

The acid gas feed (191,000 std m³/day, 38°C) is composed of 75.1% H₂S, 24.7% CO₂, and 0.2% hydrocarbons. (Monsanto Entro-Chem.)

Location	Temperature, C°	Location	Temperature, C°
1	1049	6	166
2	379	7	208
3	149	8	224
4	258	9	133
5	332	10	538

Fig. 4.2. Claus-type sulfur recovery unit of the Okotoks plant.

fuels have to be burned, sulfur oxides must be removed by stack gas cleaning methods, or by new combustion techniques designed to remove sulfur during burning.¹⁰

SULFUR FROM OTHER SOURCES. Because of stringent air pollution regulations, sulfuric acid plants are being installed to remove and utilize SO₂ in gases resulting from the roasting of sulfide ores, smelting of ores, and burning of spent acid or acid sludge from petroleum refining. Liquid sulfur dioxide is occasionally the preferred product from these sources.

Conventional copper smelters have limited sulfur recovery capability because certain portions of the off gas are too low in sulfur dioxide concentration to make sulfuric acid economically. Electrical furnaces and flash smelters produce more concentrated sulfur dioxide suitable for the recovery of elemental sulfur or sulfuric acid.¹¹

¹⁰Slack, *Sulfur Dioxide Removal From Waste Gases*, Noyes, Park Ridge, N.J., 1971; ER&E Sets Pilot Plant to Burn High-Sulfur Coal with Low SO₂ Discharge, *Oil Gas J.* **70** (47) 83 (1972).

¹¹Semrau, *Sulfur Oxides Control and Metallurgical Technology*, *J. Met.* **23** (3) 41 (1971); White, SO₂ Laws Force U.S. Copper Smelters into Industrial Russian Roulette, *Eng. Min. J.* **179** (7) 61 (1971).

Several commercial processes for recovering elemental sulfur from pyrite ores include the Outokumpu flash-smelter process, the Orkla process, and the Noranda process. Only the Outokumpu process is still being used commercially. The Outokumpu flash smelter, as well as the Mitsubishi and Noranda continuous smelters, are also being used for continuous smelting of copper ores and delivering high-strength sulfur dioxide gases for sulfuric acid manufacture.

Today, pyrite and zinc sulfide ores are usually roasted in fluidized¹² bed roasters although a few flash roasters and multiple hearth roasters still exist. Acid sludges from petroleum refining are being successfully regenerated¹³ to produce clean recycled sulfuric acid. The recovery of sulfur from stack gases in power stations has not materialized except for a few small installations. Power plants, when required to treat their stacks, usually treat the gases with alkaline solutions of lime or sodium and discard the residue, usually calcium sulfate and/or sulfite.

Sulfur derived from pyrite roaster and smelter off gases amounted to almost 20×10^6 t worldwide in 1980.

SULFURIC ACID

It is difficult to believe that a very active chemical such as sulfuric acid is at the same time one of the most widely used and most important technical products. It is the agent for sulfate formation and for sulfonation, but more frequently it is used because it is a rather strong and cheaply priced inorganic acid. It enters into many industries, though infrequently appearing in the finished material. It is employed in the manufacture of fertilizers, leather, and tin plate, in the refining of petroleum, and in the dyeing of fabrics.

HISTORICAL.¹⁴ The origin of the first sulfuric acid is unknown, but it was mentioned as far back as the tenth century. Its preparation, by burning sulfur with saltpeter, was first described by Valentinus in the fifteenth century. In 1746, Roebuck of Birmingham, England, introduced the lead chamber process. This interesting, but now obsolete process is described in detail in the third edition of this book and elsewhere.¹⁵

The contact process was first discovered in 1831 by Phillips, an Englishman, whose patent included the essential features of the modern contact process, namely, the passing of a mixture of sulfur dioxide and air over a catalyst, followed by the absorption of the sulfur trioxide in 98.5 to 99% sulfuric acid. Phillips' invention was not a commercial success for more than 40 years, probably because (1) there was a lack of demand for strong acid, (2) inadequate knowledge of catalytic gas reactions, and (3) the slow progress of chemical technology. Development of the dye industry resulted in a rising demand for concentrated acids for the manufacture of alizarin and other organic coloring matter. In 1889, it was demonstrated that an excess of oxygen in the gaseous mixture for the contact process was advantageous. The contact

¹²Fluidized Bed Technique Pays Off in New Sulfuric Acid Plant, *Chem. Eng.* 62 (8) 288 (1955); Guccione, From Pyrite: Iron Ore and Sulfur, *Chem. Eng.* 73 (4) 122 (1966); Hester, Johannsen, and Danz, Fluidized Bed Roasting Ovens, *Ind. Eng. Chem.* 50 1500 (1958).

¹³Sander and Daradimos, Regenerating Spent Acid, *Chem. Eng. Prog.* 74 (9) 57 (1978); Duecker and West, op. cit., chap. 18.

¹⁴Duecker and West, op. cit., Fairlie, *Manufacture of Sulfuric Acid*, Reinhold, New York, 1936. Both are standard reference books with bibliographies and sketches.

¹⁵Faith, Keyes, and Clark, *Industrial Chemicals*, 4th ed., Wiley-Interscience, New York, 1975; Fairlie, op. cit.

process has been improved in all details and is now one of industry's low-cost, automatically controlled, continuous processes¹⁶ (see Fig. 4.4). All the new sulfuric acid plants use the contact process. One of the disadvantages which led to the demise of the chamber process is that it can produce acid of only 78% strength. Concentration is expensive, thus by 1980, only one chamber plant was still in operation in the United States.

PROPERTIES OF SULFURIC ACID. Sulfuric acid is a strong dibasic acid. In addition, it is also an oxidizing and dehydrating agent, particularly toward organic compounds. Its dehydrating action is important in absorbing water formed in such chemical conversions as nitration, sulfonation, and esterification, thus ensuring high yields.

Solutions of sulfuric acid may be concentrated economically to about 93% by weight of H_2SO_4 . Stronger acids may be made by dissolving sulfur trioxide in 98 to 99% acid. Sulfuric acid forms many hydrates that have fairly definite melting points, as shown in Table 4.1. The irregularities in the relation between strengths of the sulfuric acids and the corresponding specific gravities and freezing points are due to these hydrates.

Sulfuric acid is widely sold in the form of various solutions of H_2SO_4 in water, or of SO_3 in H_2SO_4 . The latter, called oleums, are marketed on the basis of the percentage of SO_3 present; 20% oleum means that, in 100 kg, there are 20 kg of SO_3 and 80 kg of H_2SO_4 . This 20% oleum, if diluted with water to make 100% acid (monohydrate), would furnish 104.5 kg total weight. Previously, when much of the acid was made by the chamber process, solutions of sulfuric acid in water were sold according to their specific gravity or their Baumé (Bé°) degrees. Table 4.2 illustrates the standard sulfuric acids of commerce. For sulfuric acid the usual temperature to which specific gravity, or Baumé degrees, are referred is 15°C. The specific gravity of sulfuric acid increases gradually to 1.844 at 15°C for 97% acid, after which it decreases to 1.839 at 15°C for 100% acid. Consequently, in this upper range, i.e., above 95%, the strengths must be determined by means other than density. For some of the medium-range oleums, however, density is again helpful. Electrical conductance, refractive index, and sonic transmittance are being used to measure continuously acid strength in modern plants.

As contact plant acid has displaced chamber plant acid, the H_2SO_4 percentage is now normally specified. Acid containing 93.19% H_2SO_4 (66° Bé acid) is the normal acid of commerce in North America. This acid is cheap to transport as it has little water and can be stored and shipped in steel tanks and containers. Its freezing point (-7°C) is lower than that of 96% acid. Acid of somewhat higher strength (about 95% H_2SO_4) is normally used in Europe. Lesser

¹⁶For a listing of sulfuric acid plants in the United States, see *Chem. Mark. Rep.* May 7, 1979.

Table 4.1 Hydrates of Sulfuric Acid

	Formula	Melting Point, °C	Specific Gravity
Sulfuric, acid, fuming	$\text{H}_2\text{S}_2\text{O}_7$	35	1.9 ^{20°}
100%	H_2SO_4	10.37	1.834 ^{18°/4}
Monohydrate	$\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	8.48	1.842 ^{15°/4}
Dihydrate	$\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$	-38.57	1.650 ^{0°/4}

SOURCE: Rubin and Giaque, The Heat Capacities and Entropies of Sulfuric Acid and Its Mono- and Dihydrates from 15 to 300 K. *J. Am. Chem. Soc.* 74 800 (1952).

Table 4.2 Commercial Strengths of Sulfuric Acid

	Degrees Bé. 15.6°C	Specific Gravity, 15.6°C	Sulfuric Acid, %
Battery acid	29.0	1.250	33.33
Chamber acid, fertilizer acid, 50° acid	50	1.526	62.15
Glover or tower acid, 60° acid	60	1.706	77.67
Oil of vitriol (OV), concentrated acid 66° acid	66	1.835	93.19
98% acid		1.841	98.0
100% H ₂ SO ₄		1.835	100.0
20% oleum, ° 104.5% acid		1.915	104.5
40% oleum, 109% acid		1.983	109.0
66% oleum		1.992	114.6

*For oleums, percent means free SO₃.

SOURCE: Duecker and West, *Manufacture of Sulfuric Acid*, ACS Monograph 144, Reinhold, New York, 1959, pp. 2 and 411 (modified).

quantities of 98% acid and oleum are shipped. Acid of 93% H₂SO₄ strength is completely suitable for fertilizer manufacture, which is the major use for sulfuric acid.

The normal strengths of commercial oleums fall into three categories, expressed as percent free sulfur trioxide: 10 to 35%, 40%, and 60 to 65%. The freezing point of 35% oleum is about 29°C, and of 40% oleum about 34°C; consequently, small amounts of nitric acid are sometimes added (where this is tolerable) to these grades to inhibit freezing during winter shipment.

PRODUCTION AND USAGE. Fertilizer manufacture, as shown in Table 19.3, is the greatest single use of sulfuric acid. When superphosphate was the usual phosphatic fertilizer, the chamber process sulfuric acid plant and the superphosphate plant were built and operated at the same site. These were small plants located near farming areas.

More concentrated fertilizers are now required in order to reduce the costs of transportation and application. Plants for triple superphosphate are more capital intensive than ordinary superphosphate plants. They are built on a much larger scale, and, like previous superphosphate plants, operate at the same site as the contact plant. The product acid has a strength of

Table 4.3 Major U.S. Markets for Sulfuric Acid
(million metric tons 100% H₂SO₄ and percentage)

	1979	%	1980	%
Phosphate fertilizer	23.2	60.9	26.0	64.5
Petroleum refinery	2.4	6.3	2.6	6.5
Chemicals	2.3	6.0	2.0	5.0
Ore processing	2.5	6.6	2.0	5.0
Pulp and paper products	0.8	2.1	0.7	1.7
Paints and pigments	0.6	1.6	0.7	1.7
Nitrogen fertilizer	0.5	1.3	0.7	1.7
Steel pickling	0.9	2.4	0.3	0.7
All other	4.9	12.8	5.3	13.2
Total	38.1	100.0	40.3	100.0

SOURCE: *End Uses of Sulfur and Sulfuric Acid in 1980*; Mineral Industry Surveys, U. S. Bureau of Mines, May 27, 1981.

93.2% H_2SO_4 , which can be safely stored in steel tanks. It is diluted as part of the phosphate-producing facility if lower strength is desired.

When chamber plants supplied acid, several different grades were supplied, each with a particular use. Grades of 53 to 56°Bé were employed in superphosphate manufacture, so the chamber plants could supply this acid without expensive concentration. Battery acid is even more dilute. The 60°Bé grade was used in the manufacture of sulfates of ammonia, copper (bluestone), aluminum (alums), magnesium (Epsom salts), zinc, iron (copperas), etc., and organic acids such as citric, oxalic, acetic, and tartaric; and for pickling iron and steel before galvanizing and tinning, refining and producing heavy metals, electroplating, and preparing sugar, starch, and syrup. Strong sulfuric acid, 93 to 99%, is utilized in the purification of petroleum products, preparation of titanium dioxide, alkylation of isobutane, manufacture of many nitrogen chemicals, synthesis of phenol, recovery of fatty acids in soap manufacture, and manufacture of phosphoric acid and triple superphosphate. Oleums are needed for petroleum, nitrocellulose, nitroglycerin, TNT, and dye manufacture as well as for fortifying weaker acids. There are many other uses; in fact, few chemical products are manufactured without the use of sulfuric acid.

Free world production capacity for sulfuric acid for 1979 and 1980 is shown in Table 19.4. This shows that the 1980 installed free world capacity is 431,000 t/day, equivalent to about 155×10^6 t/year. U.S. capacity in 1980 was 153,000 t/day, equivalent to approximately 50×10^6 t/year.

U.S. usage was 40.3×10^6 t for 1980, indicating that plants in the United States were then producing at about 80% of capacity.

Manufacture

When the sole problem involved was forming H_2SO_4 at a reasonable concentration from SO_2 generated by burning sulfur or pyrites and when energy was cheap, plants were relatively uncomplicated. When energy prices increased sharply, the high-level energy resulting from the oxidation of sulfur and sulfur dioxide became a valuable commodity. Major changes in plant design were instituted to use this heat to generate high-pressure steam for generating electrical energy, thereby maximizing energy recovery while minimizing process energy use. This combination of a chemical plant and an electrical (or steam) generation system is known

Table 4.4 Sulfuric Acid Capacity in the Free World (in thousands of metric tons per day)

	1970	1980	1990 (estimated)
World	250.9	430.9	614.5
United States	92.7	152.7	189.1
Europe	99.1	170.9	200.0
Japan	20.9	27.3	36.4
Canada	10.0	15.5	22.7
Mexico	6.8	8.9	5.6
North Africa	4.0	18.6	35+
Brazil	2.3	7.1	16+

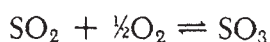
SOURCE: Monsanto Enviro-Chem.

as cogeneration. A modern sulfuric acid plant is, therefore, an electrical generating system. Of course, this secondary function complicates the plant's operating system, but it sharply reduces the cost of the acid produced. Plants have become larger to utilize the economies of large scale; a 2800-t/day plant was brought on stream in 1982.

MANUFACTURE BY THE CONTACT PROCESS. Until 1900, no contact plant had been built in the United States, although this process had become very important in Europe because of the need for oleums and for high-strength acids for sulfonation, particularly in the dye industry. A substantial number of contact plants were built in the period 1900 to 1925, using platinum catalysts. In the middle 1920s, vanadium catalysts came into use and have gradually completely replaced platinum. By 1930, the contact process could compete with the chamber process regardless of the strength of acid desired. Since the mid-1920s most new facilities built have used the contact process with vanadium catalysts.

There have been many improvements both in equipment and catalyst. Typical flowcharts are shown in Figs. 4.3, 4.4, and 4.5. Parts of the process vary considerably, depending upon the type of raw material used. Sulfur-burning plants are the simplest and cheapest since special purification of burner gases to protect the catalyst is not required. In the single-absorption configuration, which was the normal procedure until the 1970s, little attention was directed to planning efficient heat recovery so that all heat evolved by combustion and conversion could be recovered in the form of relatively high-pressure steam. When using other raw materials such as sulfide ores and spent or sludge acids, extensive gas purification is required and the heat evolved in the catalytic reaction is needed to preheat SO_2 gas in heat exchangers prior to catalytic conversion. The heat evolved in roasting the ore or in burning the spent acid usually is recovered in the form of low-pressure steam.

The contact process has been gradually modified to use double absorption (also called double catalyst), which increases yields and reduces stack emission of unconverted SO_2 . Recently, U.S. government regulations have specified maximum allowable emissions of SO_2 from acid plants and require that all new plants either use the double-absorption process or else be fitted with stack gas scrubbing systems to achieve comparable emission levels. For sulfur-burning plants, allowable emissions are equivalent to 99.7 percent conversion of SO_2 , and for plants using smelter gases to about 99.0 to 99.5 percent conversion. Conversions using the single-absorption contact process were typically about 97 to 98 percent. Although some units use alkali scrubbers on the tail gases to stay within the limit, most new plants use double absorption. In this flow configuration, the gases leaving the first absorbing tower are reheated by heat exchange with the bottom converter gases and reenter the final stage of the converter. Because of the lower content of sulfur trioxide, the reaction



is able to proceed farther in the desired direction and the higher recovery of 99.7 percent can be achieved. The gases leaving this final stage are cooled and the SO_3 is absorbed in a final absorber tower.

The heat of combustion of sulfur is utilized in a waste heat boiler or boilers and economizers to generate steam for melting the sulfur and for power purposes around the plant. Steam is one of the products of the plant. Modern plants generate steam at 6 MPa, which can be compared with the 2 MPa of a few years ago. Friedman¹⁷ has made an excellent analysis of the energy use in sulfuric acid plants. The steam generated in the larger sulfur-burning plants

¹⁷Friedman, Sulfuric Acid Energy Design for the 80's, *Chem. Eng. Prog.* **78** (2) 51 (1982).

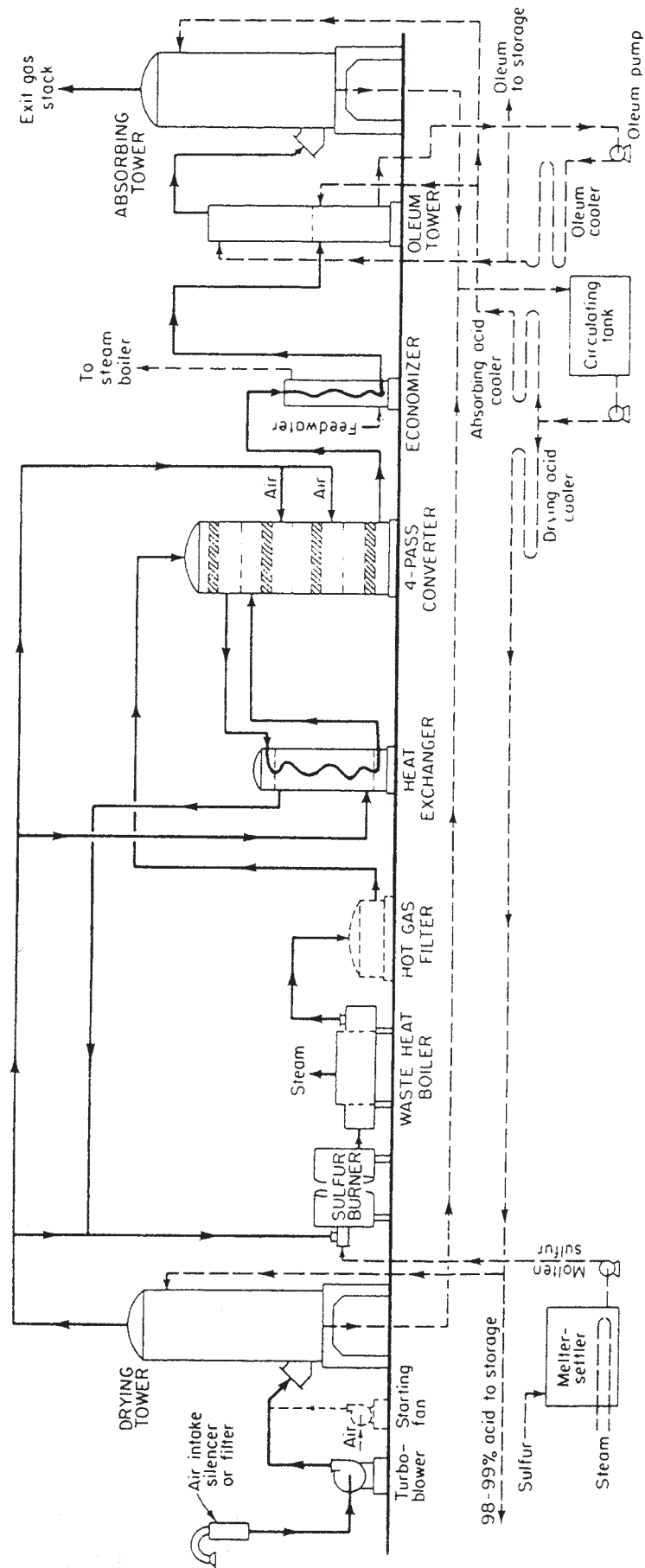


Fig. 4-3. Typical flowchart for a sulfur-burning single-absorption contact sulfuric acid plant with air injection (dilution) cooling between stages. (Monsanto *Enviro-Chem.*)

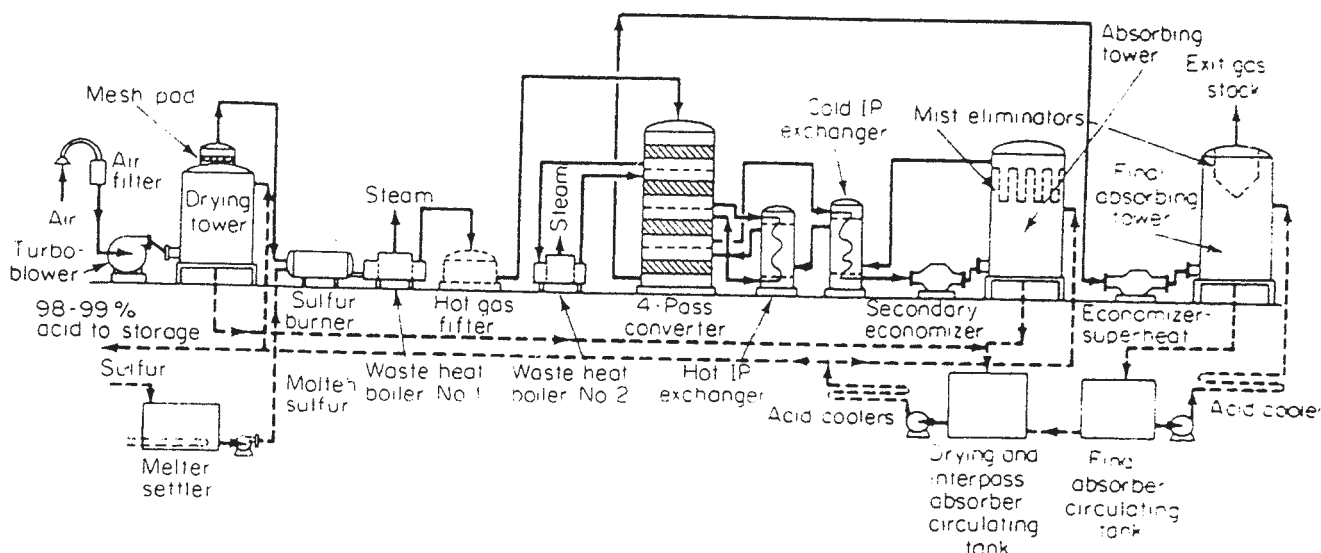
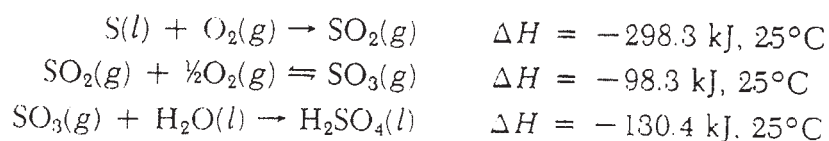


Fig. 4.4. Typical flowchart for a sulfur-burning double-absorption contact sulfuric acid plant. (Monsanto Enviro-Chem.)

(Fig. 4.5) normally exceeds 1.3 t per metric ton of acid produced. However, much less steam can be produced when a gas purification system is required. In Sweden¹⁸ a 2200-t/day plant delivers 52 MW of heat to a district heating system, saving 35,700 t of fuel oil per day.

The reactions are:



The oxidation of sulfur dioxide in the converters of the contact plant is an example of the many industrial applications of the principles of physical chemistry.

The reaction from SO_2 to SO_3 is an exothermic reversible reaction. An equilibrium constant¹⁹ for this reaction, calculated from partial pressures according to the law of mass action, may be expressed by:

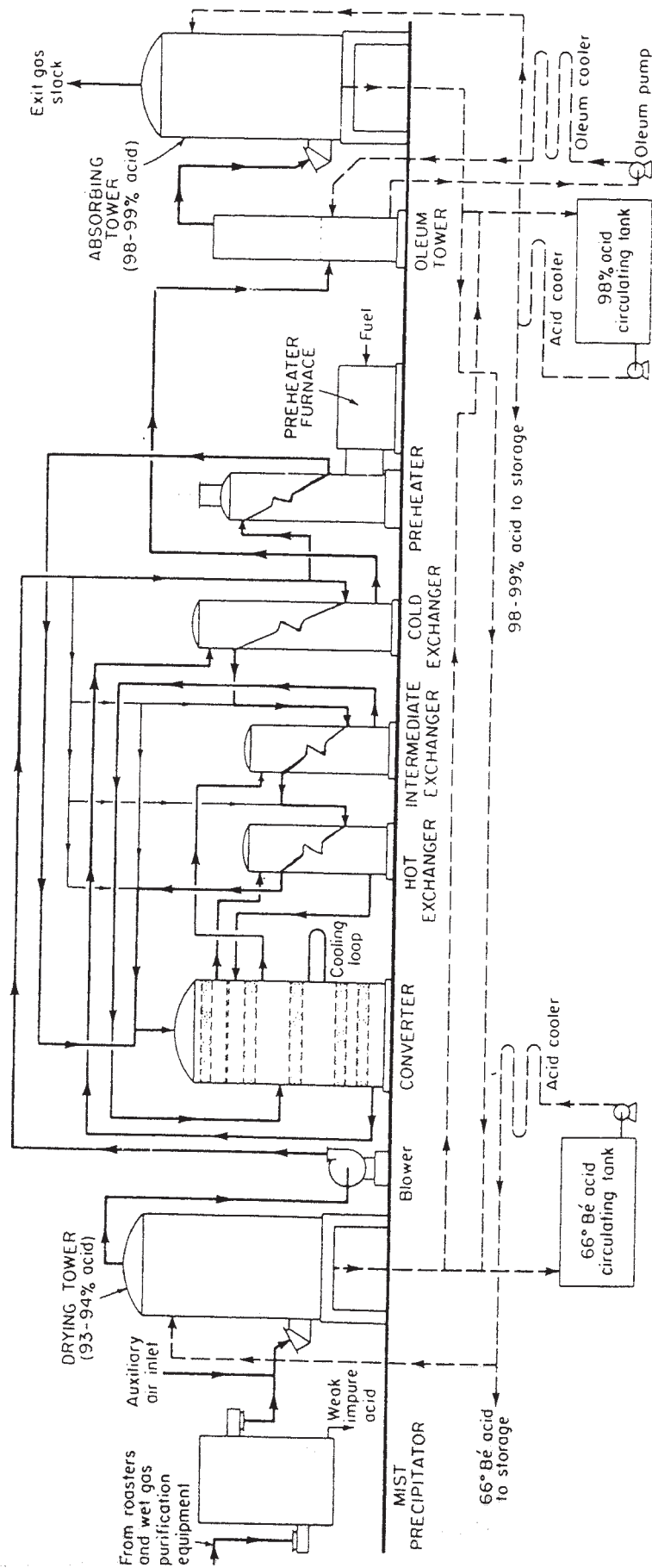
$$K_p = \frac{p_{\text{SO}_3}}{p_{\text{SO}_2} \times p_{\text{O}_2}^{1/2}}$$

Values for K_p have been experimentally determined, based on p in atmospheres, as presented in Table 4.5, and are constant for any given temperature. These experimental values are in satisfactory agreement with the values of K_p calculated from thermodynamic data.

Figure 4.6 shows the equilibrium conversion of SO_2 to SO_3 as a function of temperature for two feeds of different initial SO_2 concentrations. These equilibrium conversions were calculated from the experimental values of K_p (Table 4.5), assuming that all gases are ideal and that the total pressure is 101 kPa (1 atm).

¹⁸The Changing Sulfuric Acid Industry, *Chem. Week* 130 (6) 40 (1982).

¹⁹Duecker and West, op. cit. p. 135 ff.



Investment: 3 to 4 times as much as in sulfur-burning plant including roasters, and gas purifiers.

Fig. 4.5. Typical flowchart for an ore-roasting single-absorption contact sulfuric acid plant (Monsanto Enviro-Chem.)

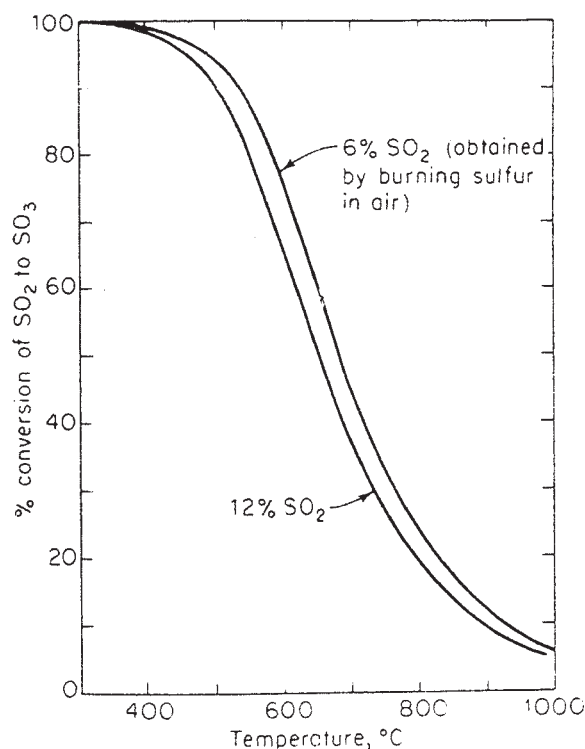


Fig. 4.6. Equilibrium-temperature relation for SO_2 conversion to SO_3 . (Monsanto Enviro-Chem.)

The equilibrium conversion data in Fig. 4.6 show that the conversion of sulfur dioxide decreases with an increase in temperature. For that reason, it is desirable to carry out the reaction at as low a temperature as practicable. At 400°C , where from Fig. 4.6 the equilibrium condition is seen to be very favorable, being almost 100 percent, the rate of attainment of this equilibrium is slow. The rate at 500°C is 10 to 100 times faster than at 400°C ; at 550°C , it is still faster. Since the reverse reaction, $\text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2}\text{O}_2$, does not become appreciable until 550°C , it is advisable to run the reaction initially at this temperature in order to get high rates, giving a maximum conversion with a minimum of catalyst.²⁰ There is here the usual conflict between favorable conversion equilibrium at lower temperatures and favorable rates at higher temperatures. The actual procedure in a contact plant takes advantage of both rate and equilibrium considerations by first allowing the gases to enter over a part of the catalyst at about 425 to 440°C , and then allowing the temperature to increase adiabatically as the reaction proceeds. The reaction rate increases as the temperature rises, but then begins

²⁰Lewis and Ries, Influence of Reaction Rate on Operating Conditions in Contact Sulfuric Acid Manufacture, *Ind. Eng. Chem.* 17, 593 (1925); 19, 830 (1927).

Table 4.5 Equilibrium Constants for Sulfur Dioxide Oxidation

Temperature, $^\circ\text{C}$	K_p	Temperature, $^\circ\text{C}$	K_p
400	397	800	0.915
500	48.1	900	0.384
600	9.53	1000	0.1845
700	2.63	1100	0.0980

SOURCE: *Z. Elektrochem* 11 373 (1905).

to slow down as equilibrium is approached. The reaction essentially stops when about 60 to 70 percent of the SO_2 has been converted, at a temperature in the vicinity of 600°C . Then the gas, before it passes over the remainder of the catalyst, is cooled in a heat exchanger, in a waste heat boiler, or by other means until the temperature of the gases passing over the last portion of the catalyst is not over 430°C . The yields using this procedure are 97 to 98 percent, and the overall reaction rate is very rapid. Figures 4.3, 4.4, 4.5, and 4.7 illustrate how these conditions are applied in practice and how the heat of reaction is used.

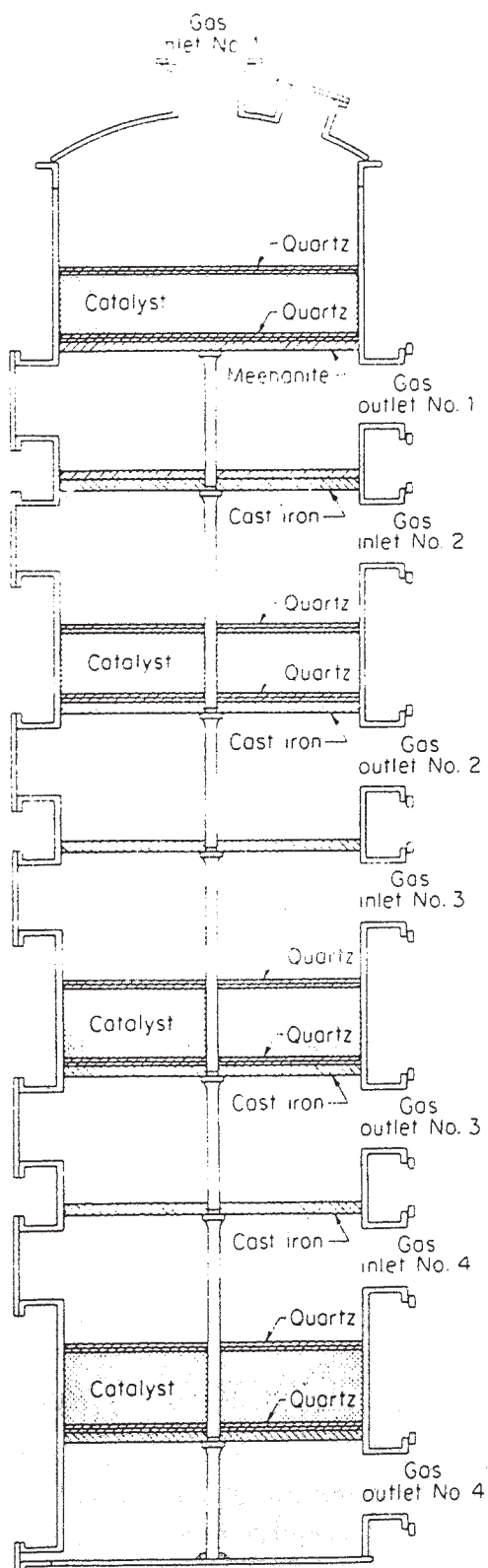


Fig. 4.7. Monsanto four-pass converter. In plants in which cold SO_2 gas must be heated by means of heat in the SO_2 gas, each of the four gas outlets except No. 3 is connected to a tubular heat exchanger. Each of the gas outlets except No. 4 is for the return connection from the exchanger. Gas outlet No. 3 and inlet No. 4 are connected to a small flue cooler from which the heat may be discarded because it is small in amount and not needed for preheating SO_2 gas (Fig. 19.5). In sulfur-burning plants, many variations are used for SO_3 gas cooling. Any of the gas outlets may be connected to a heat exchanger, waste heat boiler, steam superheater, or other cooling equipment. Any one of them may also be used for the injection of cold, dry air (Fig. 19.3). (*Monsanto Enviro-Chem.*)

Rewriting the expression for K_p in terms of mole fractions and total pressures for the equation $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$, we get:

$$K_p = \frac{N \times n_{\text{SO}_3}^2}{n_{\text{SO}_2}^2 \times n_{\text{O}_2} \times P}$$

where n = number of moles of each component, N = total moles, and P = total pressure
By rearranging, we get

$$n_{\text{SO}_3}^2 = \frac{n_{\text{SO}_2}^2 \times n_{\text{O}_2} \times K_p \times P}{N}$$

This expression shows that an increase in either SO_2 or oxygen increases the conversion to SO_3 . Oxygen enrichment of converter gas was attempted but was not a commercial success. If the concentration of oxygen in the burner gas increases, that of SO_2 decreases, and vice versa. An increase in pressure, according to the principle of Le Chatelier, also increases the conversion to SO_3 , but the effect is not large. A superatmospheric plant²¹ has recently been built in France, and some advantages have been claimed. However, the expected cost savings appear not to have materialized. The number of moles of SO_3 formed at equilibrium is inversely proportional to N , the total number of moles in the above equation. This shows that if the mixture of gases going through the converter is diluted with an inert gas, such as nitrogen, the conversion to SO_3 is decreased.

The conversion of SO_2 to SO_3 is a reversible reaction. If a portion of the SO_3 is removed, more SO_2 will be converted in order to reestablish the equilibrium. This fact is being used to increase the overall conversion efficiency and decrease the quantity of SO_2 being released to the atmosphere (Fig. 4.4). The gases leaving the converter (Fig. 4.7), after having passed through two or three layers of catalyst, are cooled and passed through an intermediate absorber tower where some of the SO_3 is removed. Mist eliminators are essential when inter-pass cooling is used. The gases leaving this tower are then reheated, and they flow through the remaining layers of catalyst in the converter. The gases are then cooled and passed through the final absorber tower before being permitted to flow into the atmosphere. In this manner more than 99.7 percent of the total SO_2 is converted into SO_3 and subsequently into product sulfuric acid.

CATALYSTS.²² In all catalytic reactions, the function of the catalyst is to increase the *rate* of the reactions. A typical sulfur dioxide-converting catalyst consists of a diatomaceous earth impregnated with upward of 7% V_2O_5 . Commercial catalysts contain appreciable amounts of potassium salts (sulfates, pyrosulfates, etc.) in addition to V_2O_5 . At operating temperatures the active ingredient is a molten salt held in a porous silica pellet. Sometimes two grades are charged into the converter, a less active but harder type being used in the first pass of the converter and a more active but softer type in passes subsequent to the first. These catalysts are long lived, up to 20 years, and are not subject to poisoning, except for fluorine, which damages the siliceous carrier. Trouble is also encountered with arsenic, and vanadium can be

²¹Bauer and Vidon, The Uguine Kuhlmann Pressure Process, *Chem. Eng. Prog.* 74 (9) 68 (1978).

²²Fairlie, op. cit., discusses patents and patent litigation. Duecker and West also give some later details. Both are pretty well out of date.

removed as volatile oxychlorides if large amounts of chlorides are present. Plugging with dust and acid mist can be a problem. Dust can be removed from first-pass catalyst by removal and screening. Conversions are high, up to 98 percent, depending on the SO_2 gas strength and on O_2/SO_2 ratios in single-absorption plants and up to 99.8 in double-absorption-type plants. Clean SO_2 must, of course, be provided. Monsanto Enviro-Chem, American Cyanamid, Halder-Topsoe, and other vanadium catalysts are extensively used.

The higher conversions accomplished in double-absorption plants are not the result of increased catalytic efficiency per se, but are accomplished by passing the gas through the converter a second time after the majority of the sulfur trioxide has been scrubbed out of the gas, thus the equilibrium is disturbed.

Iron oxide and platinum catalysts were used before the 1930s but are now normally not used, having been replaced by vanadium. Catalysts are formed into larger cylindrical shapes and into hollow cylinders in order to reduce the pressure drop in the converter while retaining a large superficial surface. There are changes in the formulation, but present-day catalysts are all vanadium-impregnated diatomaceous earth.

Contact Process Equipment

Duecker and West²³ detail the many variations in the equipment employed and include materials of construction. All recent plants have the "outdoor" type of construction, which reduces initial capital investment. These plants are insulated where necessary to conserve heat but are otherwise completely exposed to the elements, often having only the control room enclosed.

BURNERS. Sulfur and some sulfide ores are the usual raw materials. Because of its superior purity and lower transportation costs, sulfur is frequently brought in and stored in molten condition. It is then pumped from a storage tank through heated lines and sprayed into a furnace using burners very similar to those usually used for burning fuel oil. In sulfur burning plants, the strength of the SO_2 gas allowed to enter the converter has increased over the years from a strength of about 8% SO_2 by volume to the present practice of 11% SO_2 with the newest plants handling 12% successfully.

Ores are burned in fluidized beds or rotary roasters.

TREATMENT OF THE BURNER GAS. Sulfur dioxide burner gas may contain carbon dioxide, nitrogen, such impurities as chlorine, arsenic, fluorine, and a small amount of dust. Arsenic and fluorine are present only when materials other than elemental sulfur are burned. To prevent corrosion from the burner gas, it is customary to dry the air for burning the sulfur, and oxidizing the SO_2 until the moisture content is below 35 mg/m^3 , as shown in Figs. 4.3 and 4.4, and to dry the roaster gases before oxidizing the SO_2 as is shown in Fig. 4.5. Such drying is done in towers, usually with 93 to 98% sulfuric acid. The sulfur burner gas has much of its heat removed in waste heat boilers for the generation of steam. If sulfide ore is roasted, efficient dust collectors, cooling and scrubbing towers, and electrostatic mist precipitators may be added.

HEAT EXCHANGERS AND COOLERS. Before the gases are fed to the first stage of the converter, they are adjusted to the minimum temperature at which the catalyst rapidly increases

²³Duecker and West, op. cit., discuss burners in chaps. 8 and 9, converters in chap. 14.

the speed of the reaction, usually 425 to 440°C. The gases must be cooled between catalyst stages to achieve high conversion. For this purpose, cold air may be introduced (to cool by dilution), or boilers, steam superheaters, or tubular heat exchangers may be employed. Heat exchangers usually consist of large cylinders containing many small tubes. The SO₃-containing gases usually pass through the tubes and the SO₂-containing gases surround the tubes.

CONVERTERS. The chemical conversion of sulfur dioxide to sulfur trioxide is designed to maximize the conversion by taking into consideration that:

1. Equilibrium is an inverse function of temperature and a direct function of the oxygen to sulfur dioxide ratio.
2. Rate of reaction is a direct function of temperature.
3. Gas composition and amount of catalyst affect the rate of conversion and the kinetics of the reaction.
4. Removal of sulfur trioxide formed allows more sulfur dioxide to be converted.

The commercialization of these basic conditions makes possible high overall conversion by using a multipass converter wherein, at an entering temperature of 425 to 440°C (the ignition temperature), the major part of the conversion (60 to 75 percent) is obtained in the first catalyst bed with an exit temperature of 600°C or more, depending largely on the concentration of SO₂ in the gas. Table 4.6 gives the temperatures and percent conversions for each stage of a four-pass converter.²⁴ The successive lowering of the temperature between stages ensures an overall higher conversion. Conversion in a four-stage converter of a single-absorption plant is 98 percent or slightly higher. In the multipass converter shown, about 20 percent of the total catalyst is in the first stage, where 70 to 75 percent of the conversion may take place.

²⁴Slin'ko and Beskov, Calculation of Contact Equipment with Adiabatic Catalyst Layers for Oxidation of Sulfur Dioxide, *Int. Chem. Eng.* 2 (3) 388 (1962).

Table 4.6 Temperatures and Conversions in Each Stage of a Monsanto Converter (using relatively rich SO₂ gas from sulfur)

Location	Temperature, °C	Equivalent Conversion, %
Gas entering first pass	410.0	
Gas leaving first pass	<u>601.8</u>	
Rise in temperature	191.8	74.0
Gas entering second pass	438.0	
Gas leaving second pass	<u>485.3</u>	
Rise in temperature	47.3	18.4
Gas entering third pass	432	
Gas leaving third pass	<u>443</u>	
Rise in temperature	11	4.3
Gas entering fourth pass	427.0	
Gas leaving fourth pass	<u>430.3</u>	
Rise in temperature	3.3	1.3
Total rise	253.4	98.0

SOURCE: Based on Duecker and West, *Manufacture of Sulfuric Acid*, ACS Monograph 144, Reinhold, New York, 1959, p. 252.

In the converter shown in Fig. 4.7, the hot conversion gases are progressively cooled between stages and, in a double-absorption plant, after leaving the third stage, pass through heat exchangers and sometimes an economizer, before the SO_3 -containing gas enters the first 98 to 99% absorbing tower, having previously passed through an oleum tower if this product is desired. The gas leaving the 98 to 99% tower is reheated in heat exchangers and reenters the converter at the fourth pass. On leaving this, it again goes through heat exchangers and or an economizer to enter the final 98 to 99% absorbing tower. The converter depicted in Fig. 4.7 is provided with trays for supporting the catalyst and manholes for access to it. Converters have usually been made of cast iron and aluminum-coated steel, but stainless steel is now the preferred material of construction. Pressure drop through the converter must be minimized to reduce power consumption. The converter is the "heart" of a contact sulfuric acid plant and there are many variables. All these must be optimized to secure the maximum yield and profit. Converters as large as 14 m in diameter are being built. Studies have been made regarding use of computers²⁵ for converter design.

SULFUR TRIOXIDE ABSORBERS. It has been known for a long time that a concentration of acid between 98.5 and 99% sulfuric acid is the most efficient agent for the absorption of sulfur trioxide, probably because acid of this strength has a lower vapor pressure than any other concentration. Acid of this strength is used in the intermediate and final absorbers for essentially complete absorption of the SO_3 before the partially converted gas reenters the converter and the waste gas is vented to the atmosphere. Water cannot be used because direct contact of sulfur trioxide and water results in an acid mist that is almost impossible to absorb. Since the absorbing acid is continuously becoming more concentrated, it is necessary to provide some means of diluting that part of the acid which is discharged from the absorbers and which is to be recirculated. The recirculated acid is diluted by adding dilute sulfuric acid or water in the amount required, cooling the absorbing acid, and withdrawing any excess acid from the system for sale.

The 20% oleum is made in an oleum absorber²⁶ as shown in Figs. 4.3 and 4.5, if the plant includes such an oleum tower, by adding 98 to 99% acid to the oleum which is circulating over this tower. If an oleum of 60 to 65% is wanted, it may be prepared by producing 30 to 35% oleum in the tower and distilling it in steel boilers. The trioxide driven off may be absorbed in a separate stream of oleum or condensed and blended with other oleum to get the desired concentration. The usual oleum tower may be able to produce 30 to 40% oleum in smaller quantities. If full capacity for such oleum is required, it may be necessary to use two oleum towers in series ahead of the first 98 to 99% absorber. Most absorbers are equipped with mist eliminators, such as Monsanto's Enviro-Chem.

The tower, which dries the air or SO_2 gas by contacting it with circulating 98 to 99% acid, is made of steel lined with acid-proof brick and packed with ceramic shapes to effect intimate contact of acid with air or gas. The air or gas enters the lower part of the tower and leaves by a flue at the top. A 98.5 to 99% absorbing tower 7.1 m in diameter, inside the lining, with a packed volume of 200 m^3 and an acid flow of approximately 9.5 m^3/min can readily absorb 909 t of sulfur trioxide per 24 h with an apparent gas velocity of 62 cm/s measured at standard conditions of 0°C and 101 kPa. For oleum, the steel tower need not be lined.

²⁵Homme and Othmer, Sulfuric Acid, Optimized Conditions in Contact Manufacture, *Ind. Eng. Chem.* 53 979 (1961); Shannon Digital Computer, *Chem. Eng.* 72 (20) 84 (1965); Shannon, Computer Simulation, *Chem. Eng. Prog.* 62 (4) 49 (1966); Donovan, Palermo, and Smith, Sulfuric Acid Converter Optimization, *Chem. Eng. Prog.* 74 (9) 51 (1978).

²⁶Duecker and West, op. cit., pp. 226, 255.

BLOWERS. Blowers are used to propel the air and/or sulfur-containing gases (SO_2 and SO_3) through the processing equipment. These are located in the flow so that they can handle either air or sulfur dioxide-containing gas (usually after the air or gas has passed through the drying tower). They are electric motor- or steam turbine-driven single-stage centrifugal compressors of cast iron, cast steel, or fabricated steel. Pressure differentials as high as 55 kPa are obtained using only one main blower in each contact acid plant, with capacities up to 3000 t/day. The blower is the major energy consumer in the plant.

ACID PUMPS. Vertical shaft centrifugal submerged pumps of cast iron construction with alloy impellers and shafts are used to circulate acid over the drying and absorption towers. The pumps are usually immersed in brick-lined steel pump tanks within the process area. These may be driven by electric motors or steam turbines.

For transferring acid from one place to another, horizontal shaft pumps of alloy construction are generally used.

SULFUR PUMPS. Vertical shaft submerged centrifugal pumps of cast iron construction are also used to pump sulfur from a pit to the atomizers in the sulfur burner. These pumps have steam-jacketed discharge piping to prevent cooling and solidification of the sulfur, which has a melting point of about 115°C .

ACID COOLERS. The acid circulating over the absorbing towers must be cooled to remove the heat of absorption and the sensible heat of the incoming gas. The acid circulating over the drying tower must be cooled to remove the heat of dilution and heat of condensation of moisture from the incoming gas or air. Formerly this was done by passing water over coils or special cooler sections of cast iron through which the circulating acid was pumped. Recently, shell-and-tube-type heat exchangers of alloy steel, often anodically protected, have been introduced to replace cast iron. Plate coolers of special alloys are also being used. Cast iron (having numerous flanged joints and potential places for acid leakage) has been replaced by these newer coolers in most plants now being built.

GAS PURIFICATION. Plants which must handle impure sulfur dioxide gases, such as those leaving smelters, ore roasters, and other processes, may include waste heat boilers (for heat recovery while cooling the gases), electrostatic dust precipitators (for recovering valuable calcine while also cleaning the gases), scrubbing or wash towers (for further cooling the gases in order to adjust the temperature for water balance in the acid plant while also removing additional dust), and finally electrostatic mist precipitators for removal of acid mist and residual dust and fume. The gases are then ready to enter the drying tower.

MATERIALS OF CONSTRUCTION. After the moisture has been removed in the drying tower, ordinary steel and cast iron are satisfactory materials of construction for use in handling the gas or air and the strong acid. Because of the corrosive and erosive effect of hot acid on steel, the drying and absorbing towers and the acid pump tanks associated with these towers are constructed of brick-lined steel. The brick lining of the oleum tower and pump tank may be omitted if desired. Good quality cast iron is the material normally used as piping for the acid circulating over the drying and 98 to 99% absorbing towers. Cast iron is not suitable for use in the oleum system. For reasons not yet understood, cast iron fails catastrophically in oleum service.

In the gas purification system, steel is used for handling sulfur dioxide gases having temperatures above the acid dew point. For temperatures below the acid dew point and for

liquids, lead, lead-lined steel, with or without a brick lining, alloy steels, and plastic materials are used for specific service conditions. In the United States, the mist precipitators are usually fabricated of lead, with lead collector tubes. Tubular mist precipitators of plastic materials have been built in Europe.

The weak acid coolers in the gas purification system cannot be fabricated of cast iron or steel, which would corrode rapidly. Instead of the lead coil-type coolers used in older plants, modern plants may use shell and tube heat exchangers of graphite or plate-type coolers of special alloys.

PLANT COST. It is difficult to give the approximate general cost of a plant, because of variations in design and in prices in different places and because of continuing inflation. Yet it may be said that a modern double-absorption sulfur-burning contact plant producing 1800 t/day, 100% H_2SO_4 basis, cost roughly \$25 million in the early 1980s. To this figure must be added whatever is required for storage, extension of utilities, and necessary off site facilities. A metallurgical-type plant burning sulfide ores, such as that shown in Fig. 4.5, would cost three or four times the figure given for a sulfur-burning plant, since it would include ore roaster and extensive gas cooling and purification facilities.

Figure 4.8 is a photograph of the 2800-t/day sulfur-burning sulfuric acid plant at the Texasgulf Inc. phosphate operation in North Carolina, which started operating early in 1982.

SULFUR TRIOXIDE²⁷

Liquid sulfur trioxide is used for sulfonation, especially in the manufacture of detergents (Chap. 29). In the past, the difficulty was the instability of the sulfur trioxide. However, under the trade name Sulfans, stabilized forms of sulfur trioxide are commercially available; crystallization or conversion to a polymer is inhibited by several patented inhibitors, such as boron compounds, methane sulfonyl chloride, sulfur, tellurium, and phosphorus oxychloride.²⁸ This product is manufactured by distillation of strong oleums.

RECOVERY OF USED SULFURIC ACID

Much used sulfuric acid is recovered for recycling. This used acid is often referred to as waste acid, a misnomer. Many users do not consume the acid but dilute and contaminate it. Some of it can be recovered and reused at a cheaper cost than virgin (new) acid. Some of it must be recovered in order to meet environmental restrictions or to avoid the cost of neutralization. About 2×10^6 t of spent acid is reused each year: (1) spent alkylation acid catalyst is black, but still relatively strong, and not too heavily contaminated (about 90% H_2SO_4 , 5% water, and 5% hydrocarbons), (2) nitration spent acid is diluted and only slightly contaminated, (3) spent sludge acids result from petroleum refining. These latter are usually dirty, low in acidity,

²⁷Enter, Trioxide Intermediates, *Chem. Week* 102 (8) 31 (1965).

²⁸*McGraw-Hill Encyclopedia of Science and Technology*, vol. 13, McGraw Hill, New York, 1982, p. 299.

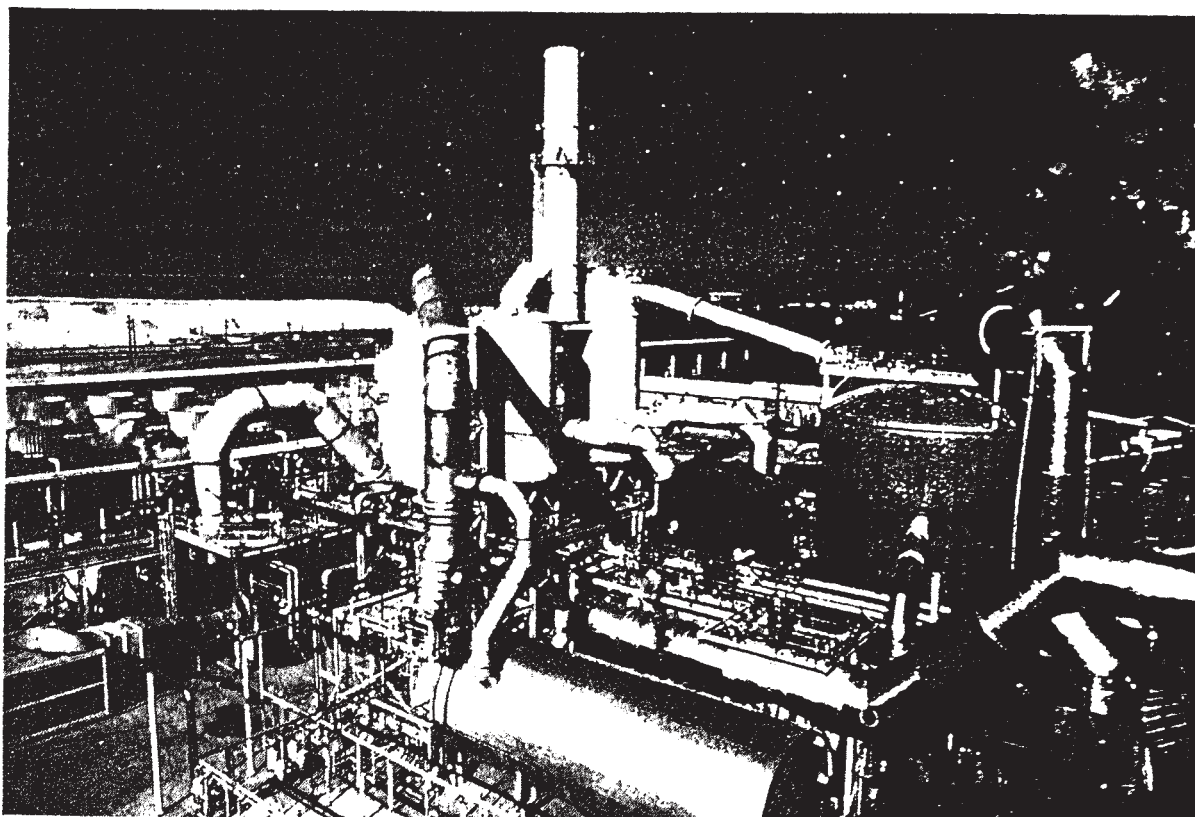


Fig. 4.8. Double-absorption, energy-efficient sulfuric acid plant with a capacity of 2800 t/day. (Texasgulf, Inc.)

heavily contaminated, and many contain up to 75% H_2SO_4 and up to 20% or more hydrocarbons, the balance being water. Occasionally, they can be added in small percentages to spent alkylation acid or reduced to sulfur dioxide by heat with coke as a by-product, but the process is expensive. Other spent acids, which have been used for their ability to absorb water, such as in the production of alcohols, in drying hydrochloric acid gas, etc., can sometimes be recovered by simple concentration.

Some sulfuric acid is still being used in the steel industry for pickling, that is, the preparation of plate for tinning or galvanizing. Because of the need to eliminate the discharge of spent liquors into streams, and because of the difficulty in treating such liquors for the recovery of the acid values, sulfuric acid is being replaced by hydrochloric acid. Spent hydrochloric liquor can be treated to recover acid values and to avoid stream pollution.

A residual liquor similar to steel mill pickle liquor is obtained from titanium pigment plants which use sulfuric acid to produce titanium dioxide from ilmenite. Most titanium dioxide pigment is made by the chloride route to avoid the disposal problem associated with the use of sulfuric acid.

Spent alkylation acid is being economically recovered²⁹ by atomizing it, burning it in a furnace, and cooling and purifying the gases in a manner similar to that used for smelter gases. The sulfur dioxide gas resulting from the combustion is then converted into new, virgin-pure acid in a contact plant.

²⁹Galstaun, Steigerwald, Ludwig, and Garrison, What Does it Cost to Desulfurize Fuel Oil? *Chem. Eng. Prog.* 61 (9) 49 (1965); Mills and Perry, Fossil Fuel Yields Power plus Pollution, *CHEMTECH* 13 (3) 53 (1973); Robinson and Robbins, Gaseous Sulfur Pollutants from Urban and Natural Sources, *J. Air Pollut. Control Assoc.* 20 (4) 233 (1970).