₂, NO, NO₂, N₂

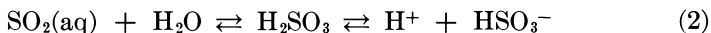
Fly ash: Na, Cl, K, Fe, Ca, Mg, Si

The main reactions in calcium based scrubbing are:

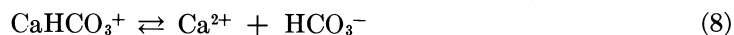
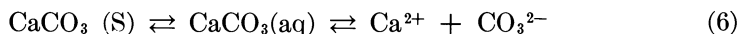
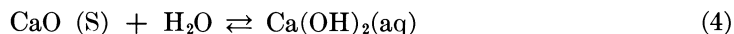
1. Diffusion of sulfur dioxide from the gas phase into the liquid phase,



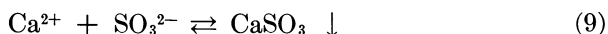
2. Hydrolysis to form sulfurous acid, bisulfite, sulfite, and hydrogen ions,



3. Dissolution and hydration of lime or limestone in an acid medium containing carbon dioxide from the flue gas to form calcium and bicarbonate ions,



4. Reaction of calcium ions from calcium oxide, calcium hydroxide, or calcium carbonate with sulfite ions from sulfuric acid to form and precipitate calcium sulfite.



There is data indicating that the hydration of sulfur dioxide to sulfuric acid, H⁺, and HSO₃⁻, the dissociation of HSO₃⁻ to SO₃²⁻, the reaction of lime and limestone in an acidic medium to form Ca²⁺ ions, and the final reaction of Ca²⁺ and SO₃²⁻ ions to precipitate calcium sulfite are rapid reactions (10). The rate controlling mechanisms are, therefore, either

gas or liquid diffusion, hydration of calcium oxide, or dissolution of the calcium carbonate or calcium hydroxide salts.

In most cases, the gas phase mass transfer sulfur dioxide and the source of calcium reagent, its introduction into the system, and its dissolution are the controlling reactions. Reaction rates are increased by minimizing the gas-liquid interface resistance, maximizing contact surface area, and increasing dissolution rates. The solid-phase calcium source is important in this consideration. Naturally occurring calcium carbonate (limestone) reacts slowly with weak acids. However, freshly precipitated calcium carbonate formed by carbonation of calcium hydroxide with the carbon dioxide from the flue gas has a higher specific surface area than limestone and dissolves faster. When carbon dioxide is not present, an even faster reaction occurs between calcium hydroxide and sulfur dioxide since calcium hydroxide has a higher solubility than calcium carbonate. Increasing gas velocity and reactant contact area increases the gas phase sulfur dioxide mass transfer rate. Reactant contact area is enhanced by smaller reagent particle size and higher reagent liquid rates, stoichiometry, calcium salt concentrations, and liquid hold-up.

At low sulfur dioxide concentrations (<1000 ppm) gas diffusion is the controlling reaction. There is negligible liquid-phase resistance because sufficient absorbent is being dissolved to react with the sulfur dioxide. However, at increased sulfur dioxide concentrations liquid-phase resistance may become controlling. In this case the rate of absorbent dissolution may not increase fast enough to react with the sulfur dioxide.

Commercial System Design

Sulfur dioxide and particulate removal are more easily controlled than the scaling and plugging which reduces system availability. System reliability was of paramount importance in the design of Research-Cottrell's various sulfur dioxide control systems. Information developed in the Howden-ICI programs provided the technical background from which the areas of concern could be investigated and better defined. Recent EPA studies have supported many of the concepts expressed by Howden-ICI and investigated by Research-Cottrell in its development programs (3).

The areas which were found to be particularly important are: absorption surface selection, control of reagent desupersaturation, reagent pH profiles, and closed-loop water balance.

Absorption Surface Selection

In the selection of the absorption surface the following requirements must be considered:

1. Provide even liquid and gas flow distribution
2. Be non-choking with regard to solids
3. Have good absorption characteristics
4. Handle a wide range of liquid rates without flooding
5. Have adequate gas turn down characteristics
6. Have a low pressure drop
7. Have a high surface/volume ratio
8. Have a resistance to scale formation
9. Have reasonable capital and operating economics.

Research-Cottrell's process uses a Munters' polypropylene wetted film packing. The cross flow flutes aid in uniform liquid and gas flow distribution. The packing has a specific surface area of 40–70 ft²/ft³ and good absorption characteristics.

Table I. Calculated Flooding Points for High Capacity Packings

Gas Velocity (ft/sec)	Liquid/Gas Ratio (gal/1000 ACF)		
	<i>Munters</i> <i>Packing</i>	<i>Pall</i> <i>Rings</i>	<i>Intalox</i> <i>Saddles</i>
4	690	580	420
8	190	130	90
12	85	47	22
24	16	—	—

Table I lists calculated flooding mass velocities for Munters and other high capacity packings. Munters' packing can tolerate a wider range of conditions without flooding. Table II lists the mass transfer coefficients obtained in the experimental work with Munters packing (6).

Control of Reagent Desupersaturation

The reagent stream must be controlled to permit calcium salt desupersaturation external to the scrubber and absorber while maintaining adequate concentration levels for good absorption efficiency. In order to do this a reagent stream containing 8–15% solids is circulated. The solid portion is composed of some fly ash components but mainly calcium carbonate, sulfite, and sulfate. Sulfur dioxide removal efficiency dictates the carbonate level. Sulfite crystals enhance and control desupersaturation of calcium sulfate while providing nucleation sites for crystal growth (11).

In the absorber tank, time for external desupersaturation is provided and fresh reagent is added to raise the pH and thereby promote desupersaturation of the spent reagent stream. The delay tank provides contact time for crystal growth and sulfite and sulfate salt precipitation.

Table II. Mass Transfer Coefficients with High Sulfur Coal–Limestone Scrubbing

<i>Sulfur Dioxide Inlet Concentration (ppm)</i>	<i>Limestone Stoichiometry (%)</i>	<i>Mass Transfer Coefficient (lb-moles/hr sq ft atm)^a</i>
1000	100	.385
1000	120	.510
1000	140	.843
1600	100	.252
1600	120	.308
1600	140	.385

^a Packing = 68 sq ft/cu ft, height = 5 ft, G = 70 lb-moles/hr sq ft, P = 1.0 atm, Limestone grind = 75%–200 mesh, L/G = 45 gals MCF.

Reagent pH Profiles

Liquid reagent pH profiles must be controlled to prevent major pH changes in the scrubber which will change salt saturation levels and cause precipitation and eventual scale formation. The Research–Cottrell limestone process controls the quantity of sulfur dioxide removed in each absorption stage and the contact time for each processing step, making it possible to maintain the pH and sulfur dioxide concentration within desired levels. By measurement of the mass flow of sulfur dioxide into the scrubbing system, reagent addition is controlled at about 90% utilization. As a result, the slurry entering the scrubber circuit has a pH of 6.5 and exists at about a pH 5.8. The slurry pH is used only to monitor the process and not to control it since the system is highly buffered by the action of carbonate–bicarbonate and sulfite–bisulfite and does not react readily to reagent feed rate changes. However, in a lime-based scrubbing system pH profiles are more distinct and some control schemes are possible.

Water Balance Maintenance

Thickening, filtration, and centrifugation are generally used to reduce the water content of calcium salts produced in the process. Spent water which is saturated with various salts is returned to the system. Only water contained in the effluent sludge and evaporated in the quenching operation leave the process. The quantity of make-up water is very limited, and considerable thought must be given to where and how it is used in the system.

Pump seals and demister wash receive priority on fresh water additions. In the Research–Cottrell process, two demisting stages insure adequate mist removal. Water sprays are mounted below and above the

first demister to keep it free from salt deposits and to provide a relatively salt-free mist to the second demisting stage.

Conclusion

The pollution control industry has made significant technical contributions to the sulfur dioxide control field. As we gain more experience, process reliability will increase and operating and investment costs will decrease. Customer acceptance will improve when it is realized that pollution control equipment permits greater flexibility in fuel selection and possibly reduced fuel expenses.

Prior to the energy crisis, it could be demonstrated that the cost differential between high and low sulfur fuels would balance the increased expenses for operating pollution control equipment. With the current erratic fuel pricing situation it is difficult to make such a comparison. However, Research-Cottrell offers processes capable of meeting federal particulate and sulfur dioxide requirements and thereby allows the user more freedom in his fuel selection.

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Lime–Limestone Scrubbing: Factors Affecting the Concentration of Sulfur Dioxide-Absorbing Species in Solution

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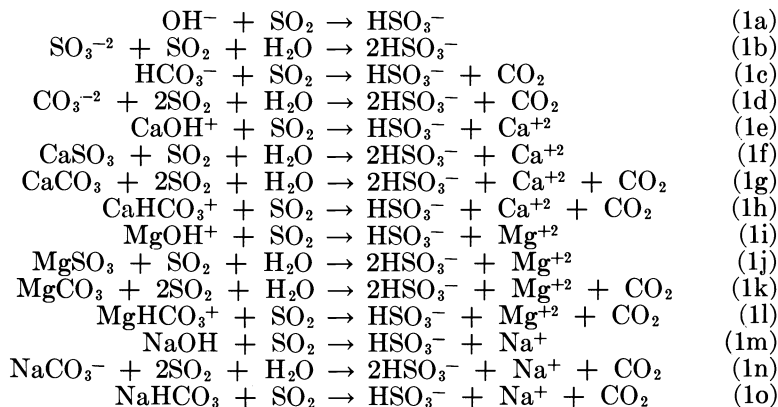
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The basicity of the aqueous phase in lime and limestone slurries for scrubbing a sulfur dioxide stack gas is increased by increasing the magnesium content in solution and by other factors less subject to control. The computer simulation study of the aqueous phase of the system $\text{CaO-MgO-Na}_2\text{O-SO}_2\text{-SO}_3\text{-CO}_2\text{-HCl-N}_2\text{O}_5\text{-H}_2\text{O}$ included variations in the contents of magnesium oxide, sodium oxide, and hydrochloric acid at various values of pH and carbon dioxide partial pressures and for several degrees of saturation of the salts $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Sodium and chloride largely offset each other. Complex interrelations between the pH, the degree of saturation of $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$, and the carbon dioxide partial pressures occur at constant composition of other components, giving essentially isobasic solutions.

The removal of sulfur dioxide from stack gas by scrubbing with a suspension of lime or limestone involves dissolution, precipitation, and oxidation in a nine-component system: $\text{CaO-MgO-Na}_2\text{O-SO}_2\text{-SO}_3\text{-CO}_2\text{-HCl-N}_2\text{O}_5\text{-H}_2\text{O}$. Other components also are present, but their concentrates are not significant. All alkali components—sodium, potassium, and ammonium oxides—are considered as sodium oxide. Lowell (1) has summarized the present knowledge of the chemical data for the aqueous system including parameters for activity coefficients, solubility products, Henry's Law constants, and ionization constants for aqueous species. This paper is concerned with the basicity of the aqueous phase of the system, because the mass transfer of sulfur dioxide from the stack

gas to the liquid is dependent largely on the availability of basic species to absorb the acidic gas. A computer simulation study was made of factors that affect the total basicity of the aqueous phase.

Species in solution are considered basic to sulfur dioxide if they will react with sulfur dioxide to form a bisulfite (HSO_3^-) species. In the nine-component system under consideration the following reactions may occur:



Thus, if the total number of equivalents of basic species in a given volume of liquid is equal to the number of moles of sulfur dioxide in the volume of gas contacted by the liquid, the stoichiometry is satisfied and there should be as complete sulfur dioxide absorption as mass transfer allows, provided the sulfur dioxide partial pressure of the resulting solution is sufficiently low.

System $\text{CaO-SO}_2\text{-SO}_3\text{-CO}_2\text{-H}_2\text{O}$

To define a set of variables representing the nine-component system, equilibrium was studied in the five-component system, $\text{CaO-SO}_2\text{-SO}_3\text{-CO}_2\text{-H}_2\text{O}$. In this system, a knowledge of four properties is sufficient to define the aqueous phase composition and the concentration of all aqueous species. These properties may be chosen from the total concentration of components, the activities of any aqueous species, the degrees of saturation of any solids, or the partial pressures of any gases—provided no two chosen properties involve a single component solely. Experience in determining liquid phase properties from pilot plant samples at various points in the limestone scrubbing system indicated that the pH varied from 4.5 to 8; the degree of supersaturation of $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$, S_1 , varied from 2 to 12, and of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, S_2 , from 1 to 2; and the partial pressure of carbon dioxide varied from very low values over ponds and hold tanks to about 0.15 atm in the stack gas. We chose, therefore, to

Table I. Liquid Phase Compositions in the

No.	<i>mmoles/kg H₂O</i>			<i>P_{CO₂}</i> (atm)			
	<i>CaO</i>	<i>SO₂</i>	<i>SO₃</i>	<i>pH</i>	<i>S₁^a</i>	<i>S₂^a</i>	<i>BASE^b</i>
1	21.35	3.26	19.41	5.5	2.0	1.25	0.629
2	20.61	0.907	19.83	6.5	2.0	1.25	0.644
3	25.48	11.74	18.38	5.5	8.0	1.25	2.489
4	22.70	3.60	19.63	6.5	8.0	1.25	2.534
5	30.40	2.79	28.69	5.5	2.0	1.953	0.621
6	29.77	0.845	29.03	6.5	2.0	1.953	0.634
7	34.20	10.46	27.74	5.5	8.0	1.953	2.464
8	31.80	3.36	28.87	6.5	8.0	1.953	2.496
9	29.71	14.10	22.06	5.0	4.0	1.563	1.232
10	25.32	1.41	23.96	7.0	4.0	1.563	1.295
11	24.46	0.705	23.95	6.0	1.0	1.563	0.317
12	30.77	10.64	22.97	6.0	16.0	1.563	4.972
13	18.35	3.13	16.15	6.0	4.0	1.00	1.274
14	36.92	2.49	35.06	6.0	4.0	2.441	1.235
15	25.74	2.78	23.72	6.0	4.0	1.563	1.254

$$^a S_1 = a_{Ca^{+2}} \cdot a_{SO_3^{-2}} \cdot a_{H_2O^{+5}} / K_{sp}(CaSO_3 \cdot 0.5H_2O)$$

$$S_2 = a_{Ca^{+2}} \cdot a_{SO_4^{-2}} \cdot a_{H_2O^2} / K_{sp}(CaSO_4 \cdot 2H_2O)$$

fix the values of the pH of the solution, the values of S_1 and S_2 for supersaturation of calcium sulfite and sulfate salts, and the partial pressure of carbon dioxide at various levels. Fifteen solutions were simulated at a carbon dioxide partial pressure of 0.0003 atm (the normal carbon dioxide content of the earth's atmosphere) in a Box-type central composite design (2) in the three variables: pH, S_1 , and S_2 . The solution composition was calculated, and the contents of the components calcium oxide, sulfur dioxide, and sulfur trioxide were held constant while the partial pressure of carbon dioxide was increased from 0.0003 to 0.15 and again to 1.0 (pure carbon dioxide). The results (Table I) are reported in terms of the sum of all basic species (BASE) and show the effect of increasing P_{CO_2} at constant composition upon pH, S_1 , and S_2 .

The fixed levels selected for pH, S_1 , and S_2 are listed in columns 5, 6, and 7 of Table I for the atmospheric conditions, *i.e.*, where the partial pressure of carbon dioxide, P_{CO_2} , is 0.0003 atm. The compositions of the liquid in terms of concentrations of calcium oxide, sulfur dioxide, and sulfur trioxide that satisfy these fixed levels of pH, S_1 , S_2 , and P_{CO_2} are given in columns 2, 3, and 4. The P_{CO_2} was increased to 0.15 and 1.0 atm, the contents of calcium oxide, sulfur dioxide, and sulfur trioxide were held constant, and new values of pH, S_1 , and S_2 were calculated. The sums of all basic species, BASE, are given in columns 8, 12, and 16. The first eight compositions represent the factorial portion (cube) of the design; the next six compositions show the variation of each variable to

System $\text{CaO-SO}_2\text{-SO}_3\text{-CO}_2\text{-H}_2\text{O}$ at 122°F

P_{CO_2} (atm)							
0.15				1.0			
pH	S_1^a	S_2^a	BASE^b	pH	S_1^a	S_2^a	BASE^b
5.18	1.07	1.256	0.639	4.64	0.33	1.259	0.684
5.41	0.46	1.260	0.653	4.70	0.10	1.261	0.694
5.38	6.44	1.257	2.492	5.03	3.29	1.271	2.509
5.82	3.86	1.276	2.537	5.20	1.29	1.291	2.549
5.16	1.05	1.959	0.634	4.62	0.33	1.961	0.684
5.37	0.47	1.963	0.646	4.67	0.11	1.963	0.694
5.37	6.38	1.961	2.468	5.02	3.21	1.976	2.487
5.78	3.90	1.979	2.499	5.17	1.33	1.993	2.516
4.93	3.44	1.565	1.239	4.67	1.98	1.570	1.275
5.65	1.21	1.581	1.300	4.95	0.31	1.586	1.325
5.12	0.21	1.567	0.335	4.46	0.05	1.566	0.407
5.77	12.02	1.583	4.973	5.35	5.98	1.612	4.983
5.53	1.91	1.013	1.279	4.93	0.57	1.021	1.300
5.48	1.88	2.454	1.244	4.88	0.57	2.461	1.274
5.51	1.90	1.576	1.260	4.91	0.57	1.583	1.285

^b BASE = millimoles/kg H_2O of total aqueous species that are basic to HSO_3^- (see Equations 1a-1o).

extreme levels (octahedron); and the last composition is the center of the design.

The data in Table I show an excellent correlation (Figure 1) of all the values of BASE with the degree of supersaturation of calcium sulfite at $P_{\text{CO}_2} = 0.0003$ and no significant effect of pH , S_2 , or P_{CO_2} at constant composition of calcium oxide, sulfur dioxide, and sulfur trioxide upon the

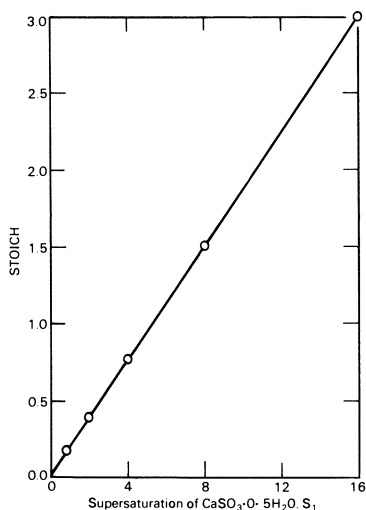


Figure 1. Effect of calcium sulfite supersaturation on the concentration of the absorbing species in the liquid phase. $P_{\text{CO}_2} = 0.0003$ atm.

simulated response, BASE. Increasing the partial pressure of carbon dioxide at constant composition of the other components decreases both the pH and S_1 greatly, whereas the values of S_2 and BASE are affected only slightly. Figures 2 and 3 show the changes in pH and S_1 , respectively, with increase in P_{CO_2} for various values of the variables.

The effect of S_1 on BASE implies the predominant influence at low P_{CO_2} of the aqueous species calcium sulfite which reacts according to Equation 1f. The aqueous equilibria



among ions, neutral species, and solid involve two constants. K_8 , the dissociation constant of the aqueous species calcium sulfite and K_{15} , the solubility product. The constants are numbered in the order listed in Table IV-2 of Lowell (1). At saturation, $S_1 = 1.0$, the activity of the basic species, calcium sulfite, equals the ratio K_{15}/K_8 , which is independent of pH or any other solution property. An increase in the degree of saturation of $CaSO_3 \cdot 0.5H_2O$ causes a corresponding increase in the activity of the aqueous species calcium sulfite, that is

$$M_{CaSO_3} \cong a_{CaSO_3} = S_1 \cdot K_{15}/K_8 \quad (3)$$

Thus, the linear relation of BASE with S_1 shown in Figure 1 is caused by the increase in the species calcium sulfite in solution which is the pre-

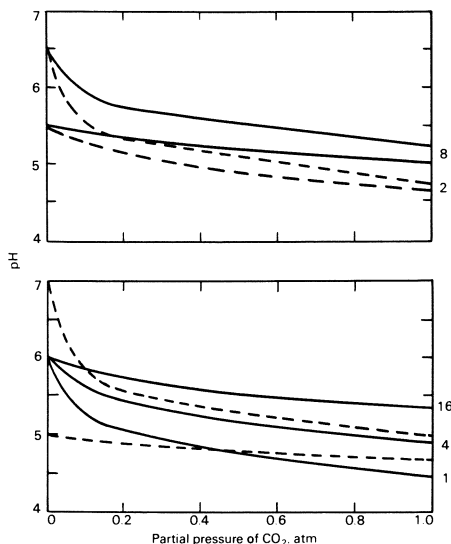


Figure 2. Effect of CO_2 pressure on the pH of simulated solutions in the system $CaO-SO_2-SO_3-CO_2-H_2O$. Numbers on curves indicate degree of supersaturation of $CaSO_3 \cdot 0.5H_2O$, S_1 , when $P_{CO_2} = 0.0003$.

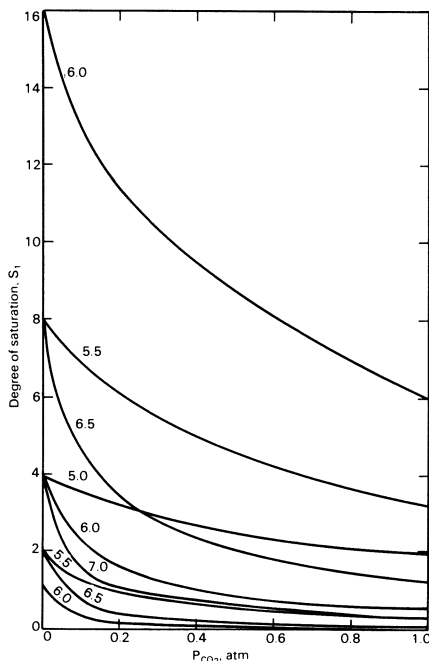


Figure 3. Effect of CO_2 pressure on the degree of saturation of $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$. Numbers on curves denote pH when $P_{\text{CO}_2} = 0.0003$.

dominant basic specie at low carbon dioxide partial pressures. As P_{CO_2} increases at constant composition, S_1 (and, therefore, the amount of calcium sulfite) decreases by being replaced by the basic carbonate species, CaCO_3 and CaHCO_3^+ .

The results of the five-component study show that at low values of P_{CO_2} the factor S_1 is more important than pH in determining the basic species concentration. However, the interrelations between pH, S_1 , and P_{CO_2} (Figures 2 and 3) show that all three factors are important in correlations with the basicity of the simulated solutions. The degree of saturation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, S_2 , has no appreciable effect and can be eliminated from consideration. The effect of the carbon dioxide partial pressure would be expected to depend on the level of S_1 , the pH, and the concentration of other cations that form basic carbonate species in solution.

System $\text{CaO-MgO-Na}_2\text{O-SO}_2\text{-SO}_3\text{-CO}_2\text{-HCl-N}_2\text{O}_5\text{-H}_2\text{O}$

Choice of Variables. Determining the properties of the aqueous phase in the full system requires the same procedure, except that eight properties must be known. We have chosen to fix two quantities in order to reduce the variables to a more manageable number for study. The fixed quantities were saturation with gypsum ($S_2 = 1.0$) because of its minor influence on basicity and $\text{N}_2\text{O}_5 = 10^{-6}$ equivalents/kg water be-

cause nitrate forms no sulfur dioxide reacting species and its effect could be expected to be similar to that of chloride. The six variables chosen for study are shown in Table II.

Table II. Six Variables in the Full System

Coded Factor	Name	Coded Levels				
		-2	-1	0	1	2
x ₁	pH	5.0	5.5	6.0	6.5	7.0
x ₂	saturation degree of CaSO ₃ · 0.5H ₂ O, S ₁	0	1	2	3	4
x ₃	total Mg (mm/kg H ₂ O)	0	50	100	150	200
x ₄	total Na (mm/kg H ₂ O)	0	50	100	150	200
x ₅	total Cl (mm/kg H ₂ O)	0	50	100	150	200
x ₆	P _{CO₂} (atm)		0.0003	0.075	0.15	

Experimental Design. The Box-type central composite design (2) was used for the first five factors, x₁-x₅, with each test made at all three levels of carbon dioxide partial pressure, x₆. The values of BASE are listed in Table III for the simulated solutions, and in Table IV the fractions of BASE caused by magnesium and sodium species are given. There is an important difference between these tables and Table I. In Tables III and IV, the five factors, x₁-x₅, were kept constant as P_{CO₂} was increased from 0.0003 to 0.075 and 0.15, allowing the composition to change. In Table I the composition of calcium oxide, sulfur dioxide, and sulfur trioxide was kept constant as P_{CO₂} was increased, allowing the properties of pH, S₁, and S₂ to change.

Figure 4 shows the effects of pH and P_{CO₂} on the basicity when the degree of supersaturation of calcium sulfite is 2.0 and the contents of Mg, Na, and Cl each are 100 mmoles/kg H₂O. These fixed conditions are the values at the design center and are in the range that occurs frequently in limestone scrubbing. The increase in basicity with increased P_{CO₂} is extremely great at high pH, indicating that additional basic carbonate species add greatly to the sulfur dioxide absorption capacity at high pH. Increasing the partial pressure of carbon dioxide at constant pH, S₁, and magnesium content causes a very slight decrease in the concentration of total sulfite at all isopleths of pH. However, there is a 0.1% increase in calcium content at pH 5.0 and a 15% increase at pH 7.0 at a supersaturation of 2.0 for calcium sulfite as P_{CO₂} changes from 0.0003 to 0.15 atm. The additional carbonate that goes into solution also decreases the sulfate content to maintain electroneutrality and to satisfy the gypsum saturation.

Figure 5 shows the effects at pH 6.0 on the basicity of each of the variables, S₁, Mg, Na, and Cl, at three levels of P_{CO₂}. In each case the other variables were held at their values corresponding to the center of the design. The effect of the supersaturation of calcium sulfite is linear

Table III. The Basicity of the Liquid Phase as Affected by Solution Properties at 122°F

<i>Solution Properties</i>		<i>BASE^a (mmoles/kg H₂O) When P_{CO₂} (atm) is</i>					
<i>pH</i>	<i>S₁^b</i>	<i>mmoles/kg H₂O</i>			<i>0.0003</i>	<i>0.075</i>	<i>0.15</i>
		<i>Mg</i>	<i>Na</i>	<i>Cl</i>			
5.5	1	50	50	50	0.641	1.006	1.373
6.5	1	50	50	50	0.661	4.351	8.070
5.5	3	50	50	50	1.870	2.235	2.602
6.5	3	50	50	50	1.934	5.608	9.312
5.5	1	150	50	50	1.395	1.812	2.230
6.5	1	150	50	50	1.425	5.651	9.900
5.5	3	150	50	50	4.053	4.468	4.887
6.5	3	150	50	50	4.178	8.372	12.592
5.5	1	50	150	50	0.780	1.154	1.531
6.5	1	50	150	50	0.804	4.571	8.359
5.5	3	50	150	50	2.272	2.647	3.022
6.5	3	50	150	50	2.353	6.106	9.880
5.5	1	150	150	50	1.556	1.978	2.403
6.5	1	150	150	50	1.586	5.868	10.171
5.5	3	150	150	50	4.525	4.947	5.370
6.5	3	150	150	50	4.654	8.907	13.181
5.5	1	50	50	150	0.447	0.862	1.279
6.5	1	50	50	150	0.465	4.674	8.935
5.5	3	50	50	150	1.322	1.739	2.155
6.5	3	50	50	150	1.352	5.554	9.809
5.5	1	150	50	150	1.104	1.548	1.993
6.5	1	150	50	150	1.132	5.639	10.176
5.5	3	150	50	150	3.220	3.663	4.106
6.5	3	150	50	150	3.311	7.788	12.296
5.5	1	50	150	150	0.598	0.991	1.387
6.5	1	50	150	150	0.618	4.588	8.588
5.5	3	50	150	150	1.752	2.145	2.541
6.5	3	50	150	150	1.805	5.762	9.750
5.5	1	150	150	150	1.313	1.753	2.195
6.5	1	150	150	150	1.342	5.808	10.298
5.5	3	150	150	150	3.827	4.266	4.708
6.5	3	150	150	150	3.934	8.369	12.831
5.0	2	100	100	100	1.837	1.966	2.096
7.0	2	100	100	100	2.004	15.360	28.878
6.0	0	100	100	100	0.007	1.294	2.587
6.0	4	100	100	100	3.811	5.088	6.370
6.0	2	0	100	100	0.658	1.792	2.934
6.0	2	200	100	100	3.489	4.915	6.346
6.0	2	100	0	100	1.531	2.834	4.145
6.0	2	100	200	100	2.250	3.547	4.850
6.0	2	100	100	0	2.401	3.628	4.859
6.0	2	100	100	200	1.448	2.826	4.213
6.0	2	100	100	100	1.939	3.221	4.508

^a Σ aqueous species basic to HSO_3^-

^b Degree of saturation of calcium sulfite

Table IV. Fraction of Basic Species Caused by Magnesium and Sodium at 122°F

<i>Solution Properties</i>					<i>Fraction as Mg and Na Species When P_{CO_2} (atm) is</i>		
<i>pH</i>	<i>S₁^a</i>	<i>mmoles/kg H₂O</i>			<i>0.0003</i>	<i>0.075</i>	<i>0.15</i>
		<i>Mg</i>	<i>Na</i>	<i>Cl</i>			
5.5	1	50	50	50	0.401	0.287	0.233
6.5	1	50	50	50	0.397	0.138	0.117
5.5	3	50	50	50	0.394	0.343	0.307
6.5	3	50	50	50	0.398	0.195	0.153
5.5	1	150	50	50	0.654	0.542	0.471
6.5	1	150	50	50	0.649	0.296	0.245
5.5	3	150	50	50	0.650	0.605	0.568
6.5	3	150	50	50	0.650	0.411	0.331
5.5	1	50	150	50	0.396	0.297	0.247
6.5	1	50	150	50	0.392	0.148	0.124
5.5	3	50	150	50	0.393	0.350	0.318
6.5	3	50	150	50	0.393	0.209	0.165
5.5	1	150	150	50	0.643	0.541	0.475
6.5	1	150	150	50	0.639	0.301	0.248
5.5	3	150	150	50	0.641	0.600	0.566
6.5	3	150	150	50	0.639	0.416	0.337
5.5	1	50	50	150	0.283	0.193	0.162
6.5	1	50	50	150	0.281	0.120	0.111
5.5	3	50	50	150	0.279	0.235	0.208
6.5	3	50	50	150	0.282	0.145	0.125
5.5	1	150	50	150	0.632	0.506	0.436
6.5	1	150	50	150	0.627	0.288	0.250
5.5	3	150	50	150	0.627	0.574	0.532
6.5	3	150	50	150	0.628	0.381	0.314
5.5	1	50	150	150	0.363	0.260	0.216
6.5	1	50	150	150	0.360	0.143	0.127
5.5	3	50	150	150	0.358	0.311	0.278
6.5	3	50	150	150	0.360	0.187	0.154
5.5	1	150	150	150	0.641	0.527	0.459
6.5	1	150	150	150	0.636	0.299	0.255
5.5	3	150	150	150	0.637	0.591	0.553
6.5	3	150	150	150	0.637	0.402	0.329
5.0	2	100	100	100	0.546	0.520	0.496
7.0	2	100	100	100	0.544	0.216	0.194
6.0	0	100	100	100	0.229	0.145	0.144
6.0	4	100	100	100	0.549	0.445	0.383
6.0	2	0	100	100	0.000	0.016	0.020
6.0	2	200	100	100	0.703	0.560	0.481
6.0	2	100	0	100	0.525	0.351	0.286
6.0	2	100	200	100	0.547	0.399	0.330
6.0	2	100	100	0	0.562	0.413	0.339
6.0	2	100	100	200	0.499	0.334	0.277
6.0	2	100	100	100	0.552	0.388	0.317

^a Degree of saturation of calcium sulfite

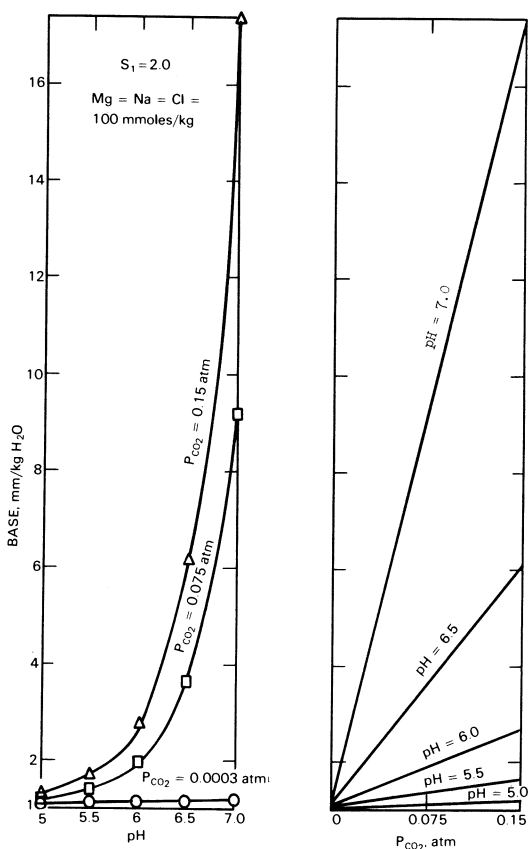


Figure 4. Effects of pH and P_{CO_2} of liquid phase on its basicity for SO_2 absorption

at constant values of Mg, Na, and Cl, and the isobars of carbon dioxide partial pressure are parallel. The simulated basicity response caused by increasing the magnesium content is slightly concave upward, particularly at $P_{CO_2} = 0.15$ atm. Increasing the sodium content or decreasing the chloride content causes the basicity to increase approximately linearly. In each case the isobars of carbon dioxide partial pressure show an increase in basicity resulting from the additional carbonate species. Increasing the magnesium and sodium increases the basicity because of greater abundance of their basic species; adding a mole of magnesium increases the basicity about seven times that caused by adding a mole of sodium under the same conditions.

Increasing the chloride content at constant value of other variables causes the basicity to decrease. This results from the requirements of electroneutrality and the constant saturation values assumed. An increase

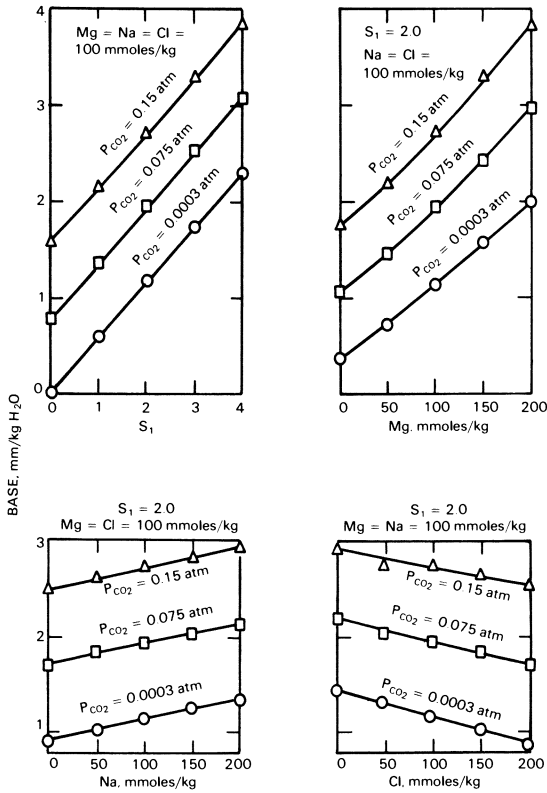


Figure 5. Effects of P_{CO_2} in combination with S_1 and contents of Mg, Na, and Cl on the basicity at pH 6.0

in chloride results in a decrease in other anionic components such as sulfite and sulfate, which also are controlled by a constant degree of saturation in this simulation; this results in lower quantities of sulfite, sulfate, and carbonate attached to cationic species (Ca, Mg, and Na) and consequently in lower values of sulfur dioxide-absorbing species. The ionic strength also will increase as chloride is increased but this will have a minor effect on the basicity because many of the basic species are neutral (no ionic charge).

Combined Effect of pH, Magnesium Content, P_{CO_2} , and Degree of Saturation of Calcium Sulfite. The addition of large quantities of magnesium at different values of pH and degrees of saturation of calcium sulfite is shown in Table V for three values of carbon dioxide partial pressure when the solution contains 100 mmoles NaCl/kg and is saturated with gypsum. The basicity values are given in the upper section of Table V while the lower listing gives the values of the logarithm of the

solubility product (3) of dolomite, $\text{CaMg}(\text{CO}_3)_2$. When $\log K_{\text{sp}} = -1$, 0, and $+1$, solutions are 1/10 saturated, saturated, and 10-fold saturated, respectively, with dolomite. It is evident that at pH 6.5 and at carbon dioxide partial pressures of 0.075 and 0.15 the solutions become supersaturated with dolomite even at moderate Mg contents. These simulated compositions that are supersaturated with dolomite may never exist in actual scrubbing solutions because of the pH- P_{CO_2} relationship shown in Figure 2; they are presented to complete the factorial design of Table V and to demonstrate the effects of the variables on the basicity of the aqueous phase.

Figure 6 shows the effects of the partial pressure of carbon dioxide at pH 5.5 and 6.0 for various combinations of magnesium contents and degrees of supersaturation of calcium sulfite. The slopes of the linear relation between the basicity and P_{CO_2} are essentially constant as S_1 increases, they increase slightly as the magnesium content increases, and they increase greatly as pH increases.

Precipitation of Carbonate Salts. In the Appendix, equations are given for the calculated degrees of saturation of calcite, S_3 , and of dolomite, S_4 , based on regression of these properties at the conditions shown in Table III. Figure 7 shows the effects of pH and P_{CO_2} for solutions that are saturated with calcite or dolomite. In each case the solutions are saturated with calcium sulfite and gypsum, and the content of sodium chloride is 200 mmoles/kg H_2O .

In Curve 1 of Figure 7 the magnesium content is very low, 0.001 mmole/kg, and calcite saturates at a lower carbon dioxide partial pressure for any given pH than dolomite. When the magnesium content is increased to 100 mmoles/kg, Curve 2, dolomite saturates at a lower partial pressure of carbon dioxide than calcite for any given pH. The same is true for Curve 3 where the magnesium content is 200 mmoles/kg. An extrapolation of the dolomite solubility to 600 mmoles Mg/kg (14,600 ppm Mg), Curve 4, shows that very low carbon dioxide partial pressure is needed to saturate dolomite from solutions with these high magnesium contents.

Application of the Study Results

The concentration of absorbing species in the scrubber solution is obviously an important consideration in scrubbing stack gas with lime-limestone slurry. Thus, the results of this study are useful both in understanding solution absorptivity and in pointing the way to possible improvement.

In a typical limestone scrubbing system a slurry of finely ground limestone plus product solids and perhaps fly ash is circulated through

Table V. Properties of Solutions Containing

		<i>BASE^a when P_{CO_2} (atm) is</i>		
		<i>0.0003</i>		
<i>pH</i>	<i>S₁^b</i>	<i>200 Mg^c</i>	<i>600 Mg</i>	<i>1000 Mg</i>
5.5	1	1.75	5.34	9.26
	2	3.45	10.53	18.28
	3	5.09	15.59	27.07
6.0	1	1.76	5.36	9.29
	2	3.49	10.61	18.36
	3	5.18	15.74	27.25
6.5	1	1.78	5.39	9.32
	2	3.52	10.65	18.42
	3	5.23	15.81	27.34
Log S₄^d				
5.5	1	-8.825	-8.534	-8.359
	2	-8.813	-8.526	-8.351
	3	-8.802	-8.517	-8.344
6.0	1	-6.833	-6.541	-6.365
	2	-6.829	-6.539	-6.364
	3	-6.825	-6.537	-6.362
6.5	1	-4.835	-4.543	-4.367
	2	-4.834	-4.543	-4.367
	3	-4.833	-4.543	-4.368

^a Σ aqueous species basic to HSO_3^-

^b Degree of saturation of calcium sulfite

^c Magnesium content in mmoles/kg H_2O

a loop composed of the scrubber and a delay, or hold, tank. The slurry is held in the tank to allow the reactions started in the scrubber to go to completion and also to allow the supersaturation of $CaSO_3 \cdot 0.5H_2O$ and $CaSO_4 \cdot 2H_2O$ to dissipate as much as possible. Both salts supersaturate to a high degree which may cause scaling in the scrubber unless crystallization can be induced in the delay tank.

The feed limestone usually is fed into the delay tank. A sidestream of slurry is withdrawn from the tank or at a point just before the tank, the solids are separated and discarded, and the liquid phase is returned to the scrubber. Thus, the system is in a continuous dynamic state rather than at equilibrium.

In such a system, the solution is in continuous contact with the major solid phases— $CaCO_3$, $CaSO_3 \cdot 0.5H_2O$, and $CaSO_4 \cdot 2H_2O$. The composition of the liquid phase is continually changing as solids go into and come out of solution and as sulfur dioxide and carbon dioxide are absorbed or desorbed. Mass transfer is an important consideration, both of sulfur dioxide into the liquid and of the various solids into and out of

100 mmoles NaCl/kg Water at 122°F

BASE^a when P_{CO₂} (atm) is

0.075			0.15		
200 Mg	600 Mg	1000 Mg	200 Mg	600 Mg	1000 Mg
2.20	5.95	10.00	2.65	6.56	10.75
3.90	11.14	19.02	4.35	11.75	19.76
5.54	16.19	27.81	5.99	16.80	28.55
3.19	7.29	11.66	4.63	9.23	14.04
4.92	12.53	20.72	6.35	14.45	23.08
6.60	17.65	29.59	8.03	19.57	31.94
6.37	11.64	17.05	10.98	17.90	24.80
8.08	16.85	26.09	12.67	23.08	33.77
9.77	21.98	34.94	14.35	28.16	42.57

Log S₄^d

-4.028	-3.738	-3.563	-3.426	-3.136	-2.961
-4.017	-3.730	-3.555	-3.414	-3.127	-2.953
-4.006	-3.721	-3.548	-3.403	-3.119	-2.946
-2.035	-1.744	-1.569	-1.432	-1.142	-0.966
-2.032	-1.742	-1.567	-1.428	-1.140	-0.965
-2.028	-1.740	-1.566	-1.424	-1.138	-0.964
-0.034	0.255	0.430	0.573	0.859	1.033
-0.033	0.255	0.429	0.574	0.859	1.032
-0.032	0.255	0.429	0.576	0.859	1.031

^d S₄ = $a_{Ca} \cdot a_{Mg} \cdot a^2_{CO_2} / K_{sp}$ (dolomite). Negative values are unsaturated solutions, positive values are supersaturated solutions.

the liquid. Thus, equilibrium data such as obtained in the present study can only be an indication. The actual situation will depend also on the design of the particular scrubber installation and its operating conditions since these affect the mass transfer rate in addition to the equilibrium driving forces.

Lime scrubbing is quite similar to limestone scrubbing except that the pH in the delay tank is higher, about 8–10 as compared with 5.8–6.0 in limestone scrubbing. The pH apparently drops quickly when the slurry returns to the scrubber, caused by absorption of carbon dioxide and sulfur dioxide, so that the scrubber exit pH is about 5.4–5.8 no matter which absorbent is used.

Calcium Sulfite Supersaturation. One of the more effective ways to increase absorbing species concentration, as shown in Figures 1, 5, and 6, is to increase the supersaturation of CaSO₃ · 0.5H₂O. In practice such an increase probably could be accomplished by decreasing delay time and by separating and recycling the liquid phase from the product solids

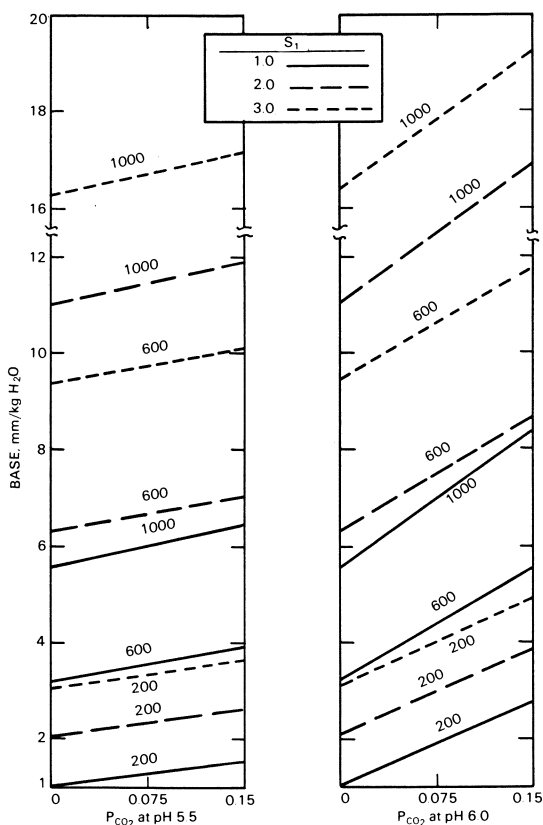


Figure 6. Basicity of solution with 100 mmoles NaCl/kg and saturated with gypsum. Numbers on curves denote mmoles Mg/kg H_2O .

as quickly as possible. However, since this is likely to aggravate scaling it is hardly a practical course.

Thus, the beneficial effect of sulfite supersaturation comes only from the minimum value below which it cannot be decreased (by extended delay time, crystal seeding, and high liquid-to-gas ratio) in the effort to avoid scaling. The maximum level, which occurs when the pH is highest, appears to be 8–10. Supersaturation of calcium sulfite is decreased when pH decreases (by absorbing carbon dioxide and sulfur dioxide), and it is increased by dissolving lime or limestone which adds calcium and increases the pH.

Magnesium Content of Limestone. It has been generally accepted (until recently) that the magnesium content of the limestone should be minimized to prevent the presence of polluting soluble magnesium salts in the product solids. There is now a general trend, however, to stabilize

the solids against leaching no matter what the composition. In this situation it would appear reasonable to use dolomite or dolomitic limestone if there were any benefit in the scrubbing step.

If the limestone is used as is, however, the dissolution rate of the dolomite fraction is so slow that the overall effectiveness appears to be decreased. It may be that with enough delay time the dolomite would react adequately in the delay tank with bisulfite species formed in the scrubber, but suitable data on this do not appear to be available.

When the dolomitic limestone is calcined, the resulting magnesium oxide hydrates and reacts just as it does in those processes using mag-

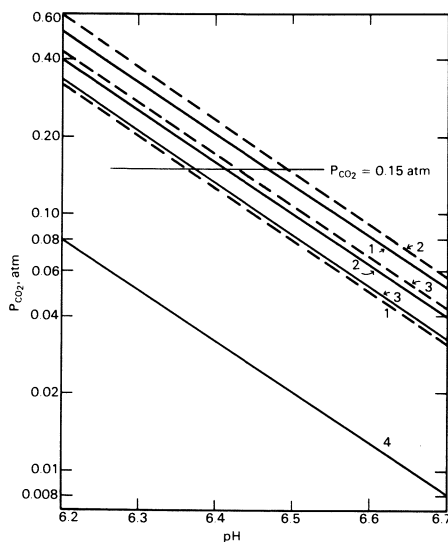


Figure 7. Effects of pH and P_{CO_2} on solutions saturated with dolomite (—) or calcite (---) at 50°C. All solutions saturated with $CaSO_3 \cdot 0.5H_2O$ and $CaSO_4 \cdot 2H_2O$ and contain 200 mmoles NaCl/kg.

nesium oxide as the primary absorbent. In recent commercial tests a major increase in absorption was noted when the lime was dolomitic rather than calcitic. The reason for this is shown in Figure 5, where only 0.2 mole Mg^{+2}/kg H_2O more than doubled the concentration of the absorbing species. Figure 6 shows increasing amounts of sulfur dioxide-absorbing species as the magnesium content is increased to 1 molal.

It should be noted, however, that there is a theoretical maximum solubility for Mg^{+2} species above which dolomite may precipitate (Table IV and Figure 7). Dolomite has never been precipitated, to our knowledge, under conditions likely to be encountered in lime or lime-limestone

stack gas scrubbing. The possibility, nevertheless, exists from thermodynamic reasoning. Magnesium losses through formation of magnesian calcite or aragonite is another possibility. Fortunately, the factors affecting precipitation tend to offset each other. In the delay tank the low carbon dioxide partial pressure offsets the precipitating tendency of the relatively high pH, and in the scrubber the low pH offsets the effect of the higher carbon dioxide pressure. The combination of high pH in the slurry returning to the scrubber and the high carbon dioxide pressure in the scrubber might cause precipitation. However, the pH of the return solution appears to drop rapidly to the generally low pH level throughout the scrubber.

The steady state concentration of magnesium species in a scrubber system using dolomitic lime will depend on several factors, including magnesium content of the limestone, system purge rate, and limiting maximum solubility. Whatever the concentration obtained, it seems likely to have a significant beneficial effect on absorption.

Addition of Magnesium Salts. The addition of magnesium sulfate increased the sulfur dioxide removal in closed-loop limestone slurry scrubbing (4). In the present simulation study of the concentrations of magnesium, sodium and chlorine (Table II), the extent to which $Mg + 0.5Na$ exceeds $0.5Cl$ is approximately equivalent to adding magnesium sulfate because of the requirements of electroneutrality and the constant value of S_2 .

At high magnesium concentrations in limestone slurries the bulk of the absorbing species concentration is in the form of magnesium sulfite, making the system similar to magnesium scrubbing processes such as Chemico-Basic and Grillo. In lime slurry scrubbing, the bulk of absorbing species concentration is in the form of magnesium carbonate and $MgHCO_3^+$ at high magnesium concentrations.

Use of Cooling Tower Blowdown. In some areas the general shortage of water makes it desirable to use cooling tower blowdown as makeup water. As a result, very high concentrations of dissolved salts—on the order of 12%—are attained in the scrubber loop at steady state. The composition will vary depending on the number of cooling tower cycles and on the mode of operation of the scrubbing system. Usually sodium and chloride are the main constituents, with lesser amount of magnesium, calcium, and sulfate.

The results of this study indicate that the sodium and chloride largely offset each other (Figure 5) when in comparable molar concentrations. The magnesium, of course, is helpful.

Use of Salt Water. In some coastal areas the use of sea water as makeup water is economical. Again, there should be little effect on the concentration of absorbing species except that caused by ionic strength.

Stoichiometry and Solids Dissolution. One thousand cu ft of gas at standard conditions contains 3.16 g moles of sulfur dioxide when the sulfur dioxide content of the gas is 2500 ppm. At a liquid-to-gas ratio of 50 gal/standard 1000 cu ft, 16.7 mmoles of basic species/l. are required to react with this amount of sulfur dioxide. Very few of the simulated solutions in Tables III and IV attained this basicity except under extreme conditions of the variables, conditions unlikely to be controlled consistently in lime or limestone scrubbing. Consequently, under most conditions, additional basic species must enter the liquid phase in the scrubber to neutralize the dissolving gas. These species come from the dissolution of calcium carbonate or calcium sulfite in the scrubbing tower. The amount of solids dissolution required to achieve stoichiometry is reduced greatly by the presence of large amounts of magnesium in solution.

Appendix

Saturation of the Aqueous Phase With Calcite or Dolomite. Tables similar to Table III for the degree of saturation of calcite, CaCO_3 , and for dolomite, $\text{CaMg}(\text{CO}_3)_2$, were calculated, and the results were quantitatively represented by the equation

$$\begin{aligned} \log S_j = & b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_5x_5 + \\ & b_6 \log P_{\text{CO}_2} + b_{33}x_3^2 + b_{44}x_4^2 + b_{55}x_5^2 + b_{12}x_1x_2 + b_{34}x_3x_4 + \\ & b_{35}x_3x_5 + b_{45}x_4x_5 + b_{345}x_3x_4x_5 \end{aligned} \quad (1A)$$

where x 's are coded values of the independent variables, namely,

$$x_1 = 2(\text{pH}-6) \quad (2A)$$

$$x_2 = S_1 - 2 \quad (3A)$$

$$x_3 = (\text{Mg}-100)/50 \quad (4A)$$

$$x_4 = (\text{Na}-100)/50 \quad (5A)$$

$$x_5 = (\text{Cl}-100)/50 \quad (6A)$$

The degree of saturation of calcite, S_3 , and of dolomite, S_4 , are defined as follows

$$S_3 = a_{\text{Ca}^{+2}} \cdot a_{\text{CO}_3^{-2}} / K_{\text{sp}}(\text{calcite}) \quad (7A)$$

$$S_4 = a_{\text{Ca}^{+2}} \cdot a_{\text{Mg}^{+2}} \cdot a_{\text{CO}_3^{-2}}^2 / K_{\text{sp}}(\text{dolomite}) \quad (8A)$$

The values of the constants in Equation 1A are

Constant	For	
	Calcite	Dolomite
b_0	-0.056	0.123
b_1	0.995	1.989
b_2	0.006	0.006

<i>Constant</i>	<i>For</i>	
	<i>Calcite</i>	<i>Dolomite</i>
b_3	-0.117	0.077
b_4	-0.094	-0.132
b_5	0.126	0.175
b_6	1.003	2.006
b_{33}	0.032	0.000
b_{44}	0.010	0.014
b_{55}	0.007	0.006
b_{12}	-0.004	-0.005
b_{34}	0.038	0.051
b_{35}	-0.041	-0.047
b_{45}	-0.025	0.009
b_{345}	0.011	0.009

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Kinetics of the Reaction of Half-Calcined Dolomite with Sulfur Dioxide

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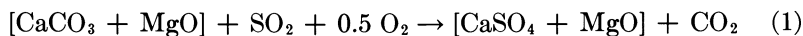
Kinetics of the reaction of sulfur dioxide with half-calcined dolomite have been studied using gravimetric techniques. The reaction rate depends significantly on the presence of water in the reactant gas mixture. With water, the reaction is first order with respect to the sulfur dioxide concentration. Without water, the reaction rate is slower, and the reaction is 0.76 order with respect to sulfur dioxide concentration. This suggests that the rate-determining step differs depending on whether or not water is present. The reaction has an apparent activation energy of 7.3 kcal/mole with water present in the reactant gas.

This paper reports the initial results obtained by a small basic-chemistry support program associated with developing a fluidized-bed combustor for high-sulfur coal. The combustion of fossil fuels in a fluidized bed containing a material that reacts with and fixes sulfur dioxide in the bed is only one of many processes presently being developed to permit the use of high sulfur fuels in an environmentally acceptable way. The fluidized-bed concept has several variations, but in most cases the sulfur-fixing material is limestone in a form that reacts with sulfur dioxide to produce calcium sulfate. It is hoped that these initial results will also be useful in developing other processes for sulfur dioxide control such as panel-bed filters.

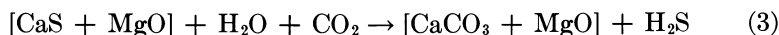
The active material used in this program is half-calcined dolomite, which reacts with sulfur dioxide as indicated in Equation 1:

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For economic and environmental reasons, it is desirable to regenerate the reactive material from the product by some scheme such as shown in Equations 2 and 3



in which the hydrogen sulfide resulting from Equation 3 is concentrated enough to permit sulfur recovery in a Claus plant.

A considerable amount of work, including detailed kinetic studies (1, 2), has been reported on the reaction of calcined limestones with sulfur dioxide (Equation 4)



in connection with both the fluidized-bed combustion and dry-limestone injection processes. The respective reactions of fully calcined and half-calcined limestones with hydrogen sulfide



have been studied in some detail in connection with other desulfurization schemes (2, 3, 4, 5, 6). Some results have also been reported on the reactions of work discussed here (7, 8, 9). Exploratory experiments applying the system considered here to panel-bed filtration (9) have indicated its feasibility. The following conclusions can be drawn from this prior work:

1. Dolomite limestones (fully calcined or half-calcined) are more effective reagents than calcite and show considerable promise in sulfur emission control.

2. The reduction of the sulfation product to the sulfide (Equation 2) appears to be satisfactory.

3. The active reagent can be more readily regenerated (by Equation 3) from sulfide produced by direct sulfidation with hydrogen sulfide than from sulfide formed by reduction of the sulfated product resulting from reaction with sulfur dioxide.

In the light of this prior work, the goals of this program are to determine the detailed kinetics of Equations 1, 2, and 3, to elucidate plausible mechanisms for these reactions, and to determine the conditions that optimize each of these reactions. Kinetic results for Equation 1 are presented here.

Experimental

Apparatus. The experimental apparatus is similar to that used by other workers (3, 5, 8) and is schematically depicted in Figure 1. The reactant gas mixture, which is prepared by controlling the flow of each constituent by means of a diaphragm-type regulator and calibrated rotameters, flows upward through the heated reaction tube, past the sample, and exits through a condenser and a series of scrubbers. Total flow can be controlled from 200 to 400 cm³/min with an accuracy for the total flow and for each constituent of about $\pm 2\%$. The water content of the reactant gas is controlled by a thermostated humidifier. Sulfur dioxide is added to the stream after humidification. The sample is suspended in a platinum basket from one arm of a recording balance. The balance, which provides continuous weight data from 0.2 to 1.0 g with an accuracy of ± 0.1 mg, is protected from corrosive gases by a purge flow of nitrogen. Temperature in the reaction zone is controlled by a Marshall furnace with an accuracy of $\pm 5^\circ\text{C}$ up to about 950°C and is recorded along with sample weight on a recorder.

Materials. The apparatus is fabricated from quartz and type 304 stainless steel. Commercial research-grade cylinder gases are used to make up the reactant gas stream. The stone used in these experiments was BCR-1337 dolomite obtained from Charles Pfizer and Co., Gibson-

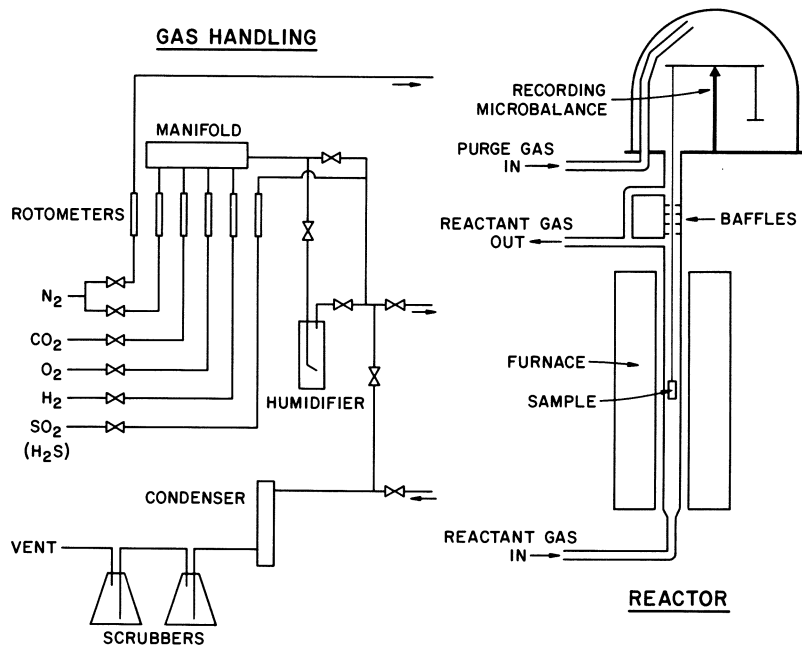


Figure 1. Schematic of the apparatus

burg, Ohio and has an empirical formula $\text{Ca}_{1.14}\text{Mg}_{0.86}(\text{CO}_3)_2$. Chemical analysis and petrographic characteristics of this stone have been reported by Harvey (10).

Procedure. In a typical experiment, ~ 200 mg of 1337 dolomite particles having diameters in a narrow range around 1.1 mm (-16 to $+18$ U.S. standard screen) are placed in the apparatus under nitrogen and carbon dioxide flow and are heated to 800°C at about $25^\circ\text{C}/\text{min}$ to half-calcine the stone. After calcination the weight change of the sample is observed. When half-calcination of the stone is complete (usually after about 45 min), the sample temperature is adjusted to that selected for the experiment, the sample is isolated under nitrogen and carbon dioxide atmosphere, and the reactant gas mixture is adjusted to the appropriate composition and flow rate for the experiment while bypassing the reaction tube. At time zero, the reactant gas is diverted through the reaction tube and the weight change of the sample is observed as a function of time. The reaction is followed until the rate of weight change is negligible, typically about 2 hr for the experiments reported here.

To study the reaction of magnesium oxide, a sample of reagent-grade magnesium carbonate was ground and pressed into a dense pellet which was then broken up to obtain a sample containing particles of the size used in the other experiments. Calcination and subsequent procedures were identical to those for other samples.

The reaction rate, r , at any time during the reaction was calculated from the equation

$$r = \frac{1}{w} \cdot \frac{dn}{dt} \quad (7)$$

where w is the total weight of the sample before calcining, n is the amount of sulfate as moles of sulfur trioxide produced, and t is time in sec.

Results and Discussion

Typical experimental results are shown in Figure 2 where the fraction of the stone reacted according to Equation 1 is plotted against time for several different sulfur dioxide concentrations. The reaction temperature and reactant gas composition are given in the figure legend. The flow rate of the reactant gas was maintained well above the rate at which gas phase diffusion affected the reaction rate. It is evident that the reaction rate, and hence the extent of the reaction at a given time, is a function of sulfur dioxide concentration. Curve a in Figure 3 shows these same data, in a plot of the logarithm of the initial reaction rate *vs.* the logarithm of the sulfur dioxide concentration. Initial rates were actually evaluated at $t = 1$ min because of scatter in the data near $t = 0$. The straight line thus obtained has a slope of 1.08 and indicates that the reaction is first order with respect to sulfur dioxide concentration in the reactant gas under these reaction conditions. Similar first-order de-

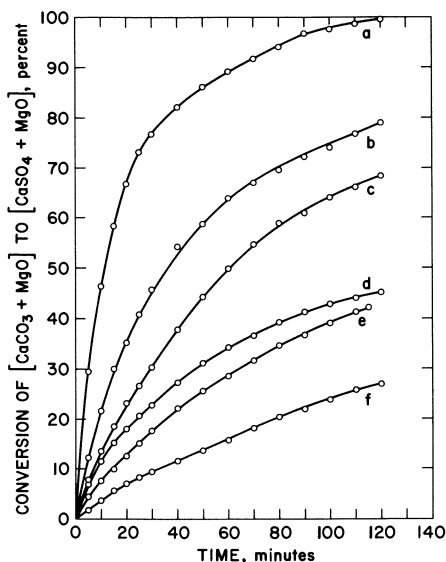


Figure 2. Percent conversion vs. time for various sulfur dioxide concentrations in the reactant gas at 750°C. Gas composition in %— SO_2 : a = 3.1; b = 1.1; c = 0.65; d = 0.39; e = 0.20; f = 0.10. CO_2 : 15.0. O_2 : 5.0. H_2O : 2.9. N_2 , balance.

pendence for the reaction of fully calcined 1337 dolomite was reported by Borgwardt (1), and, in fact, the reaction rates reported by Borgwardt are similar to those observed here.

We noticed in several early experiments that the concentration of water in the reactant gas appeared to influence the reaction rate. A series of experiments was performed in which the water concentration in the reactant gas was varied from about 1.0 to 40 mole % while the concentration of other reactants was constant. The results indicated, however, that the reaction was essentially zero order with respect to water concentration. Another series of experiments, in which the reactant gas was dry and the concentration of sulfur dioxide was varied, gave the results shown in Figure 3, Curve b. The observed slope of 0.76 indicates that the rate varies with the three-fourths power of sulfur dioxide concentration. Thus, it appears that the rate-determining step is different depending on whether or not water is present in the reactant gas. With water present, the reaction is 0.22 order with respect to oxygen concentration in the reactant gas stream.

The temperature dependence of the reaction rate with water present was examined from 550 to 850°C. At higher temperatures, the carbon

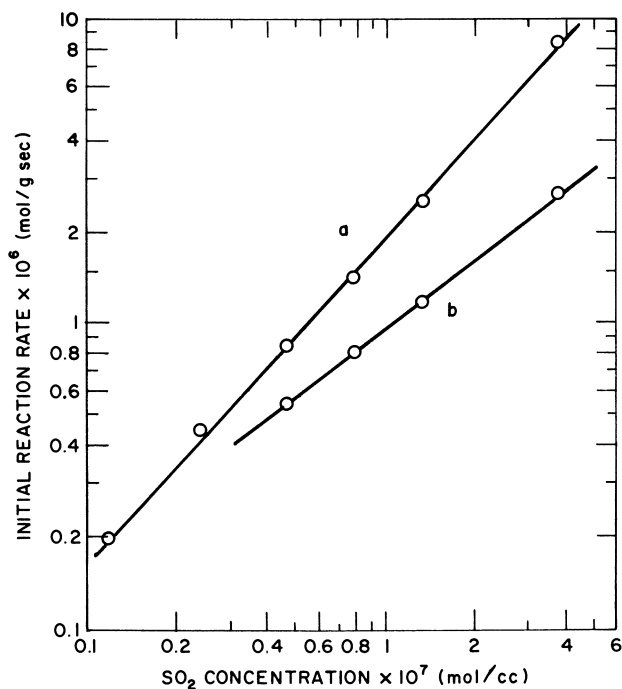


Figure 3. Curve a: initial reaction rate (see text) vs. sulfur dioxide concentration on logarithmic scales. Reaction conditions as noted under Figure 2. Curve b: initial reaction rate vs. sulfur dioxide concentration on logarithmic scales. Reaction conditions as noted under Figure 2 except that water is absent.

dioxide concentration necessary to prevent calcium carbonate decomposition (11) could not be maintained with the present apparatus. The initial reaction rate increased significantly with temperature over this range. An Arrhenius plot of the data (Figure 4) shows a linear dependence of rate on $1/T$ and yields an apparent activation energy of 7.3 kcal/mole. Although such a value does not point conclusively to a mechanism in which some chemical reaction is rate controlling, the value is somewhat greater than one might expect if the reaction were diffusion controlled.

In some experimental runs, the conversion to sulfate based on Equation 1 was greater than theoretically predicted. It has been reported that magnesium oxide undergoes sulfation (8). Accordingly, to assess the extent to which this reaction might interfere with detailed analysis of our results, the sulfation of calcined magnesium carbonate was examined. Typical results are shown in Figure 5 together with results for the half-calcined stone. The extent of magnesium oxide sulfation is not great,

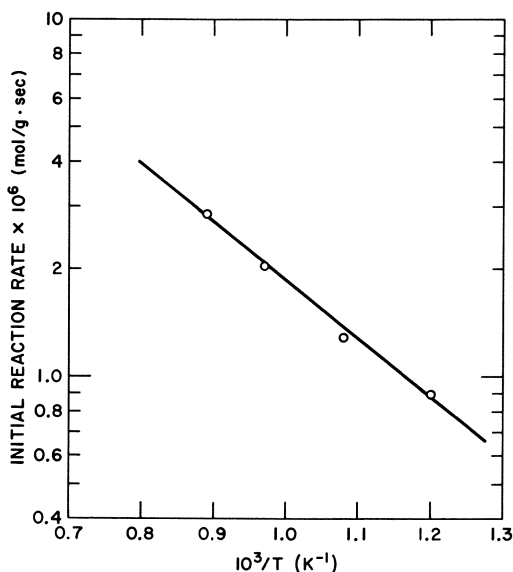


Figure 4. Arrhenius plot for the reaction of sulfur dioxide with half-calcined 1337 dolomite

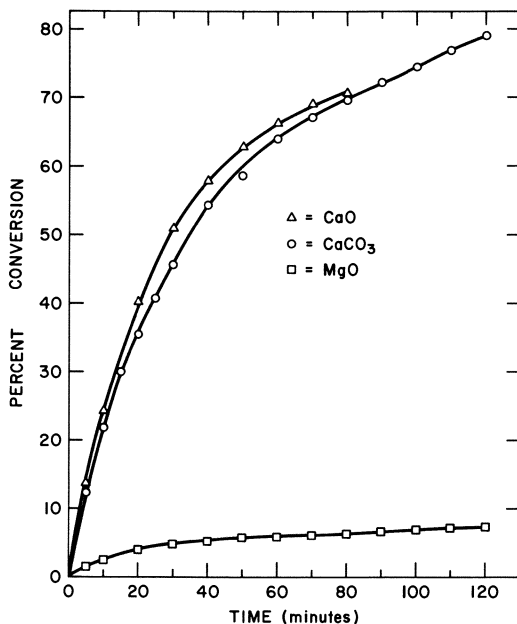


Figure 5. Percent conversion vs. time for: Δ = [CaO + MgO]; \circ = [CaCO₃ + MgO]; and \square = MgO at 750°C. Gas composition, in %—SO₂: 1.1. CO₂: Δ = 0.0, \circ = 15.0, \square = 0.0. O₂: 5.0. H₂O: 2.9. N₂, balance.

and the reaction rate is much slower than for the half-calcined stone. Nevertheless, the effect is too great to be ignored in any detailed treatment of the data for half-calcined stone. Figure 5 also shows results obtained for the sulfation of fully calcined stone under the same conditions except that carbon dioxide was absent in the reactant gas. These results are very similar to those for the half-calcined stone, as one might expect in view of the generally close correlation between this work and that of Borgwardt (1).

To date, there have been several unsuccessful attempts to fit these results to a simple model—for example, one based on a shrinking unreacted core or on reaction of a porous solid. The apparent role of water in the mechanism suggests that sulfur dioxide may be oxidized to sulfur trioxide on the surface and that sulfur trioxide diffuses through a product layer to react with calcium carbonate. This concept would be consistent with the similar kinetics observed for half- and fully calcined stone since the rate-determining step would presumably be the same in either case. This view is supported by the observation that reactivity in a fluidized bed decreases somewhat above about 850°C because the thermodynamics of sulfur dioxide oxidation become less favorable. On the other hand, Borgwardt's observations with fully calcined stone (1) suggest that the decreased reactivity is caused by hard-burning of the stone.

Further work is needed to understand the role of water in the sulfation mechanism more fully and to extend the kinetic studies to the reduction and regeneration reactions outlined above. The potential advantages of a process using dolomite in a closed cycle for sulfur dioxide control are sufficiently great to warrant continued effort.

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Recent Experience of the Wellman–Lord Sulfur Dioxide Recovery Process

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Plants producing a stack gas containing sulfur dioxide can meet provisions of the Clean Air Act by using the Wellman–Lord sulfur dioxide recovery process. The process is installed commercially at several locations in the United States and Japan and has demonstrated long term operation reliability while sulfur dioxide removal has met all applicable environmental regulations. This paper describes the process and reviews the application to tail gases from a Claus sulfur plant including capital and operating costs for a specific application.

Davy Powergas Inc., formerly Wellman–Lord Inc., developed the Wellman–Lord sulfur dioxide recovery process in the 1960's to produce a concentrated sulfur dioxide gas from lean off-gas streams. It can be used in any plant that produces a stack gas containing sulfur dioxide, including power plants, sulfuric acid plants, petroleum refineries, and metallurgical plants. Its best application, however, is treating gases which contain 0.15–3.0% sulfur dioxide by volume.

Process Description

This recovery process is based on the simple chemistry of the sodium sulfite/bisulfite system. After appropriate pretreatment, the flue gas containing sulfur dioxide enters the absorber, which reduces the sulfur concentration to the required level and can accommodate a wide range of turn-down conditions (Figure 1).

The sulfur dioxide-rich gas is contacted countercurrently in the absorber by a sodium sulfite solution. As the sodium sulfite absorbs the sulfur dioxide and forms bisulfite, the solution becomes less saturated. This allows highly reliable fouling- or scaling-free operation of the ab-

sorber which is not possible in systems having reverse relationships. After being stripped of sulfur dioxide, the gas passes out the top of the absorber. The bisulfite-rich solution is discharged at the bottom of the tower into a surge tank.

From the surge tank, the bisulfite solution flows steadily into a forced-circulation evaporator-crystallizer, which is the heart of the regeneration system. Heat can be provided by the low-pressure exhaust steam that normally would be discharged into the atmosphere. Operating plants are currently using steam at pressures as low as 15 lb/sq in., but even lower pressures can be used. In large plants such as power plants, the regeneration system should be operated as a double-effect evaporator which would reduce steam consumption by 40–45%.

In the evaporator, the bisulfite solution is thermally decomposed to sodium sulfite and sulfur dioxide. The resulting vapor is partially condensed in one or more stages to remove water and to achieve the desired product quality.

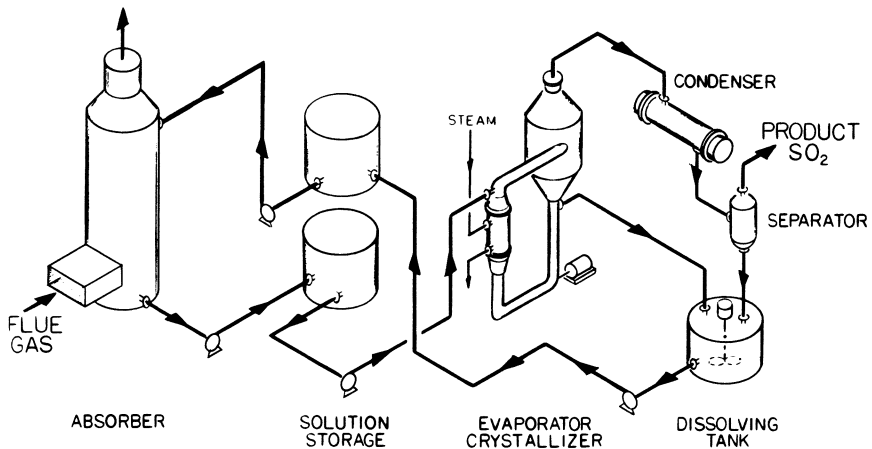


Figure 1. Basic flow diagram of the Wellman-Lord sulfur dioxide recovery system

The sodium sulfite precipitates out of the bisulfite solution and builds a dense slurry of crystals in the evaporator. A portion of this slurry is withdrawn from the evaporator and sent to a dissolving tank where water from the condenser system is added to dissolve the sulfite crystals. The resulting solution is sent to another surge tank and is then fed back into the absorber to complete the process loop.

As the solution contacts the gases in the absorber, a moderate amount of the circulating solution is oxidized to non-regenerable sulfate by the oxygen or sulfur trioxide in the gas. To control the sulfate level, a small stream of the solution is purged from the system. This purge stream

can be acidified and neutralized to produce a sodium sulfate stream containing essentially no chemical or biological oxygen demands so that it may be discharged as an innocuous effluent. A selective crystallization system may also be used to enrich the sulfate in the stream to minimize the sodium loss. These crystals can then be dried for sale.

Current Status

Ten Wellman–Lord installations presently operating in the United States and Japan have an aggregate operating experience of more than 10 yr. The total flue gas volume handled by these operating units is approximately 1 million standard cu ft/min (SCFM). Twelve other plants are in the design and construction stage. The overall capacity of installations which are operating or in design is about 4 million SCFM.

The first commercial application of the Wellman–Lord process was at the Olin Corp. sulfuric acid regeneration plant in Paulsboro, N. J. This plant regenerates 700 tons of sulfuric acid/day and handles a variety of spent acids. The sulfur dioxide content of the tail gas varies as the blends of these acids change.

Olin's absorber system can process 45,000 SCFM of tail gas containing up to 6,000 ppm sulfur dioxide by volume. The cleaned gas, containing less than 500 ppm of sulfur dioxide, is discharged into the atmosphere. The recovered sulfur dioxide vapor is returned to the acid-regeneration plant to produce sulfuric acid.

At Chiba, Japan, the Japan Synthetic Rubber Co. has two steam boilers with evaporation rates of 130 metric tons/hr, each equipped with Wellman–Lord sulfur dioxide recovery units. The load to each scrubber is essentially constant, but sulfur dioxide concentration varies from 400 to 2,000 ppm because of the varying quantities of waste process gas from the plant.

More than 90% of the sulfur dioxide is removed, producing outlet concentrations that are consistently less than 200 ppm. Only one-half man/shift is required to operate the system, including waste disposal and production. This installation began operation in July 1971 and has operated for 3 yr with essentially 100% reliability.

One of the most important uses for the Wellman–Lord process is treating off-gases from Claus sulfur plants. Standard Oil Co. of California (SOCAL) is using this process at its El Segundo refinery near Los Angeles (Figure 2). Additional units are being designed and will be installed at the El Segundo refinery and at the Richmond, Calif. refinery.

At El Segundo, tail gases from three 135 long-tons/day (LTPD) Claus units pass through three gas-handling trains before being dis-

charged to the atmosphere. Each train includes an incinerator, a waste heat boiler, a quench column, a gas cooler, and an absorber. A single set of surge tanks and a single chemical plant serve all three gas trains.

The chemical plant consists of a single-effect vacuum evaporator system for regenerating the solution and liberating the sulfur dioxide. Indirect heat is supplied to the forced-circulation evaporator by using exhaust steam from the refinery. The vacuum is supplied by a liquid ring vacuum pump which also pumps the sulfur dioxide back into the front of the Claus plant.

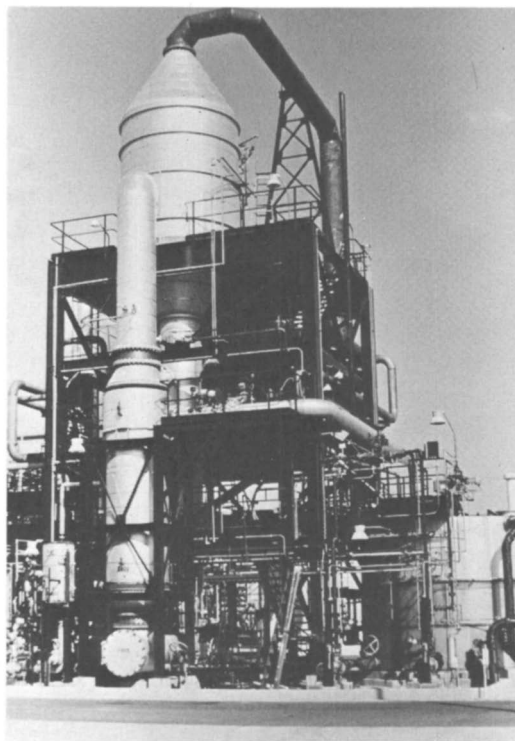


Figure 2. The sulfur dioxide recovery process installed on a Claus unit at the Standard Oil Co. of California refinery at El Segundo, Calif.

The El Segundo installation immediately lowered the emissions from the SOCAL refinery Claus plants to within the Los Angeles area limits of 500 ppm or less of sulfur dioxide. At Richmond, regulations are even lower—300 ppm or less. The Wellman-Lord recovery units being installed there are guaranteed by Davy Powergas to meet those emission levels.

Process Advantages

A basic advantage of the process is that it allows considerable flexibility in the choice of end product. The concentrated sulfur dioxide gas can be fed to conventional sulfuric acid plants, reduced to elemental sulfur, or converted to liquid sulfur dioxide. Any of these products can be sold to reclaim a portion of the recovery system's operating costs.

The absorption system can be physically separated from the regeneration system if there are space limitations within the plant. Gases from more than one unit can be treated by installing separate absorbers for each sulfur dioxide source, with all the absorbers being supplied by a common regeneration system.

Feeding solutions from the absorber system and the regeneration system through surge tanks enables the entire recovery process to operate smoothly and reliably despite frequent gas flow and concentration fluctuations. In addition, the surge tanks allow the regeneration section to be shut down for up to 3 days without interfering with the sulfur dioxide removal in the absorption section. This is possible because the absorber is the only part of the system that contacts the flue gas and removes the sulfur dioxide.

The ability to shut down the regeneration section allows time for scheduled maintenance or repairs and increases the system's reliability. Also, the need for expensive spare equipment is minimized without sacrificing basic pollution control.

Typical Cost Analysis

To illustrate the economics involved in applying the Wellman-Lord process to a Claus plant, the following hypothetical case will indicate the relationship of costs to the performance given. The basic parameters of this example are:

1. Three Claus plants at 150 LTPD each.
2. Recovery efficiency of the Claus plant of 96%.
3. In each gas handling train—one waste heat boiler, one quench cooling section, and one sulfur dioxide absorber system for each Claus Plant.
4. One common chemical plant for regeneration of the solution from all three absorbers.
5. Surge tankage for both absorber feed and absorber product solution sufficient for 3 days output from the chemical plant.

The gas flow to each absorber is 12,000 SCFM with a sulfur dioxide content of about 1100 lb/hr, so the total sulfur dioxide produced in the evaporator system will be 2900 lb/hr.

The capital cost of producing an exit gas with less than 250 ppm sulfur dioxide by volume will be approximately five million dollars. The

operating cost, including capital charges, labor, supervision, payroll, maintenance, utilities, and overhead is about \$800,000 annually.

The Japan Synthetic Rubber Co. installation at Chiba illustrates costs of a second type of application. During its first 10 mo of operation, its operating costs were broken down as follows: 50% for interest and carrying charges, 15% for steam, 10% for electric power, 10% for caustic soda consumption, and 15% for labor and miscellaneous costs.

Future Developmental Plants

The Wellman-Lord process can be a significant factor in helping domestic power plants to meet the air pollution abatement requirements of the Clean Air Act of 1970. To show its applicability to the utilities industry, Davy Powergas Inc. is building a demonstration installation at the Dean H. Mitchell Station of Northern Indiana Public Service Co. in Gary, Ind. When completed, it will consist of a Wellman-Lord sulfur dioxide recovery unit connected to an Allied Chemical Co. sulfur dioxide-to-sulfur reduction process to produce elemental sulfur. Davy Powergas guarantees emissions of 200 ppm by volume or less of sulfur dioxide at this facility.

Processes that have been successful in other industrial applications presently are being studied for inclusion in the Wellman-Lord process. This would allow the system to operate as a closed loop with total sodium and sulfur dioxide recovery and would eliminate effluent streams requiring treatment. Further test work is necessary, however, before including another idea into the commercially proved process.

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Regenerative Aqueous Carbonate Process for Utility and Industrial Sulfur Dioxide Removal

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The aqueous carbonate process (ACP) is a unique regenerative sulfur dioxide removal process which is applicable to utility and industrial installations. This process uses a dilute sodium carbonate solution to remove sulfur dioxide from flue gases. The scrubbant is atomized in a spray dryer. Sodium sulfites and sulfates are formed which are reduced and regenerated to carbonate in an aqueous regenerative subsystem which also produces sulfur. The process eliminates the great quantities of solid waste associated with open loop processes. Reheat is eliminated because the flue gas is not saturated during scrubbing. Typical economics show a capital cost of below \$70/kw (\$32 per 1000/SCF of gas throughput). Operating costs from 1 to 3 mills/kw-hr have been estimated. The process, a summary of pilot test results, integration information, and system economics are discussed.

The aqueous carbonate process (ACP) has been under development at Atomics International for the last 4½ yr. The program aims to establish a technology which eliminates or minimizes the major problems encountered in operating most other sulfur dioxide removal processes. That technology includes the use of sodium carbonate as the scrubbant in the modified spray dryer and the complete regeneration of the sulfur dioxide removal products to recover elemental sulfur and produce sodium carbonate for reuse in the spray dryer-scrubber.

The modified spray dryer provides intimate contact between the sulfur dioxide-containing waste gas and a finely atomized fog of sodium carbonate solution. Only small quantities of the reactive sodium car-

bonate solution are required to achieve excellent sulfur dioxide removal. The reaction product is a dry powder easily collected and stored, and the waste gas does not become saturated with water vapor. This kind of scrubber is not subject to scaling or plugging problems, does not require a gas reheater, and operates with a low liquid-to-gas ratio. By providing surge capacity for the sodium carbonate solution and storage capacity for the dry reaction product, the scrubbing system can be easily and inexpensively decoupled from the regeneration system. The net result is a sulfur dioxide scrubbing system with a high degree of operational reliability.

Complete regeneration in the ACP system is accomplished by three basic chemical steps. In the first step the product sodium sulfite and sulfate are reduced to sodium sulfide. Atomics International has developed a high temperature reducer which accepts the product from the spray dryer-scrubber, melts it, elevates its temperature, and reduces the sulfur-containing salts to the desired sulfide form with coke or coal. The second regeneration step involves dissolving the sulfide in water and carbonating it to reform sodium carbonate for recycle to the scrubber. A hydrogen sulfide-rich gas is evolved. Technology similar to that used in chemical recovery processes in the pulp and paper industry is used. In the final step the hydrogen sulfide is converted to elemental sulfur by a Claus process. Since elemental sulfur is the only system by-product, the problems of disposing of sludge or sulfate bleed streams are eliminated.

The ACP system combines a sulfur dioxide scrubbing system based on spray dryer technology with a regeneration system based on a unique reduction step coupled to chemical recovery and Claus technologies. This combination results in an efficient and reliable process for application to sulfur dioxide pollution problems. The remainder of this paper discusses the details of the process and typical installation characteristics and also presents process economics which indicate that the ACP system is economically feasible as well as technically sound.

Process Description

The key component of the ACP scrubbing system is a modified spray dryer which serves as a reaction chamber for the sulfur dioxide removal. In the spray dryer, the sodium carbonate solution is atomized by a high speed centrifugal atomizer and mixed with the hot gas entering the dryer through a vane-ring. The fine mist of solution droplets absorbs sulfur dioxide while the thermal energy of the waste gas vaporizes the water without saturating or excessively cooling the gas. Thus, the spray dryer produces a gas low in sulfur dioxide but containing dry particles of the reaction products from the contactor—sodium carbonate, sulfite, and

sulfate. This powder is subsequently separated from the gas and collected for disposal with the open loop system or for processing and regeneration in the regenerative version. After product collection, the treated waste gas remains relatively hot and is vented through a stack.

Figure 1 is a block diagram of the key subsystems of an ACP regenerative system which are integrated into an existing power plant where the clean gas is vented through an existing stack after it has been through the scrubber and solids removal systems. Typically, a new induced draft

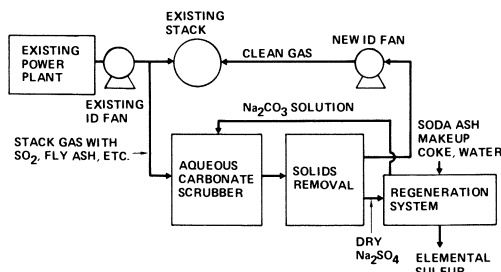


Figure 1. Regenerative ACP block diagram

fan is required to provide the pressure to move the gas through the system. Dry powder from the solids removal system is transferred to the block shown as the regenerative system. The chemicals needed by the regeneration system include makeup sodium carbonate (soda ash), a carbon source for the reduction step, and water. The products from this system are ash, which is derived mainly from the flue gas, and elemental sulfur, which is a high purity by-product. Additional detail on the scrubber system is shown in Figure 2 such as the solution feed tanks and pumps, the spray dryer, cyclones, and, in this case, for very high particulate removal, a small electrostatic precipitator. In addition, a solids transfer system is shown which conveys the dry powder from the cyclones and precipitator to a separate or adjacent regeneration system. The equipment shown in Figure 2 is suitable for retrofit into an existing plant.

An ACP regeneration system flow diagram is shown in Figure 3. This diagram represents typical processing steps without proprietary modifications or operational details. As shown, the product salt is conveyed along with coke or any other carbon source to the molten salt reducer. In the reducer the salt is heated, melted, and reduced in a single zone by adding air and coke. Air provides some reoxidation of sulfide to generate sensible heat while the coke acts directly to reduce the sulfite and sulfate to sulfide. The molten mixture is passed into a quench tank where it is dissolved and processed as a low temperature (below the boiling point of water)

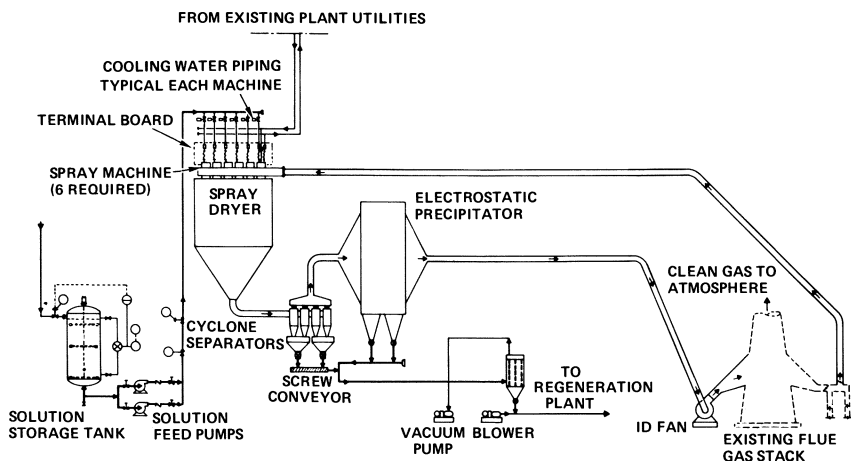


Figure 2. Scrubber subsystem loop

aqueous solution. The reducer off-gas is used as the carbon dioxide source for subsequent carbonation steps and as a source of process heat.

The aqueous solution is cooled and filtered to remove any excess coke, coke ash, or fly ash. After filtration, the solution is precarbonated with pure carbon dioxide recovered from the decomposer. Final carbonation occurs in the bicarbonator-crystallizer with carbon dioxide from the reducer off-gas. Gases evolved from both the precarbonator and the

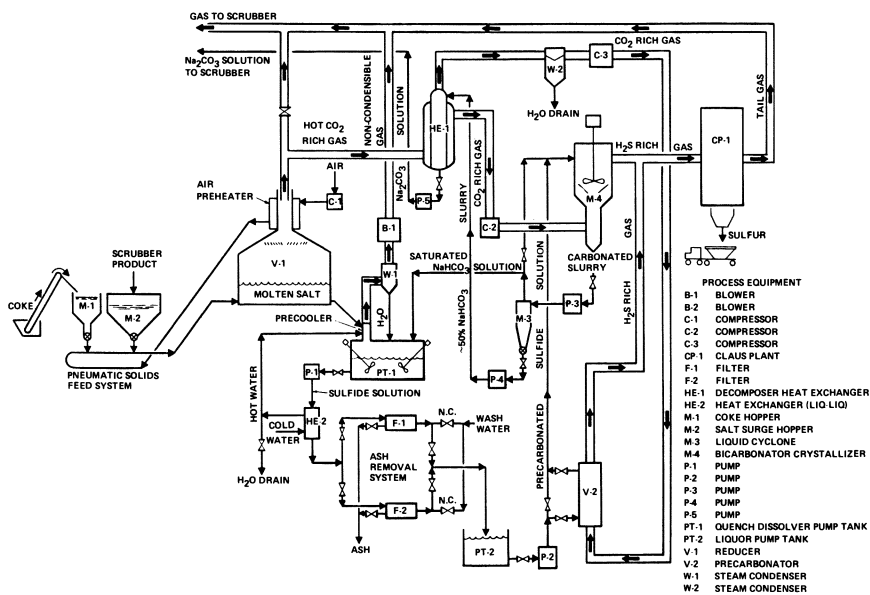


Figure 3. Regeneration subsystem

bicarbonator–crystallizer are rich in hydrogen sulfide and are combined for subsequent recovery of elemental sulfur in the Claus plant. Tail gas from the Claus plant is returned to the scrubber for final cleanup.

The product from the bicarbonator–crystallizer is a sodium carbonate–sodium bicarbonate slurry which is decomposed to produce a sodium carbonate solution for return to the scrubber to provide pure carbon dioxide for the precarbonator. This completes the regeneration cycle and closes the loop for the total ACP system. The technology involved is a combination of a unique reducer and aqueous chemical processing, most of which is commercially proved.

So far, development efforts have concentrated on pilot demonstration of the scrubbing system and the reducer. Extensive test data have been generated with 5-ft and 7-ft diameter spray dryer–scrubbers. Proprietary test results are available from 4-ft and 9-ft diameter reducers. Key operating and performance characteristics of the aqueous regeneration steps have also been tested. These pilot test results combined with existing data and technology from the spray drying and pulp and paper industries provide a firm technical base for the design and construction of large-scale ACP systems.

A key component of the regeneration subsystem is the reducer. This component is a ceramic-lined vessel which contains the molten salt at temperatures approaching 2000°F. The component is common to several other sulfur dioxide and coal gasification processes and has been demonstrated at both 4-ft and 9-ft diameter size scales. In the reducer, both the oxidation of sulfide to sulfate and the reduction of sulfate to sulfide by the coke proceed simultaneously.

Test Results

The first pilot scrubber tests were conducted using simulated flue gas to establish the feasibility of sulfur dioxide's reacting with sodium carbonate solutions and slurries in a spray dryer. Subsequent tests were conducted at the Mohave generating station, where a 5-ft diameter modified spray dryer was used to test sulfur dioxide removal from a side stream of flue gas from this coal-fired power plant (Figure 4). The spray dryer had been in operation for over 20 yr in various drying applications prior to modification to a sulfur dioxide scrubber. It was used in over 100 tests at Mohave without a single operational problem.

Most of the Mohave test data were obtained with flue gas containing 400 ppm or less sulfur dioxide since this is characteristic for a power plant burning low sulfur western coal. A few tests were run at various concentrations up to 1500 ppm, but most of the available data at high sulfur dioxide concentrations were obtained using simulated flue gas in a 7-ft

diameter spray dryer scrubber. After establishing that the data obtained at Mohave was identical to that obtained when using simulated flue gas, an extensive range of tests was run with the 7-ft unit at sulfur dioxide concentrations ranging from 200 to 8000 ppm. These data cover the range of most utility and industrial scrubbing applications and can be supple-

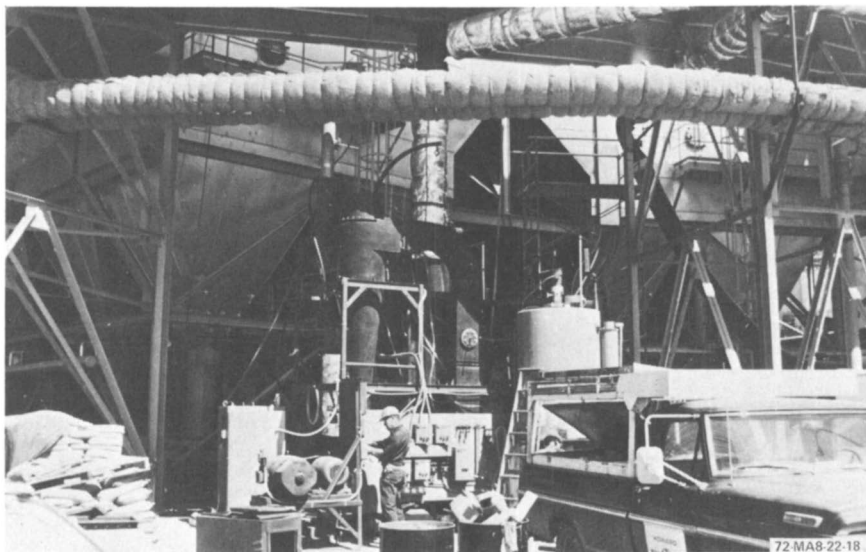


Figure 4. Pilot scrubber installation

mented as necessary in the future to cover special or unusual sulfur dioxide removal problems.

Figure 5 is a plot of some of the data taken during the Mohave test program and illustrates an important and desirable operation characteristic of a spray dryer-scrubber. Only about 0.3 gal of the 5.5 wt % sodium carbonate solution was needed/1000 standard cu ft (SCF) of flue gas to obtain greater than 90% removal of the 400 ppm inlet sulfur dioxide. Subsequent tests have confirmed that this same liquid-to-gas ratio (L/G) can be used to remove greater than 90% of the sulfur dioxide from gases containing 200–4000 ppm sulfur dioxide. The concentration of sodium carbonate in solution is adjusted in proportion to the sulfur dioxide concentration in the gas to provide sufficient alkalinity to neutralize the absorbed sulfur dioxide, but the L/G itself remains at about 0.3 gal/1000 SCF over this range of concentrations. Above 4000 ppm sulfur dioxide, it is necessary to increase the L/G to provide enough dissolved sodium carbonate to react with the absorbed sulfur dioxide. However, even at 8000 ppm sulfur dioxide, the required L/G is only about

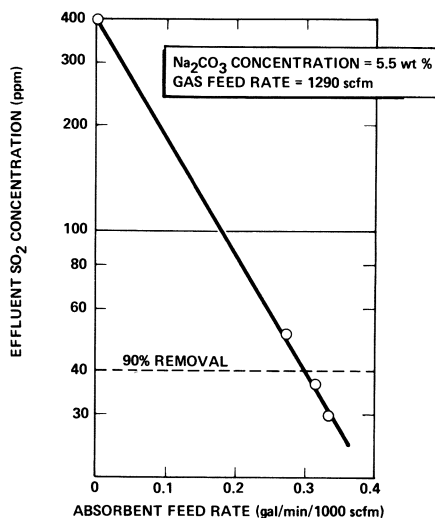


Figure 5. Sulfur dioxide removal vs. absorbent flow rate

0.6 gal/1000 SCF as compared with most other scrubbers which would require 10–100 gal/SCF for such an application.

One of the primary reasons that the spray dryer–scrubber is able to achieve excellent sulfur dioxide removal with such low liquid-to-gas ratios is the small size of the droplets produced by the high speed centrifugal atomizer. This type of atomizer also has an easily controlled turndown capability which is a desirable feature that has been demonstrated in the pilot tests. As gas flow decreases, the amount of sodium carbonate solution can be decreased in direct proportion without interfering with sulfur dioxide removal efficiency. The atomizer actually produces finer droplets at the lower liquid flow rates. This appears to compensate for any gas–liquid mixing problems that could impair performance.

The proper operation of a spray dryer–scrubber also requires that a dry product be formed and subsequently removed from the gas stream. Pilot tests have shown that the product salts will be dry and collectable if the gas temperature at the dryer outlet is maintained about 20°F above its dewpoint. This also tends to minimize plume formation. The cyclone collectors used in the pilot tests removed 89–99% of the product. Although this was excellent performance by mechanical collectors, particulate emission standards will require either replacement of the cyclones or additional collection devices in series with the cyclones. The system design presently favored involves using cyclones to remove the bulk of the product and adding a small electrostatic precipitator for final particulate removal. The sodium salts produced in the spray dryer–scrubber

have excellent resistivity properties to promote effective electrostatic precipitation.

It was observed during the Mohave tests that the fine fly ash particles entering the spray dryer were often trapped in the cyclone along with the bulk of the product salt, apparently because of agglomeration with the atomized droplets in the spray dryer. Thus, the dryer itself helps to minimize emission of fine ash particles which are normally difficult to remove even with an electrostatic precipitator. Numerous samples have been taken and extensive data have been accumulated on the physical

Table I. Typical Scrubber System Performance

<i>Inlet Flue Gas Properties</i>	<i>Low Sulfur Coal</i>	<i>3% Sulfur Coal</i>
Temperature (°F)	300	300
SO ₂ concentrations (ppm)	400	2200
Ash content (grain/SCF)	0.03 (downstream of main power plant electrostatic precipitator)	2.0 (no prior ash removal)
H ₂ O content (vol %)	14	10
<i>Spray Dryer Operating Conditions</i>		
Feed composition (wt % Na ₂ CO ₃)	4.4	20
Feed rate (gal/1000 SCF)	0.32 (0.12 lb Na ₂ CO ₃ /1000 SCF)	0.34 (0.70 lb Na ₂ CO ₃ /1000 SCF)
Gas pressure drop (in. H ₂ O, including cyclone)	9	10
<i>Exit Gas Properties</i>		
Temperature (°F)	155	155
Dewpoint (°F)	134.5	132.5
SO ₂ concentration (ppm)	40 (90% removal)	130 (94% removal)
Particulate loading (grain/SCF with cyclone)	~0.05 (<0.01 grain/SCF with electrostatic precipitator according to manufacturer's guaranteed specification)	~0.2 (estimated 0.01 with addition of precipitator)
<i>Product Composition (wt %)</i>		
Na ₂ CO ₃	6	5
NaHCO ₃	12	10
Na ₂ SO ₄	17	12
Na ₂ SO ₃	62	50
H ₂ O	1	1
Ash	2	22

and chemical properties of the product salts, both upstream and downstream of the cyclone. These data are considered adequate to specify, design, and warrant production collection systems capable of limiting emissions to less than 0.01 grain/SCF.

Typical scrubber system performance is given in Table I. It was derived from test results, and it shows two cases—one representing a power

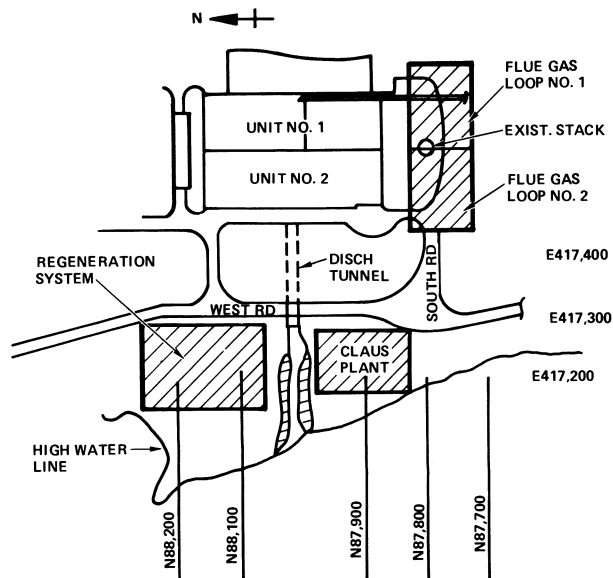


Figure 6. Typical ACP system plot arrangement

plant such as Mohave which burns low sulfur western coal and the other representing a power plant which burns 3% sulfur eastern coal. The major difference in the two cases occurs because of the water vapor and the ash content in the inlet flue gas. The inlet water vapor content in the Mohave case limits the amount of solution that can be sprayed into the gas and thereby limits sulfur dioxide removal. The inlet ash content in the second case causes a slightly higher ΔP and adds a significant burden to the particulate collection equipment. The high percentage of ash in the product will also complicate regeneration.

Bench and pilot scale tests of the various steps in ACP regeneration have been conducted such as reduction, quenching, filtration, precarbonation, carbonation, decomposition, and hydrogen sulfide scrubbing. These tests are continuing in the laboratories and the nearby field test facility to optimize the ACP regeneration system performance and/or to develop new and better processing technology.

System Engineering

A number of engineering studies have been conducted to evaluate the size, integration ability, cost, and interfaces of full-scale ACP systems. Most of this work has been done in connection with power plant integration, but the results can be applied to both industrial and power plants. Figure 6 shows a plot plan for an ACP system that treats in excess of 825,000 standard cu ft/min (SCFM). The inlet sulfur dioxide concentration of this gas is approximately 2200 ppm. The system is designed for a 95.5% removal and an outlet particulate loading of 0.01 grain/SCF or 0.027 lb/10⁶ Btu.

Figure 7 is a plan view of the scrubber installation with twin scrubbers used to treat the 825,000 SCFM. The gas is removed from existing duct work, conveyed to the top of the scrubber, and passed through the scrubber, cyclones, precipitator, booster fans, and back to the existing stack. The existing ducting or the scrubber system, can be bypassed depending on operating and maintenance cycles in the power plant. The scrubbers are approximately the largest module size proposed for either

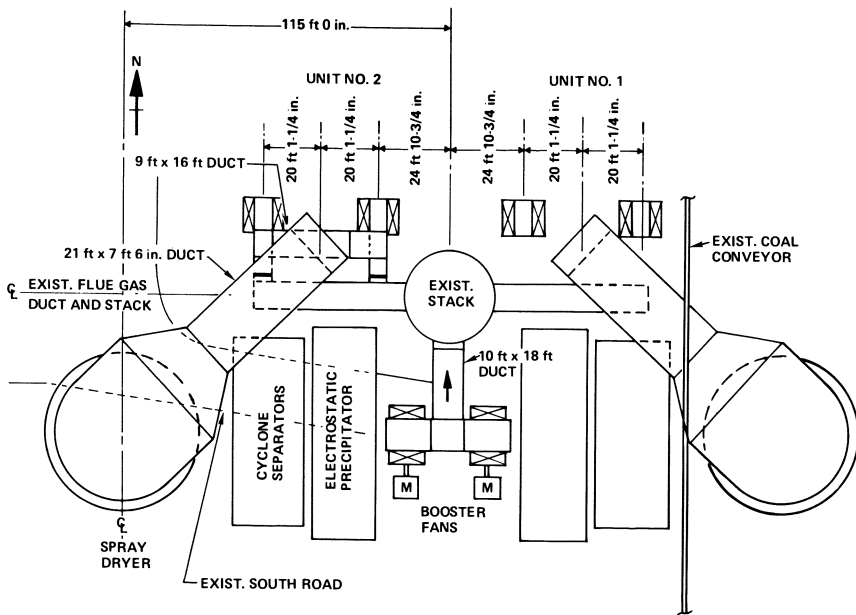


Figure 7. Scrubber installation plan view

power or industrial plants. They are 52 ft in diameter and are made of carbon steel. Figure 8 shows the scrubber installation stands 135 ft high. While the equipment is obviously large, the costs associated with these low energy scrubber systems are acceptably low. The technology is well

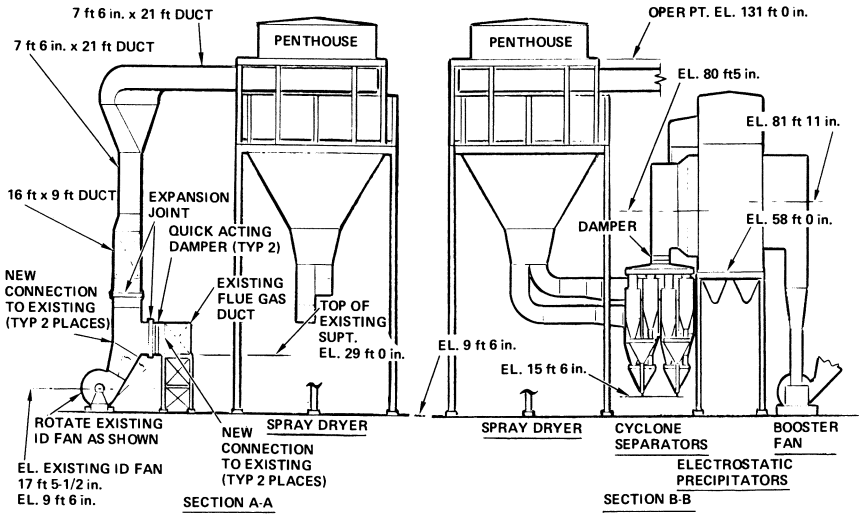


Figure 8. Scrubber installation elevation view

established, and materials such as carbon steel can be used because of the unique internal environment of a spray dryer-scrubber.

The regeneration system associated with, but decoupled from, the scrubber installation occupies a plot of about 7/10 acre (Figure 9). It contains dual reducers and multiple aqueous processing columns throughout. The system can produce 17.7 tons/hr of sodium carbonate. That

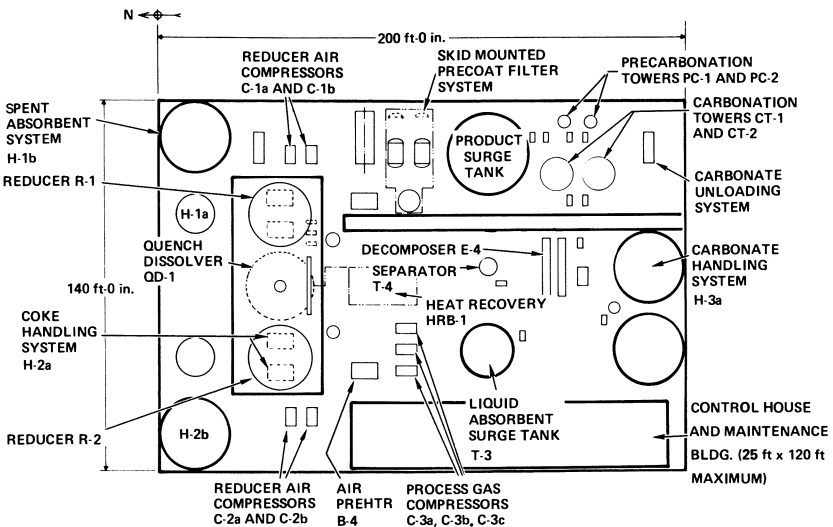


Figure 9. Regeneration system plot

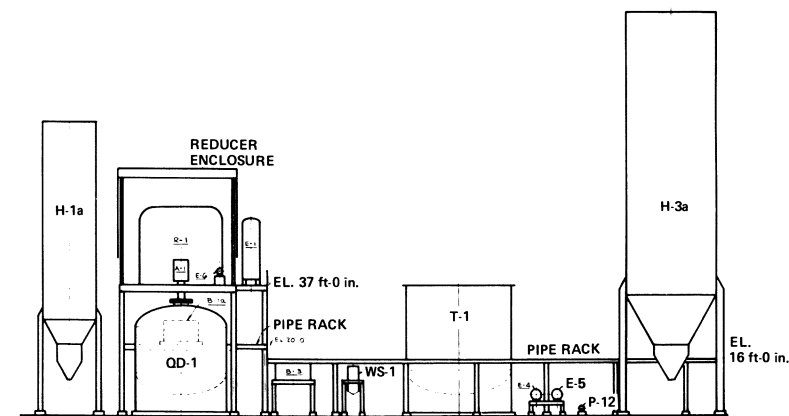


Figure 10. Regeneration elevation view

amount provides for product salt regeneration on a continuous basis when the power plant operates at full capacity on 3.5% sulfur coal. Figure 10 shows an elevation of this regeneration system. The largest equipment is associated with the regenerated carbonate handling and storage system. The reducer equipment, which is elevated above the quench tank, is about 60 ft high.

This particular regenerative ACP system including the Claus plant requires approximately 2½ acres of land, or about 300 sq ft/Mw (140 sq ft/1000 SCFM treated). The regeneration equipment can be decoupled from the scrubber system, yielding high overall ACP system reliability. The decoupling is a function of the surge capacity which is placed between the scrubber and the regeneration equipment. Table II shows the expected performance from this plant. The two columns indicate the design performance and the warranted performance. The plant will be designed for somewhat better operating performance than will be warranted. However, even the warranted performance is substantially better than many other available systems, and all federal standards are met or exceeded by the system.

Table II. ACP System Performance

	Warranty	Design
SO ₂ removal ^a (%)	90 (minimum)	95.5
SO ₂ emissions ^a (lb/10 ⁶ Btu)	0.55	0.25
Particulate emissions (grain/SCF)	0.02 ^b	0.01
Electrical power demand (kw, 24-hr average)	9900	7580
Petroleum coke (ton/hr)	8	6.6

^a 3.5 wt % sulfur coal.

^b To meet mass and opacity standards.

Economics

A thorough analysis of the capital and operating economics was made for the system described above. The basis for this estimate is shown in Table III, and relatively conservative assumptions have been made for the cost of the various utilities, maintenance, operating supplies, overhead, and capital charge rate. The analysis was based on designing the plant for the equivalent of 7000 hr/yr of full load operation. The capital costs, broken down into the gas interface loop and the regeneration system, are shown in Table IV. The cost for the scrubber loop and its asso-

Table III. Total Annual Cost Assumptions

Operation at full power—7000 hr/yr
Natural gas—\$0.40/Mcf
Coke—\$20/ton
Electrical power cost—10 mills/kw-hr
Operation labor—\$10/hr
Maintenance—3% of capital cost
Operating supplies—0.5% of capital cost
Overhead
Payroll—40% of labor
Plant—50% of labor, maintenance, and supplies
Capital charge rate—15%/yr

Table IV. Capital Cost Estimate Utility Systems for a 330-Mw Plant Using 3.5% Sulfur Coal

Gas interface loop—installed	\$ 7,343,000
Engineering and management	1,586,000
	<hr/>
Subtotal	8,929,000 (27/kw)
Regeneration system installed	9,201,000
Engineering and management	2,917,000
	<hr/>
Subtotal	12,118,000 (36.8/kw)
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Total	\$21,047,000 (63.8/kw)

ciated equipment is approximately \$27/kw. This includes all engineering, management, equipment, construction, startup, and debugging. The regeneration subsystem is somewhat more expensive and is estimated at \$36.80/kw. This cost is for regeneration associated with high sulfur fuel. The total cost then for the regenerative aqueous carbonate process on an eastern utilities site is \$63.80/kw. This compares quite favorably with the cost for non-regenerative lime and limestone systems, and the system has the advantage of being fully regenerative.

Table V shows the utilities costs for this specific plant site and conditions. The largest operating cost in the utility category is supplying petroleum coke at \$20/ton. The next largest expense is electrical power,

Table V. Utility Costs

<i>Parameter</i>	<i>330 Mw Plant (mills/kw-hr)</i>
Electricity at 10 mills/kw-hr-	0.230
Natural gas at 40°F/100	0.039
Coke at \$20/ton	0.400
Cooling water	0.0087
Process water	0.0136
Boiler feed water	0.0022
Steam	0.0114
Makeup carbonate	0.0076
Total utility cost	<u>0.7125</u>

which is to be expected with any sulfur dioxide removal system. With regard to the coke requirement, one could design this plant to use coal as the reducing agent in the reducer at some penalty in regeneration and filtration equipment. However, a net savings in operating costs could well occur because of the magnitude of the costs.

The other operating costs associated with the plant include labor, maintenance, supplies, payroll, plant overhead, capital charge, etc. Table VI summarizes utility and material costs for each subsystem, *i.e.*, the gas and regenerative subsystems, and gives total operating costs. The costs are something less than 1 mill/kw-hr for the gas interface system and about 1.8 mills/kw-hr for the regeneration system, or a total operating cost of 2.8 mills/kw-hr to provide sulfur dioxide removal. No credit whatsoever has been taken for the sulfur produced, but the total operating cost of the Claus plant is included.

If one evaluates the cost effectiveness of such a system by looking at fuel costs as a function of sulfur content and comparing total operating

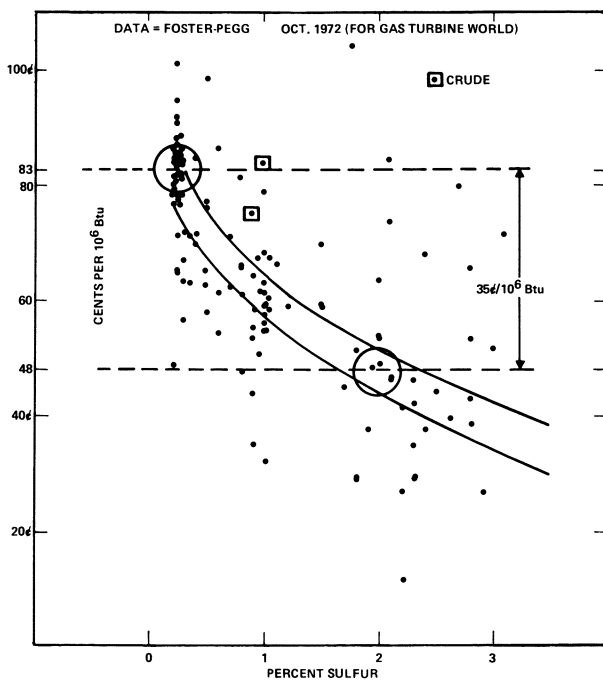
**Table VI. Annual Operating Cost Estimate (\$000)
(17.7 tons Sodium Carbonate/hr, 7000 hr/yr)**

	<i>Gas Interface</i>	<i>Regen- eration</i>	<i>Total</i>
Utilities and materials	303	1340	1643
Labor and supervision at \$10/hr	100	200	300
Maintenance at 3% depreciation base	268	364	632
Supplies at 0.5% depreciation base	44	61	105
Payroll overhead at 40% labor and supervision	40	80	120
Plant overhead at 50% labor and supervision, maintenance, and supplies	206	312	518
Capital charge at 15%	1340	1820	3160
Total (\$000/yr)	<u>2301</u>	<u>4177</u>	<u>6478</u>
Total (mills/kw-hr)	0.99	1.81	2.80

costs for the ACP system with potential savings in fuel costs, the result is quite surprising. Figure 11 is a curve from *Gas Turbine World* of October 1972 that shows fuel costs as a function of sulfur in the fuel. Although there is a great deal of scatter, it can be seen that Foster-Pegg has put in a correlation suggesting about a 35¢ per million Btu savings by going from 0.3% sulfur fuel to 2% sulfur fuel. Being able to burn 3.5% sulfur coal and still meet pollution standards probably would result in an even larger savings. Based on a conservative 35¢/million Btu, the analysis shown in Table VII shows a 6½ million dollar/yr annual cost associated with the particular plant design (as presented in Table VI), an 8.1 million dollar fuel savings, and a sulfur credit of about \$630,000. The result is a net savings of 2.25 million dollars/yr or 1.0 mill/kw-hr, as opposed to the operating loss usually associated with sulfur dioxide removal plants.

Summary

In conclusion, this second-generation sulfur dioxide removal process is now ready for full-scale installation. It promises to solve many of the



Gas Turbine World

Figure 11. Fuel cost vs. sulfur content

Table VII. ACP Cost Effectiveness

	<i>330 Mw Plant</i>
Annual operating cost (\$/yr, 000)	6480
Annual operating cost (mills/kw-hr)	2.8
Fuel savings (\$000/yr)	8100
Sulfur value at \$20/ton (\$000/yr)	630
Total credit (\$000/yr)	8730
Total savings (\$000/yr)	2250
(mills/kw-hr)	1.0

problems associated with past sulfur dioxide scrubbing systems. Specifically the ACP regenerative system:

1. Provides an economic advantage by allowing the use of high sulfur fuel while providing low sulfur dioxide emissions
2. Eliminates sludge production and the related disposal problem
3. Eliminates maintenance problems associated with scaling and plugging
4. Minimizes the impact on plant reliability by using a simple scrubbing scheme somewhat decoupled from the regeneration equipment

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Removal and Reduction of Sulfur Dioxides from Polluted Gas Streams

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This new, second generation process was primarily designed to remove sulfur dioxide from polluted gas streams. The front end of the process was developed by Bergbau Forschung and operates as a sulfur dioxide concentrator, placing the sulfur dioxide-containing gases in contact with a special carbon. Following the preferential adsorption of sulfur dioxide, the special carbon adsorbent is regenerated by thermal treatment to yield a concentrated sulfur dioxide off-gas which is converted to sulfur in a coal bed by Foster Wheeler Corporation's Resox process. This process represents a new way to achieve the desired reaction rate between sulfur dioxide and crushed coal at approximately 650–760°F.

The idea to use the various forms of coal to remove sulfur dioxide is not new and was described in an English patent as early as 1879 (1). However, massive research and development programs to develop commercially viable sulfur dioxide removal processes were not initiated until 80 years later, when ecological considerations forced public concern.

The Bergbau Forschung–Foster Wheeler sulfur dioxide removal process was originally developed for the utility industry. However, the basic system can, and will, be used to meet the specific requirements of other industries as well. This second generation sulfur dioxide removal process consists of three basic steps. The first step removes the sulfur dioxide from polluted gas streams by adsorption on carbon (activated coke). The second step regenerates the adsorbent (coke), producing a gas stream with high sulfur dioxide concentration. The third step treats the sulfur dioxide-rich stream by reducing it to elemental sulfur.

Sulfur Dioxide Removal and Adsorbent Regeneration

Physical Chemistry and Process Technology of the Sulfur Dioxide Removal System. The sulfur dioxide removal system was developed by Bergbau Forschung in Essen, West Germany and is based on and designed for a special activated coke adsorbent. The activated coke, the most critical ingredient in the system, is the result of a research and development program initiated in the late 1950s. It has excellent sulfur dioxide adsorption, high ignition temperature, and good physical strength.

The basic system consists of a gas/solid contacting device (the adsorber) and a regenerator (the desorber). Within the adsorber the activated coke moves downward in the plug flow which is contained by permanently fixed steel louvers on the gas entrance and exit sides of the unit. The polluted gas stream is passed in through the louvers, through the adsorbent, and out through louvers on the opposite side of the adsorber. The sulfur dioxide contained in the gas stream is adsorbed on the inner surface of the activated coke and is then oxidized to sulfuric acid in the presence of the oxygen and water vapor which are also in the polluted gas (2). Coincidentally, the adsorber functions as a panel bed filter to remove particulates entrained in the gas stream. The sulfuric acid content of the activated coke increases as a function of coke dwell time in the adsorber. Therefore, the coke discharged at the bottom of the adsorber contains the highest possible amount of sulfuric acid for the given conditions and adsorber geometry.

The adsorbent is regenerated after it is discharged from the adsorber and is separated from particulates by a vibrating sieve. The regeneration is effected thermally by heating the sulfuric acid-loaded adsorbent in an inert atmosphere. The regeneration conditions cause a directional change in the driving forces of the reactions in this system. The participants undergo a modified reversal of the adsorption reaction in which the fixed carbon of the adsorbent reduces the sulfuric acid to sulfur dioxide.

Technically, the regeneration is carried out in a moving bed reactor using sand as a direct heat carrier to heat the adsorbent to 600–650°C. The effluent gas of the regeneration contains 20–30% sulfur dioxide by volume as well as water and carbon dioxide. It can be fed directly to Foster Wheeler's Resox process which converts the sulfur dioxide content to sulfur.

Mechanism of Adsorption. The mechanism of the sulfur dioxide adsorption and oxidation on carbon shows that the sulfur dioxide pick-up can be divided into three subsequent phases in which phase change is a function of time. In phase one, the adsorption rate is controlled by the rate of sulfur dioxide diffusion into the inner surface of the adsorbent. As the adsorption proceeds, the number of locations available for adsorp-

tion declines, and finally most of the easily accessible inner surface becomes occupied.

It is necessary to create vacancies on the inner surface to allow continued adsorption. Vacancies, however, are created by sulfur dioxide oxidation and the subsequent transport of the generated sulfuric acid to readily accessible inner pores. Therefore, the adsorption rate is now controlled by the rate of oxidation and transport. This interdependent relationship is characteristic of this phase of adsorption.

In the third phase, the accessible inner pores start to fill up to capacity and, therefore, the transport rate approaches zero causing an excess of sulfuric acid to build up slowly on the inner surface. The continuous presence of sulfuric acid poisons the active centers, and the adsorption activity declines.

Since the bulk of the adsorption is accomplished in the second phase under stationary conditions, the adsorbent was developed to obtain high sulfur dioxide-to-sulfuric acid conversion rates for a large portion of its inner surface. The relationship between pore structure and sulfur dioxide adsorption is shown in Figure 1. The ordinate is the time, in hours, after which 10% of the inlet sulfur dioxide will pass through the carbon without being adsorbed. The mean pore diameter of adsorption pores was selected for the abscissa as the parameter to characterize the adsorbent structure (3). Adsorbents produced from bituminous coal with and without catalyst impregnation were tested. In both cases, the sulfur

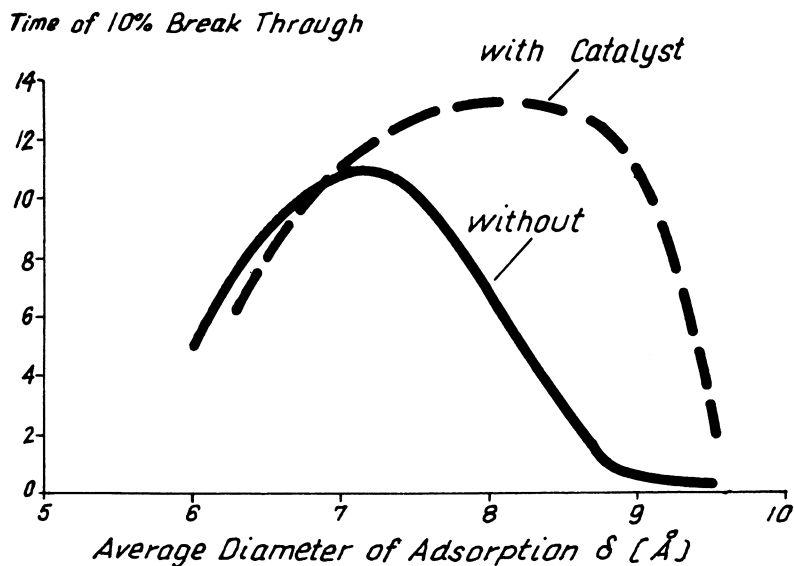


Figure 1. Sulfur dioxide sorption of various active carbons

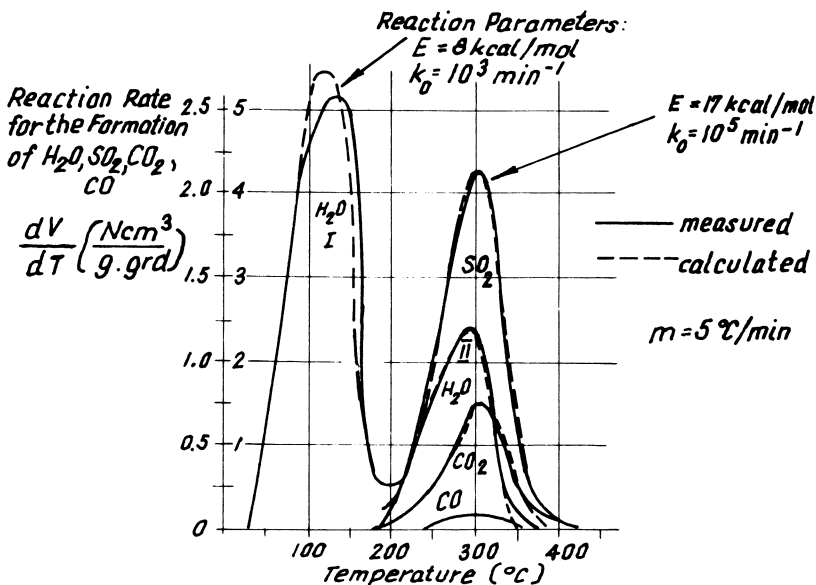
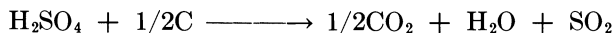


Figure 2. Nonisothermal kinetics of thermal regeneration

dioxide adsorption increases initially with increasing mean pore size diameter and then declines after reaching a maximum at about 8A and 7.2A, respectively. The data further indicate that an adsorbent with catalyst adsorbs more sulfur dioxide and therefore that pore diameters are less critical. Unfortunately, this difference in performance is not sufficient to offset economic and process considerations which favor an adsorbent without catalyst. The net result of the research and development work is an adsorbent for commercial use, which is produced from preoxidized bituminous coal and which has a particle diameter of 9 mm, a hardness of over 90%, an ignition temperature over 400°C, and a sulfur dioxide adsorption of 8–15% (4).

Adsorbent Regeneration. At temperatures above 200°C activated coke containing sulfuric acid undergoes the following reaction:



To obtain the nonisothermal reaction kinetics, the sulfuric acid-containing coke as heated at a constant rate of 5°C/min and the volume of evolving individual reaction products was monitored *vs.* the change in temperature. Under the conditions of this experiment the regeneration reaction starts around 200°C and is practically completed at 450°C as indicated by the evolution of the reaction products as shown in Figure 2.

The slow heating rate used in this experiment would be impractical for a commercial operation as the regenerator vessel would be quite large. Commercially, the regeneration heat is obtained by mixing the adsorbent with a hot solid. Sand has been found to be a satisfactory solid.

According to the laws of nonisothermal reaction kinetics, the temperature range at which a given reaction proceeds becomes higher as the heating rate is increased. The liberation curves of sulfur dioxide for different heating rates between 5 and 10,000°C/min are shown in Figure 3. The calculations are based on parameters established in laboratory experiments and shown in Figure 2. At an approximated heating rate of 500°C/min in the sand regenerator, the maximum reaction rate would be expected at 520°C with an end point of 680°C.

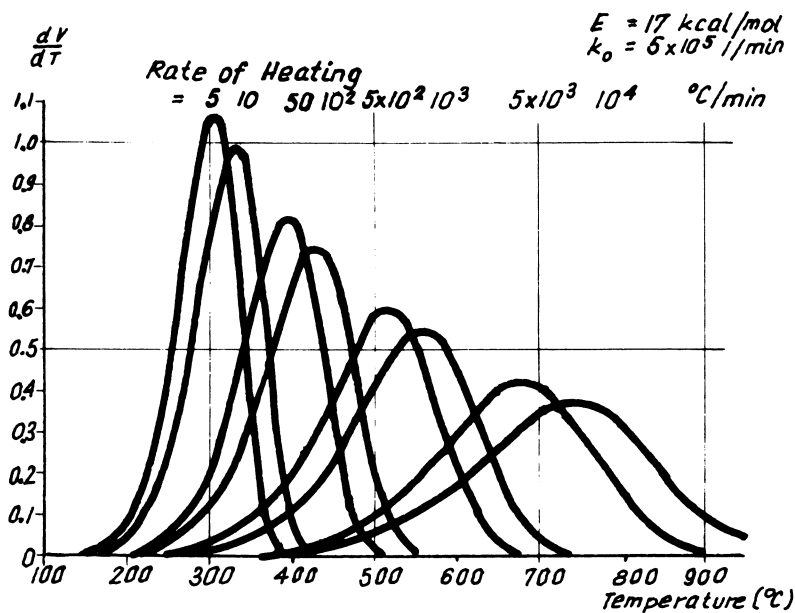


Figure 3. Liberation of sulfur dioxide for different heating rates

Pilot Plant Testing

The process described here has been tested for 2 yrs in a continuously operating pilot plant processing over 100,000 actual cu ft/hr (ACFH) (5). During 1969 the pilot unit processed 528×10^6 ACF of gas in 6000 operating hr. The desulfurization efficiency ranged between 60 and 95%. These differences were caused by deliberate changes in operating parameters such as the gas and coke residence times in the adsorber, temperature of adsorption and regeneration, etc.

Since the pilot unit and the data obtained from it are described in numerous publications only some key conclusions are mentioned here. The pilot operation established the technological feasibility of the process in general and has shown that the assumptions, calculations, and laboratory data-based conclusions concerning particular features of the process such as adsorption, regeneration at high heating rate, etc. are correct. Data obtained during the 2 yrs of operation also has proved the economical viability of the process.

Reduction of Sulfur Dioxide by Coal

The Resox process uses coal as a reducing agent to produce elemental sulfur. It was developed in Foster Wheeler Corporation's John Blizard Research Center and is the result of a research program initiated in the late 1960s.

This process is designed to reduce the sulfur dioxide in an off-gas stream to sulfur and to condense the sulfur product from the gas stream. It is capable of handling a wide range of inlet gas compositions and does not require gas cleaning, drying, or dust removal systems. Crushed coal is the only material and the only catalyst consumed. The process represents a new way to achieve the desired degree of reaction between sulfur dioxide and crushed coal at temperatures as low as 600°C.

The major process equipment consists of a reactor vessel and a sulfur condenser. In the reactor vessel, sulfur dioxide-rich gases react with crushed coal to yield gaseous elemental sulfur. This sulfur is condensed from the gas stream in the sulfur condenser. The high-purity liquid sulfur effluent of the process is a nonpolluting by-product.

Foster Wheeler Corporation's efforts toward full commercialization of this process are extended in the framework of a three phase program of process research and bench-scale feasibility studies, pilot plant operation, and large scale demonstration. Only the conclusions directly pertaining to the process are discussed here. A detailed discussion of the mechanism and kinetics of this rather involved system is beyond the scope of this paper and will be reported at a later date.

Research and Bench-Scale Feasibility Studies. The reaction between carbon and sulfur dioxide at elevated temperatures is well known and has been used for numerous processes. For example, sulfur was produced at Trail, British Columbia from 1935 to 1943 by blowing sulfur dioxide and oxygen into the bottom of a coke-fired reduction furnace. Coke was charged at the top and ash was removed on a rotary grate at the bottom of the furnace. The hot zone of the furnace was kept at 1300°C to maintain rapid reaction rates and smooth operation. Sufficient sulfur dioxide was added to the gas to react with the carbon monoxide and carbon oxysulfide contained in the reduction furnace off-gas. Coal was con-

sidered unsatisfactory as a reducing agent because of the hydrogen sulfide formation. Carbon will also react with superheated steam at elevated temperatures to yield carbon monoxide and hydrogen.

Foster Wheeler Corporation's research program was based on the assumption that while high temperatures are necessary to obtain a commercially practical reaction rate when sulfur dioxide or steam reacts individually with coal, the two reactions would interact synergistically when combined in a single integrated system. As a result of this interaction, both reactions would be promoted, and commercially practical rates for sulfur dioxide reduction could be obtained at significantly lower temperatures than those reported in the literature or used commercially. A similar behavior for the coal gasification reaction is now being studied in a separate research program.

The bench-scale study was conducted in a small pilot plant designed for the reaction of crushed coal with sulfur dioxide at carefully controlled conditions. The inlet gas composition, reaction temperature, and gas residence time were selected as the independent variables for the study. The outlet gas composition and reaction rate were monitored as dependent variables.

The relationship between sulfur dioxide conversion and the water-to-sulfur dioxide ratio is shown in Figure 4. Since the gas residence time, the reaction temperature, and the dry inlet gas composition were held constant, it is evident that the reaction rate increases with the partial

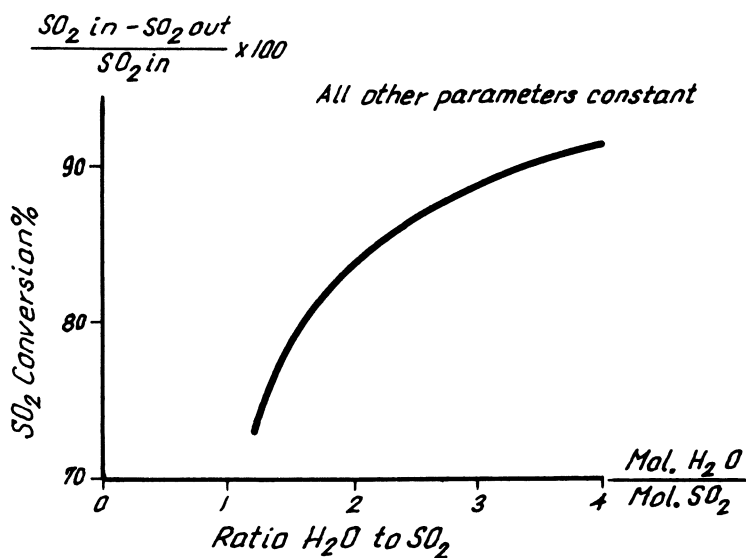


Figure 4. Relationship between sulfur dioxide conversion and the water-to-sulfur dioxide ratio

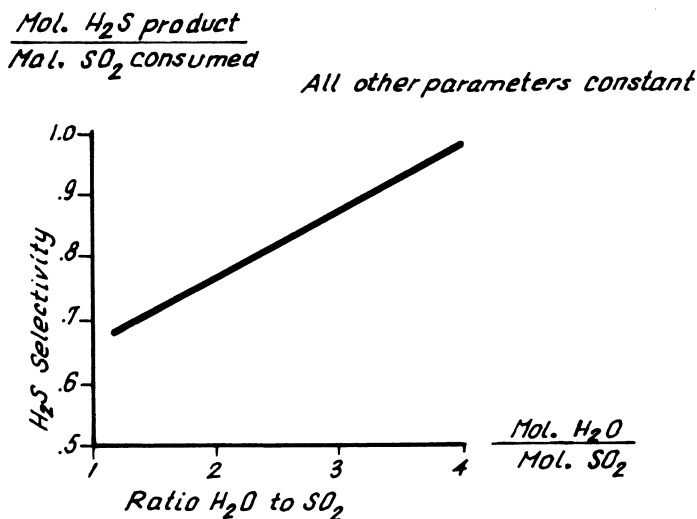


Figure 5. Relationship between hydrogen sulfide selectivity and the water-to-sulfur dioxide ratio

pressure of water in the system. The changing slope of the curve shows the different degree of increase of the reaction rate effected when the water concentration of the system is increased over different previous levels of concentration.

The water, carbon dioxide, sulfur dioxide, nitrogen gas, carbon, and the numerous other compounds resulting from different combination of the elements contained by the compounds above represent a complex system. Depending on the reaction parameters, different reaction routes will dominate the system and will yield different compounds as the major reaction products. The recent research effort concentrated on obtaining elemental sulfur or hydrogen sulfide as the principal reaction products.

In general, it was found that the selectivity of the reaction towards hydrogen sulfide increases with increasing reaction temperatures and water concentrations. The relationship between hydrogen sulfide selectivity and the amount of water in the system is shown in Figure 5.

Nearly all the sulfur dioxide entering the process was converted selectively to hydrogen sulfide between 660 and 760°C. The process was also applied to convert sulfur dioxide to sulfur at lower reaction temperatures. As shown in Figure 6, when 100% of the sulfur dioxide is converted, 90% reacts to form elemental sulfur while 10% yields different by-products such as hydrogen sulfide, carbon oxysulfide, carbon disulfide, etc. Nearly 100% selectivity to sulfur can be obtained at lower conversions corresponding to lower reaction temperatures. Lower temperatures caused lower conversions since the maximum contact time,

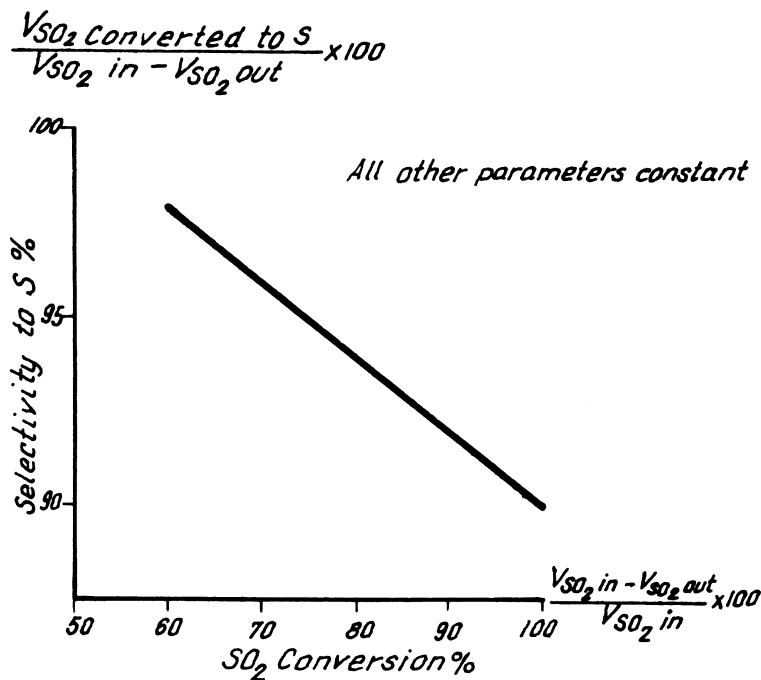


Figure 6. Sulfur dioxide consumed vs. sulfur produced

based on empty reactor volume, between sulfur dioxide-containing gas and carbon was fixed at 6 sec for all experiments.

The varying reactivity of different coals used in this work necessitated different reaction temperatures. The temperatures used were 550–700°C for bituminous coals and 650–800°C for anthracite coals. The results obtained in this phase of the program established process feasibility and showed that the initial assumptions concerning process chemistry and kinetics were correct.

Pilot Plant Operation. The pilot plant operation was the second phase of the research program and was designed to deliver the data necessary to plan, build, and operate a commercial size demonstration plant. In order to accomplish these objectives, a pilot plant of sufficient capacity was constructed and operated for an extended period of time.

A diagram of the pilot facility is shown in Figure 7. The sulfur dioxide, carbon dioxide, nitrogen, and water were metered, blended, and brought to temperature by a fired heater so that the mixture entered the reactor at a temperature and composition representative of the off-gas from the Bergbau Forschung process. The reactor of 2 cu ft volume contained a rice-size anthracite coal bed which moved downward slowly

and countercurrent to the gas stream. The coal hopper located above the reactor gravity fed the system with fresh coal as the bed volume was diminished by the reaction and by the removal of spent material.

Sample ports arranged at quarter point locations along the vertical reactor vessel permitted the gas composition to be monitored at different reactor locations, representing different gas residence times. The temperatures at each of these sample ports, as well as at the inlet and the outlet, were continuously monitored. The effluent gas of the reactor passed through the sulfur condenser. The tail gases leaving the sulfur condenser were sampled and analyzed.

A number of individual pilot runs were conducted at various process conditions to determine the cause and effect relationship of process parameters such as pressure, temperature, and residence time on the process behavior. A quantity of 1200–1500 ACFH of sulfur dioxide-containing gas was processed continuously in the pilot facility.

The integrated results of these individual runs have proved that the system is practical for large scale operations and can treat a variety of sulfur dioxide-rich effluent gases. The completed pilot test program has demonstrated that 90% of the sulfur dioxide in a typical feed gas can be converted to elemental sulfur in a prototype apparatus having design features compatible with commercial requirements.

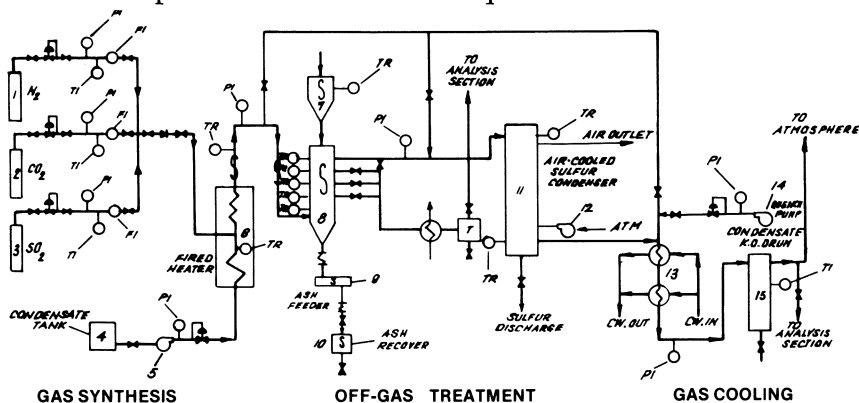


Figure 7. Foster Wheeler Resox pilot unit

Commercial Scale Demonstrations

The first commercial-size demonstration plant was completed in early 1974 by Bergbau Forschung in Lünen, West Germany. The plant, shown in Figure 8, is subsidized by the West German government. It is designed to process 5.3×10^6 standard cu ft/hr of gas. This gas is part of the



Figure 8. *Bergbau Forschung unit in West Germany*

flue gas from a 350 MW coal-fired boiler of the Steag. The plant consists of an adsorber, regenerator, and a modified Claus unit to process the sulfur dioxide-rich regeneration off-gas. Continuous operation was scheduled to start in April 1974.

Parallel with Bergbau Forschung's efforts in West Germany, Foster Wheeler Corp. is constructing the first demonstration plant in the United States. The prototype unit is being erected for Gulf Power Co. in Chattahoochee, Florida and is scheduled to be completed in September 1974. Compared with the Bergbau Forschung unit in Lünen, the Foster Wheeler plant will substitute the Resox process for the modified Claus unit and consume coal instead of natural gas to reduce the sulfur dioxide-rich regenerator off-gas.

In conclusion, when sulfur dioxide must be removed from polluted gas streams and accumulated in some form, reduction to elemental sulfur is the optimum form for accumulation, and crushed coal is the least expensive reducing agent.

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Sulfur Dioxide Absorption and Conversion to Sulfur by the Citrate Process

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The chemistry of the citrate process has been studied through its principal functional steps (absorption, regeneration, and sulfur melting) and important nonfunctional aspects (oxidation and purging). The action of hydrogen sulfide on sulfur dioxide in solution to produce sulfur by this process depends upon controlled complex interactions among a variety of sulfur-containing species including sulfite, bisulfite, thiosulfate, polythionates, and sulfur. The citrate molecule acts primarily as an efficient buffering agent allowing greater than 95% sulfur dioxide removal from industrial stack gases, high sulfur dioxide solution loading, and the recovery of high quality precipitated sulfur. Process efficiency is achieved by choosing operating conditions which yield maximum absorption and regeneration efficiency. The system will tolerate stoichiometric imbalances between absorbed sulfur dioxide and regenerant hydrogen sulfide fed to the reactors.

The citrate process for the recovery of elemental sulfur from sulfur dioxide emissions in waste gas was conceived by Bureau of Mines investigators at the Salt Lake City Metallurgy Research Center in their initial laboratory research reported in 1970 (1). This work led to a scale-up of the process to a 400 cu ft/min (CFM) pilot unit which began treating reverberatory furnace gas at a copper smelter in Arizona in November 1970. While a series of mechanical difficulties allowed only

intermittent operation of the demonstration unit and generation of limited economic and engineering data on the process, the soundness of the process chemistry was established. Details of the process to this point were reported by the Bureau of Mines in June 1971 (2).

To pursue the needed chemical and cost data on the process, the Bureau assembled a second-generation laboratory unit, incorporating modifications dictated by the results of the earlier work. This was operated as a prototype of a pilot plant designed to treat 1000 CFM of 0.5% sulfur dioxide gas, which is now constructed and operating at the Bunker Hill lead smelter, Kellogg, Idaho (3).

Pfizer had been cooperating with the Bureau of Mines on the process since its scale-up to the Arizona pilot plant. The company decided to take a more active role in the investigation and development of the process when the copper smelter demonstration was completed in 1971. Working closely with the Bureau of Mines, Pfizer constructed a laboratory pilot unit in which the viability of the process was confirmed. This was followed by a two-phase laboratory program consisting of an exhaustive study of potentially competitive absorption systems and elucidation of the process chemistry.

The first phase determined that the citrate system best met all of the critical requirements for an ideal sulfur dioxide absorption medium, including the system's capability for efficient removal of sulfur dioxide over a broad concentration range, *e.g.*, the high levels in smelter waste gas, the sulfur dioxide-lean stack gas emitted by power plants, and the intermediate range represented by Claus plants. The results of the second phase of the program, dealing with the process chemistry, forms the basis for much of this paper.

A major step was taken in the development of the citrate process within the industrial sector when, in 1972, Pfizer Inc., Arthur G. McKee and Co., and Peabody Engineered Systems became aware of their mutual interest in the citrate process—Pfizer was a leading manufacturer of citric acid and a chemical plant operator, McKee engineered and constructed process plants within which the citrate process is applicable for pollution control, and Peabody designed and manufactured pollution control equipment and systems.

In late 1972 the three companies announced plans to demonstrate the commercial feasibility of the citrate process. The prime objective was to generate hard engineering and economic data. Basically, Peabody was to fabricate and assemble a skid-mounted 2000 SCFM unit to McKee's design specifications with Pfizer providing chemical expertise, citric acid, and initial host operation of the unit on the power plant in their Terre Haute, Indiana plant site. Since June 1973, when the Terre Haute unit

began operation, it has logged over 1300 hrs of operation and has produced more than 15 tons of sulfur.

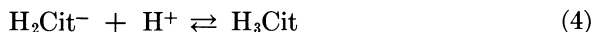
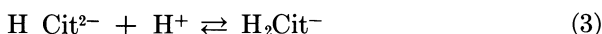
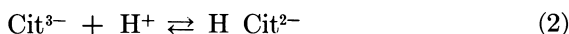
Chemistry of the Citrate Process

The chemistry of the citrate process has been considered to some extent in recent Bureau of Mines publications (2, 3). In their early work on the process, Bureau workers believed the citrate ion functioned as a complexing agent for sulfur dioxide. Subsequent work has shown, however, that the citrate ion functions primarily as a good buffering agent which facilitates efficient extraction of sulfur dioxide from stack gas, high sulfur dioxide solution loading, and the recovery of high quality precipitated sulfur.

Absorption. The solubility of sulfur dioxide in water is limited. It dissolves and sets up the equilibrium:



The solubility can be increased by removing the hydrogen ions formed. In the citrate process this is accomplished by the buffering action of the various citrate species:



The solubility of sulfur dioxide in aqueous solutions, S , can be expressed as a function of the partial pressure in the gas phase (p), Henry's Law constant (H), the hydrogen ion concentration (H^+), and the ionization constants of sulfurous acid (K_1 and K_2):

$$S = Hp \left[1 + \frac{K_1}{(\text{H}^+)} + \frac{K_1 K_2}{(\text{H}^+)^2} \right] \quad (5)$$

This relationship is plotted in Figure 1 for several assumed gas concentrations of sulfur dioxide at 50°C. The graph is approximate since molality and molarity were assumed equal. Also plotted is the concentration of total sulfur dioxide in water *vs.* pH for unbuffered solutions, Reaction 1. In the buffered region to the right of this curve, the solubility increases, rapidly approaching a 10-fold increase for each pH unit increase. Thus, for a 1000-ppm gas the solubility at pH 4.5 is 8.7 g/l., approximately 50 times that of water alone.

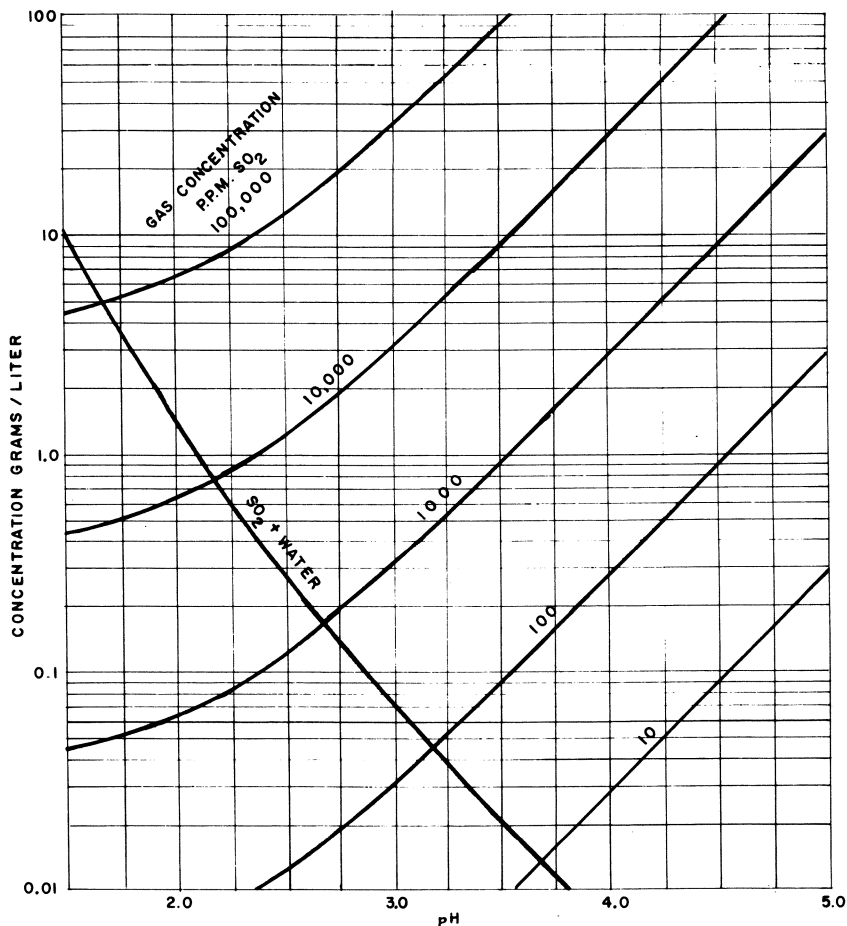


Figure 1. Calculated solubility of SO_2 in water solutions at 50°C as a function of pH for various concentrations of SO_2 in a gas at 1 atm using Equation 5. The SO_2 + water curve shows the calculated pH vs. the SO_2 concentration at 50°C for unbuffered solutions.

The practical effects of pH on sulfur dioxide absorption are shown in Figure 2. From this laboratory work it can be seen that in the range studied, an increase of 0.17 pH unit reduces the sulfur dioxide concentration in the vent gas by about one-half. In the citrate process's operating range, above pH 4.0, the vent gas contained less than 60 ppm sulfur dioxide, indicating better than 97% absorption for a 2000-ppm inlet gas.

Absorption Reactions. In practice the absorbing solution contains some thiosulfate which is formed in the regeneration step. Thiosulfate is reported (4) to form a complex with sulfur dioxide:

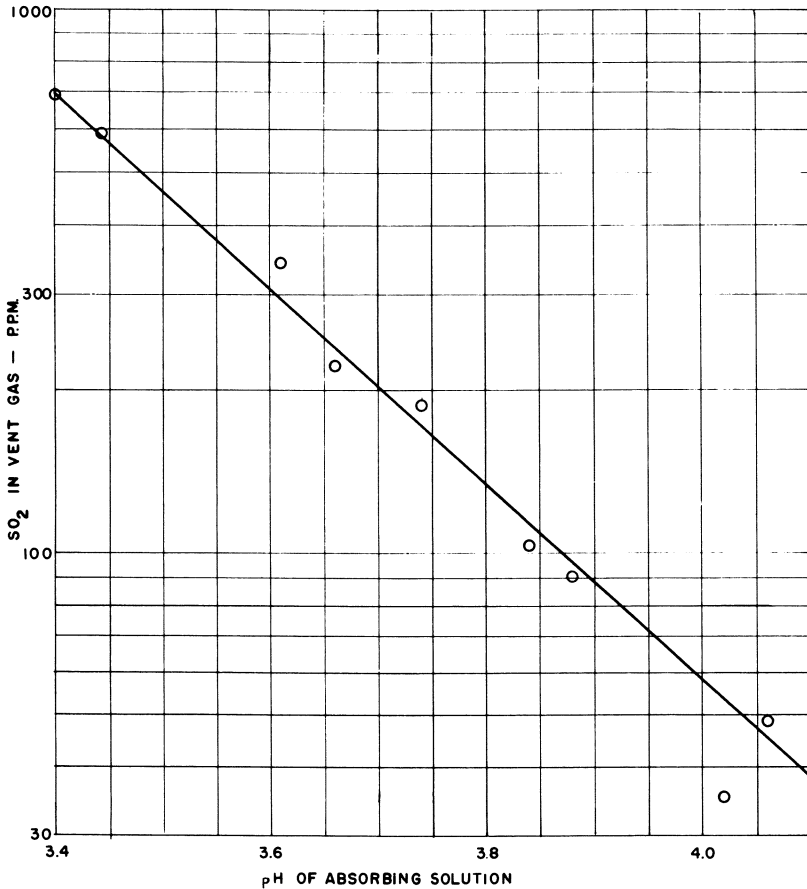
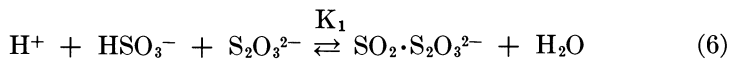


Figure 2. Laboratory absorption studies using a 2-in.-diameter packed column. The curve shows SO_2 concentration in the vent gas as a function of the pH of the absorbing solution for a 2000 ppm SO_2 -feed gas and a 0.5M citrate-feed solution.



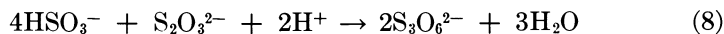
Based on spectrophotometric data, Battaglia and Miller (5) evaluated the constant K^* at pH 3.9 and 22°C, where

$$K^* = \frac{K_1(\text{H}^+)}{(\text{H}_2\text{O})} = \frac{(\text{SO}_2 \cdot \text{S}_2\text{O}_3^{2-})}{(\text{HSO}_3^-)(\text{S}_2\text{O}_3^{2-})} \quad (7)$$

Using their value for a 0.25M thiosulfate solution, about 2% of the sulfur dioxide is in the complex. Thus the presence of thiosulfate would be

expected to aid the absorption of sulfur dioxide slightly. The effect would be greater at lower pH's.

A further reaction between bisulfite and thiosulfate can result in the formation of trithionate:

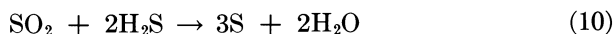


The rate expression for this reaction is reported (5) to be:

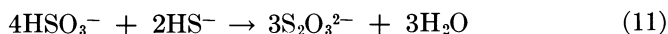
$$\frac{-d(\text{HSO}_3^-)}{dt} = k(\text{HSO}_3^-)(\text{S}_2\text{O}_3^{2-})^3(\text{H}^+)^3 \quad (9)$$

From the reported value of the rate constant at 70°C, it is estimated that for a pH of 4.0 and 0.25*M* thiosulfate, the rate of bisulfite loss is very low, 1% in about 80 hrs. Since the rate is proportional to $(\text{H}^+)^3$, the reaction would be much more significant at lower pH's.

Regeneration. The products formed by treating sulfur dioxide solutions with hydrogen sulfide depend in part on the pH. When hydrogen sulfide is added to a solution of sulfur dioxide in water, a complex mixture is formed that includes polythionic acids, thiosulfuric acid, and colloidal sulfur (in contrast to the crystalline sulfur obtained in the citrate process). This is known as Wackenroder's solution and has been extensively studied. The composition varies with the conditions used. With excess hydrogen sulfide the final product is ultimately approximately 100% sulfur (6). While the overall stoichiometry of the reaction is the same as the gas phase Claus reaction, the chemistry is more complex.

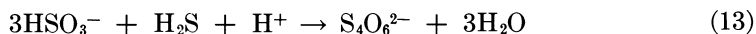
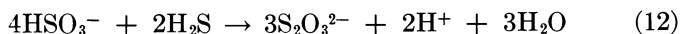


In neutral solution, almost 100% thiosulfate is formed (7):

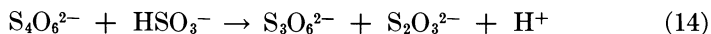


The conditions of the citrate process at pH 4.0–4.5 fall into an intermediate range between the two cases cited, and under these conditions the reaction of sulfur dioxide with hydrogen sulfide falls into two approximately separate phases.

In the first phase, in the presence of an excess of bisulfite, thiosulfate, and tetrathionate are formed by the overall reactions:

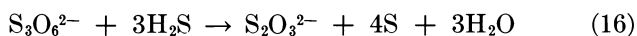
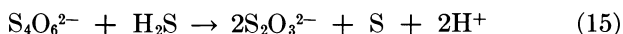


The tetrathionate can react further to form trithionate and more thiosulfate:

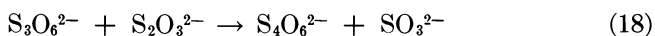


A small amount of sulfur may be formed as in Reaction 10.

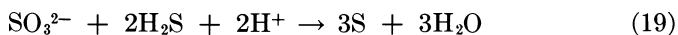
In the second phase the polythionates and thiosulfate react with hydrogen sulfide:



In addition there may be side reactions in which thiosulfate reacts with the polythionates to give the next higher polythionate and sulfite, *e.g.*:



The sulfite formed reacts with hydrogen sulfide to give sulfur.



The reaction of hydrogen sulfide with thiosulfate is much slower than with the polythionates and is rate determining for the regeneration step.

Keller's data (8) indicate that in the pH range of 3.5 to 5.5 the rate is approximated by:

$$\frac{-d(\text{S}_2\text{O}_3^{2-})}{dt} = k(\text{S}_2\text{O}_3^{2-})^{3/2} (\text{H}^+)^{1/2} \quad (20)$$

Thus, by allowing the thiosulfate concentration to build up in the system, the reaction rate is increased and smaller reactors can be used.

The rate expression also shows that the reaction is favored by a low pH. This is the opposite of the absorption step where a high pH is desired. There is, therefore, an optimum pH for the process which balances the costs of the absorption and regeneration steps. This appears to be in the range between 4.0 and 4.5.

In Figure 3 the regeneration reactions were studied by measuring the concentrations of the reactants and the products as a function of time in contact with hydrogen sulfide. For phase one, as the bisulfite decreases, there is a simultaneous buildup of polythionate and thiosulfate.

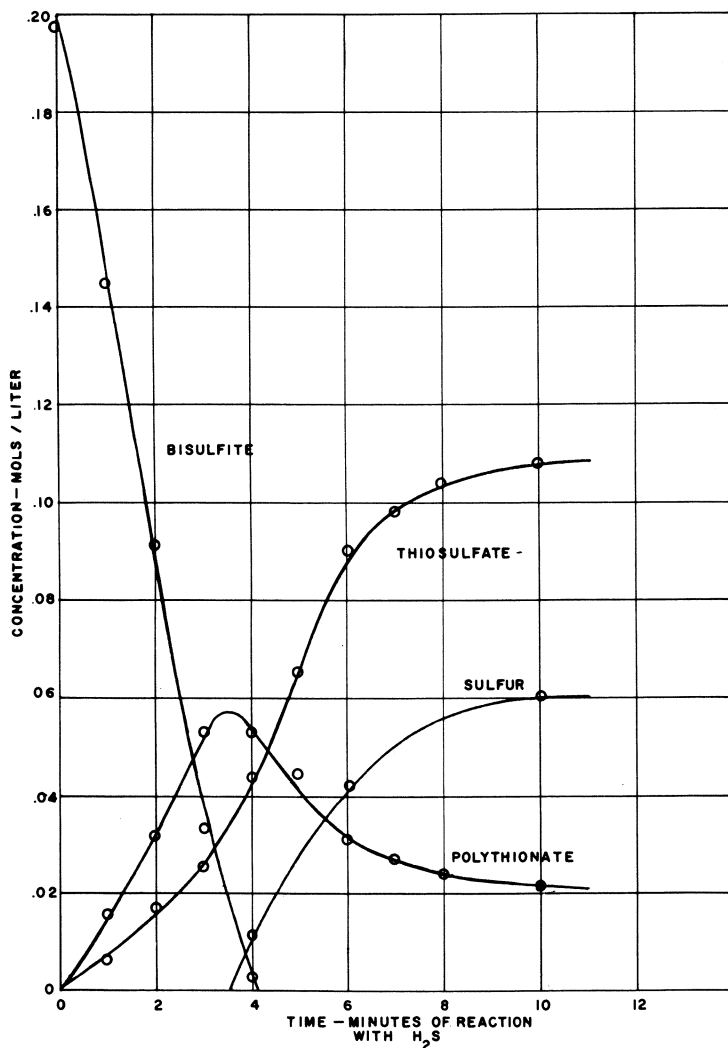


Figure 3. Reaction of H_2S with absorbed SO_2 during the regeneration step. The curves show measured concentrations of reaction mixture components as a function of reaction time with H_2S at room temperature.

As the bisulfite concentration approaches zero, the polythionate concentration levels off and sulfur precipitation begins. Then as the polythionate reacts with hydrogen sulfide, its concentration begins to decrease while the thiosulfate and sulfur concentrations continue to increase. Under the mild conditions used, there was no apparent reaction of thiosulfate or of the trithionate portion of the polythionates to form sulfur.

While the chemistry is complex, the reaction can be followed using only two simple measurements: the pH and the thiosulfate content. Calculated values are plotted in Figure 4 for a simplified batch reaction in which the hydrogen sulfide reacts consecutively with the bisulfite, polythionate, and thiosulfate.

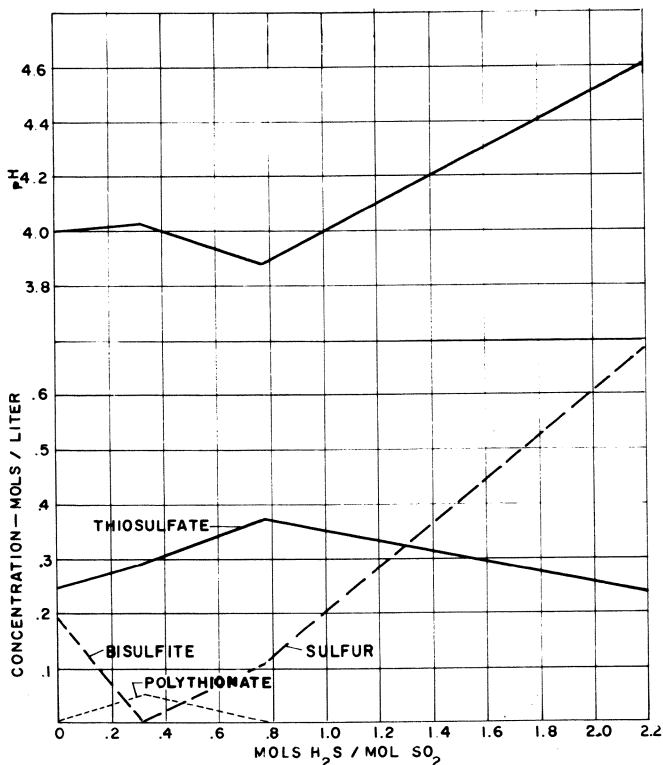


Figure 4. Calculated variation of pH and thiosulfate during the regeneration step as a function of moles of H_2S reacted per mole of SO_2 initially present. H_2S is assumed to react consecutively with bisulfite, polythionate, and thiosulfate.

thionate, and thiosulfate. In the first phase of the reaction, as the bisulfite is consumed the thiosulfate increases and the pH increases very slightly. In the first part of the second phase, as polythionates are converted to thiosulfate and sulfur precipitation begins, the thiosulfate level continues to increase and a very slight pH drop occurs. In the last part of the second phase, as thiosulfate reacts to form sulfur, the thiosulfate level steadily decreases while the pH increases.

When two moles of hydrogen sulfide/mole of sulfur dioxide have been consumed, the pH and thiosulfate concentration have returned to

the levels they had before the absorption step. Regeneration is now complete, and another cycle can begin. At this point the overall stoichiometry becomes the familiar reaction shown earlier:

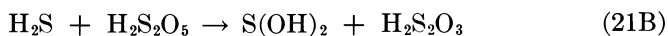
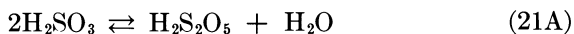


In actual practice in a continuous reaction system, the hydrogen sulfide addition rate must be controlled to obtain the final reactor conditions of pH and thiosulfate concentration. In this regard, Figure 4 illustrates an important feature of the citrate process. It can be seen that, if slightly more or less than the stoichiometric amount of hydrogen sulfide is used, the effect will be merely to cause small variations in the pH and thiosulfate content of the liquor returned to the absorption step.

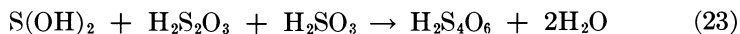
Thus, the combination of citrate buffering capacity and thiosulfate concentration provides capacity for short-term overloads of either sulfur dioxide or hydrogen sulfide. There is no need for precise instantaneous adjustment of the hydrogen sulfide flow rate to match exactly the instantaneous sulfur dioxide absorption rate. This is in contrast with the gas phase reaction where precise stoichiometry must be maintained at all times.

Regeneration Step Theory. The reaction of hydrogen sulfide and sulfur dioxide in aqueous solution has been studied extensively as the Wackenroder reaction. The consensus of various workers (9) is that the first stage of the reaction is the formation of an unstable intermediate acid that further reacts to produce the products observed, principally sulfur, thiosulfuric acid, and polythionic acids. The most prominent of the suggested intermediates are sulfoxylic acid ($\text{S}(\text{OH})_2$) (10) and thiosulfurous acid ($\text{H}_2\text{S}_2\text{O}_2$) (11). Both intermediates have schemes to explain all of the various products formed. The major overall reactions are given below.

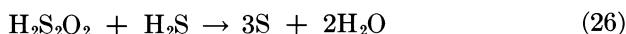
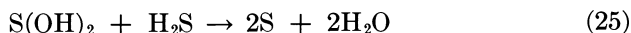
Formation of the intermediates from hydrogen sulfide and sulfur dioxide:



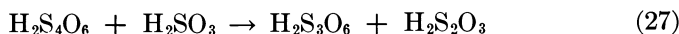
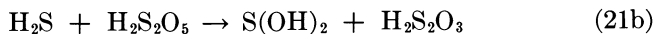
Formation of tetrathionic acid, which appears to be the first stable product:



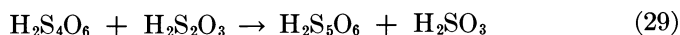
Formation of sulfur from the intermediates:



Formation of thiosulfuric acid:



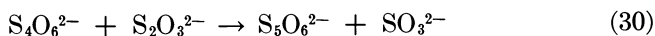
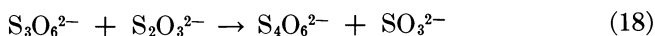
Formation of higher polythionates:



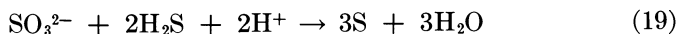
These same reactions occur, but somewhat differently, under conditions of the citrate process.

In phase 1, with the higher pH's used, the sulfur formed by Reaction 25 or 26 would be expected to react more readily to give thiosulfate by Reaction 28. Thus, sulfur formation is reduced or eliminated and a greater amount of thiosulfate is formed (12). Also in phase 1, with excess bisulfite, the polythionate chain is not built up as in Reaction 29, but rather tends to be degraded to trithionate and thiosulfate, Reactions 14 and 27.

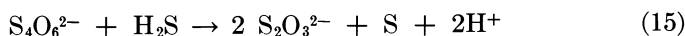
In phase 2, in the absence of bisulfite, chain buildup is possible, *e.g.*:



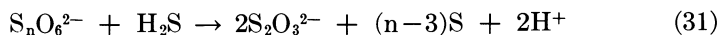
The sulfite formed would react with excess hydrogen sulfide to produce sulfur directly from the sulfoxylic or thiosulfurous intermediate, Reactions 25 and 26, without polythionate formation. The overall reaction between hydrogen sulfide and sulfite would be:



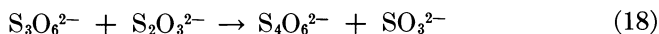
However, the pH is now more favorable for reaction of the polythionates with hydrogen sulfide (13, 14), and tetrathionate reacts as follows:



The polythionates in general react:



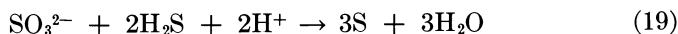
However, with trithionate at the given conditions, Reaction 31 yields one mole of thiosulfate and three moles of sulfur. In addition the reaction rate increases in the presence of thiosulfate. These suggest that the main course of the reaction with hydrogen sulfide proceeds through the initial formation of tetrathionate:



followed by:



and

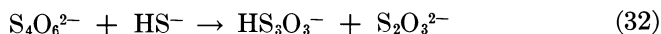


to give overall the observed reaction:

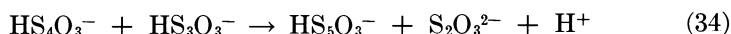
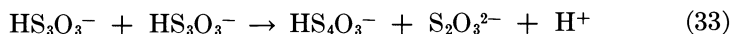


Foss (15) has postulated a mechanism for the formation of S_8 from polythionates *via* the unstable sulfanemonosulfonates as intermediates similar to that proposed by Davis (16) for acidified thiosulfate solutions.

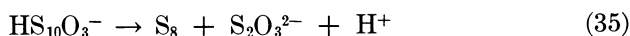
In the citrate process disulfanemonosulfonate could be formed by the attack of the HS^- ion on tetrathionate.



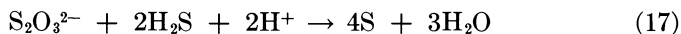
The sulfur chain would be built up by consecutive displacements of thiosulfate by disulfanemonosulfonate:



until the sulfur chain was long enough to form S_8 by ring closure.

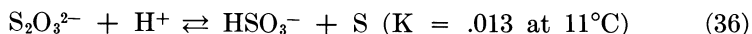


The overall stoichiometry of the reaction of thiosulfate with hydrogen sulfide is given by:



This simple equation is the result of a number of complex reactions which are discussed below.

While thiosulfate is stable in neutral solutions, in slightly acid solutions it decomposes slightly and sets up an equilibrium (14):



which stabilizes the solution and prevents further decomposition. A displacement of the equilibrium to the right will cause more thiosulfate to decompose. The use of acid to do this has been extensively investigated.

For dilute acid, the reaction rate has been studied (17). The main products were reported to be sulfur and sulfite with only small amounts of polythionates. The time of sulfur appearance was measured, and based on this the initial rate of sulfur production was expressed as:

$$\frac{d(\text{S})}{dt} = k(\text{S}_2\text{O}_3^{2-})^{3/2}(\text{H}^+)^{1/2} \quad (37)$$

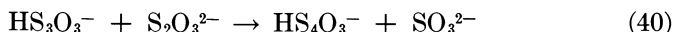
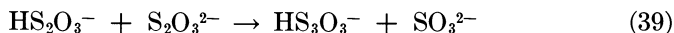
This equation is of the same form which was found to fit Keller's later data for the reaction of hydrogen sulfide with thiosulfate, Equation 20.

After the appearance of sulfur the reaction was followed by titration, and the rate of sulfite production was found to be:

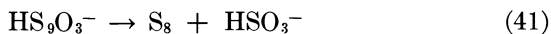
$$\frac{d(\text{SO}_3^{2-})}{dt} = k(\text{S}_2\text{O}_3^{2-})^2(\text{H}^+) \quad (38)$$

Mechanisms based on two or more consecutive reactions were proposed to explain the observed rate data (16, 18). These were the reaction of thiosulfate and bithiosulfate ion to form a complex with direct breakdown to sulfur and the reaction between the same two ions to form disulfanemonosulfonate (HS_3O_3^-), which reacts further.

As noted earlier, this last mechanism was proposed by Davis. In this case the chain buildup of the sulfanemonosulfonates is suggested to proceed by successive displacements of sulfite by thiosulfate on the unstable intermediates. The sequence is as follows:



until

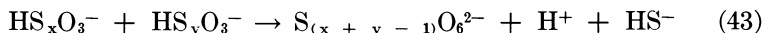


The sulfite formed in Reactions 39 and 40 is removed as bisulfite by the acid present.

Reaction between sulfanemonosulfonates was also postulated to explain the formation of polythionates (sulfanedisulfonates) as a side product in this system. Two molecules of disulfanemonosulfonate could give pentathionate:

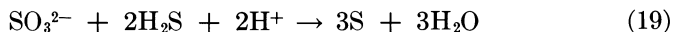


and in general

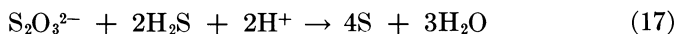


Sulfur isotope effects in the acid decomposition of thiosulfate also were studied (19), and based on these a simple bimolecular mechanism was favored.

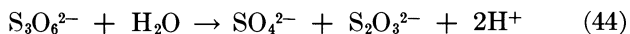
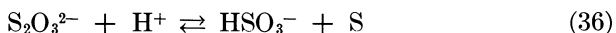
In contrast to the dilute acid decomposition of thiosulfate where the equilibrium and sulfite are acted upon by acid, this is accomplished in the citrate process by the reaction of the various sulfite species with hydrogen sulfide.



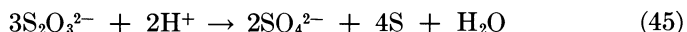
In this way the equilibrium of Reaction 36 is shifted, and the sulfite products of chain buildup in Reactions 39, 40, and 41 are removed. This results in the overall equation:



Sulfur Melting. Under the temperature conditions used in the sulfur melting step ($>125^\circ\text{C}$) there is some thiosulfate decomposition. The reaction consumes hydrogen ions and forms sulfur and sulfate as products. The ratio found of 1.37 moles of sulfur formed per mole of thiosulfate reacted suggests that the main form of the decomposition involves formation of sulfur and bisulfite from the thiosulfate, followed by decomposition of the bisulfite (5) *via* trithionate to sulfate. The sequence is:

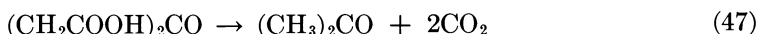


to give an overall reaction:



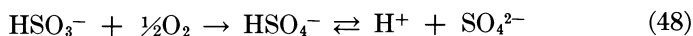
The decomposition rate does not appear to be a simple function of the thiosulfate and hydrogen ion concentrations. Rate expressions for the first two reactions in the sequence were noted earlier, Equations 37, 38, and 9. At the pH condition in the citrate process the reverse reaction in Reaction 36 also may be a factor (20).

Some slight decomposition of citrate also occurs. The main course of this appears to be *via* acetone dicarboxylic acid to form gaseous products—acetone, carbon dioxide, carbon monoxide, and water:



Based on their tests, the Bureau of Mines estimated (3) that, in a continuous sulfur melting system at 135°C, for each ton of sulfur melted, about 3 lbs of sulfate would be formed and 0.7 lbs of citrate decomposed.

Oxidation. During the absorption step some oxidation occurs:



The oxidation rate decreases with pH (21, 22) and is reported (23) to be inversely proportional to the square root of the hydrogen ion concentration:

$$\frac{-d(\text{S}_t)}{dt} = \frac{g(\text{HSO}_3^-)}{(\text{H}^+)^{1/2}} \quad (49)$$

Copper and iron act as catalyst for the oxidation.

The results of some laboratory runs demonstrating the effect of pH and the oxidation inhibiting effect of citrate are given in Table I. These show that in going from pH 4 to 5 in the citrate system the oxidation approximately doubles. In a comparison run, using a different acid, much higher levels of oxidation were found. While citric acid does chelate the heavy metals that catalyze the oxidation, this was not a factor in the

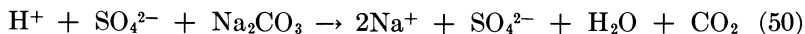
Table I. Oxidation of Sulfur Dioxide During Absorption^a

Acid	Conc. (M)	pH	Additive	Oxidation (%)
Citric	0.5	4.0	—	0.4—0.5
Citric	0.5	5.0	—	0.8—1.0
Sulfosuccinic	0.5	5.0	—	5.6—6.0
Sulfosuccinic	0.5	5.0	EDTA	5.6—6.0
Citric	0.5	5.0	Thiosulfate 0.3M	0.15

^a Temperature = 50°C. Inlet gas = 2,000 ppm SO₂, 3.5% O₂, remainder N₂.

comparison runs. This can be seen from the fact that the addition of ethylenediaminetetraacetic acid (EDTA) to the other acid did not improve its ability to inhibit the oxidation. The results also show that the addition of thiosulfate to the citrate further reduces oxidation.

The removal of sulfate as the sodium salt (Reaction 48) requires the addition of alkali to neutralize the hydrogen ions also formed:

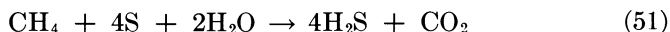


Purging. In addition to oxidation, sulfate is present from any sulfuric mist removed from the inlet gas and thiosulfate decomposition during the sulfur melting step. While the rate of sulfate formation from all these sources is small, the effect is cumulative and sulfate must be purged from the system.

This is best done by diverting a portion of the main stream and cooling it to crystallize Glauber's salt, sodium sulfate decahydrate. The solubility curve of sodium sulfate in citrate liquor is similar to that in water with the solubility decreasing greatly below about 30°C. This allows sodium sulfate removal to take place at temperatures readily attained by mechanical refrigeration.

Hydrogen Sulfide Generation. The regeneration reaction was discussed earlier from the standpoint of products formed in the reaction of sulfur dioxide solutions with added hydrogen sulfide. Thus a reliable source of hydrogen sulfide is mandatory to insure uninterrupted operation of the citrate process. Potential sources of hydrogen sulfide include demand generation, by-product from desulfurization of manufactured fuel, and separation from sour natural gas. Selection of the most appropriate source or combination of sources for a particular citrate process application will depend upon availability, logistics of transportation, and competitive economics.

The most readily available source of hydrogen sulfide often will be on-site generation by chemical synthesis according to demand. Such generation usually will require the reaction of any reducing agent feedstock with steam or water and some form of sulfur to produce dilute hydrogen sulfide.



Elemental sulfur product from the citrate process unit would be available as a feedstock for such a generator.

Several commercially proved processes for manufacturing hydrogen sulfide are available today. These generally use either methane or hydrogen as reductant, but other fuel could be substituted by applying demon-

strated fuel conversion process technology. By-product hydrogen sulfide from fuel desulfurization operations and sour natural gas production presents a potentially reliable and inexpensive source for hydrogen sulfide where it may be available.

The logistics of transportation of by-product hydrogen sulfide will play an important part in the ultimate use of this material. Intra-plant transfers will continue to be by pipeline as currently practiced in petroleum refineries and gas plants. Inter-plant transfers for more than very short distances will likely involve liquefaction of the hydrogen sulfide and movement by tank trucks or tank cars.

Liquid hydrogen sulfide has been classified as a flammable compressed gas for shipment in both tank trucks and tank cars by governmental authorities both in the United States and Canada. Department of Transportation special permits authorize use of type 105A-600W tank cars filled to a maximum density of 68%. With a capacity of 13,500 gal, these insulated tank cars will hold about 30 short tons net weight of liquid hydrogen sulfide.

Citrate Process Pilot Plant

The block flow diagram in Figure 5 indicates the principal functional sections of the citrate process, corresponding to the unit now operating in Terre Haute. A brief tour through these sections helps in gaining a perspective on the process. The 2000-SCFM gas stream being treated in the unit comes from a coal-fired spreader stoker-type boiler at 700°F with 25,000 lb/hr steam-rated capacity.

Gas cooling, cleaning, and sulfur dioxide removal is accomplished by adiabatically cooling flue gas with quench water, passing into a venturi-type water scrubber to remove fly ash, followed by absorption of the sulfur dioxide in an aqueous solution of sodium citrate and citric acid. The pilot plant has demonstrated the feasibility of a commercial plant consistently to remove more than 95% of the sulfur dioxide in the inlet gas. The pilot unit has operated for prolonged periods with exit gas of 25–50 ppm sulfur dioxide.

The sulfur dioxide-rich citrate solution in the bottom of the absorber is fed by level control through a steam-heated exchanger to a three-stage continuous stirred tank reactor system countercurrent to a flow of hydrogen sulfide gas. For this installation the gas source is a tank of liquid hydrogen sulfide.

In the reactor system, designed for 5-min retention time or less in each of the three reactors, sulfur dioxide is reduced to sulfur and citrate solution is regenerated. Sulfur slurry is pumped to a sulfur slurry surge drum and then to the sulfur separation system. Various alternative units

for separating precipitated sulfur from the solution are currently being evaluated including filtration and flotation units.

A clear or nearly clear liquor is recycled back to the clear liquor surge tank and then back to the absorption system. While developing the sulfur separation step, at times high amounts of solids containing sulfur and ash have been recycled back to the absorption system with no problem.

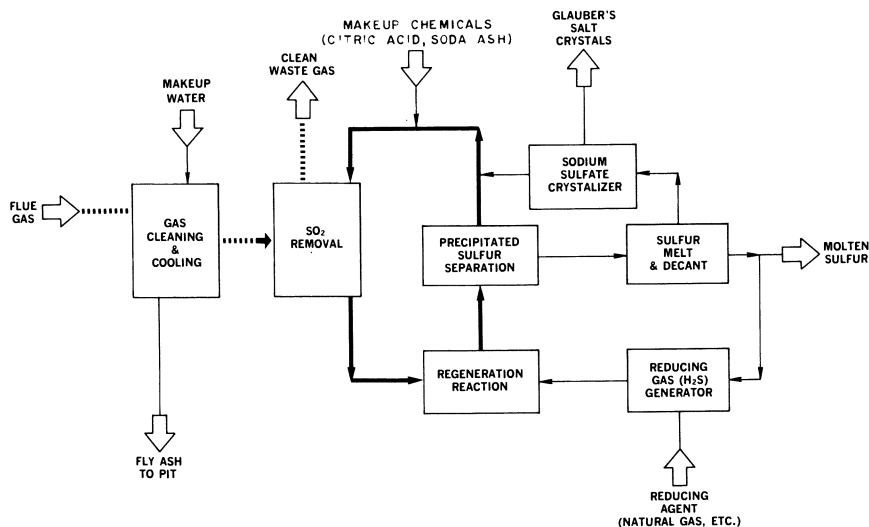


Figure 5. *Citrate process flow diagram*

The product from the sulfur separation step is fed as a slurry in citrate solution through a heater to raise the temperature above 125°C to melt the sulfur. Liquid phases are separated in a decanter under pressure. The bottom layer is drawn off as high quality molten yellow sulfur, and the citrate solution top layer is discharged to a flash drum at reduced pressure.

Citrate solution from the decanter can be bypassed around or into a vacuum crystallizer where Glauber's salt is removed from the solution by cooling to a temperature well above the freezing point of water. Current data indicate that less than 2–3% of the total sulfur dioxide is oxidized to sulfate. The amount depends to an extent on the concentration of nitrogen oxide in the input gas.

As a practical matter, the important advantages of the system's chemistry are that there is no chance of precipitation taking place in the absorber and that the circulating solution has a high capacity for short-term overloads of either sulfur dioxide or hydrogen sulfide. In other words, as already stated in the chemistry discussion, there is no need for

the hydrogen sulfide flow rate to be precisely and instantaneously adjusted to match the absorption rate of sulfur dioxide from the flue gas. The citrate solution provides adequate buffering capacity with resultant slow changes of process dependent variables. This effect is exactly the opposite of that encountered in a gas phase direct reduction system, *e.g.*, Claus reaction, where precise stoichiometry must be maintained at all times.

Operation of the unit has confirmed both the system chemistry and expected sulfur dioxide removal efficiency. It has demonstrated the inherent stability and tolerance of the system to stoichiometric imbalances between absorbed sulfur dioxide and regenerant hydrogen sulfide fed to the reactors.

Economic Projection Study

Economics for the citrate process, based on a 200 MW power plant, burning 3% sulfur coal, were presented last fall at the Purdue University Industrial Fuel Conference (24). Data coming out of Terre Haute will shortly be translated to an updated economic projection on the process.

An important consideration when comparing citrate process costs to those of throwaway processes, such as non-regenerative limestone, is the high cost of supporting off-site facilities for limestone handling and sludge disposal. The impact of waste disposal expense on overall process costs is seen from another source. In mid-1973 the Environmental Protection Agency reported (25) on their study of flue gas desulfurization economics which compared (Table II) the capital and annualized operating costs for a number of processes. Usually \$5–15/kW must be added to capital costs for waste disposal facilities.

Table II. Comparative Process Costs^a

<i>Process</i>	<i>Comparative Process Costs</i>	
	<i>Capital</i> (\$/kW)	<i>Annualized</i> (mills/kWh)
Throwaway (Capital costs do not include disposal facilities usually \$5–15/kW)		
Double alkali	24	1.95
Lime scrubbing	35	2.40
Limestone scrubbing	36	2.45
Regenerable		
Citrate	39	1.95
MgO (to S)	49	2.40
Wellman–Lord (to S)	50	2.65
Stone & Webster/Ionics (to S)	50	2.70
Cat-Ox	55	2.75

^a From (25). Basis 500 MW, 3.5% S coal, retrofit, 60% load, waste at \$3/ton wet sludge, sulfur credit at \$15/ton, particulate removal included.

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