SULFURIC ACID AND SULFUR TRIOXIDE

1. Introduction

Sulfuric acid [7664-93-9], H_2SO_4, is a colorless, viscous liquid with a specific gravity of 1.8357 and a normal boiling point of $\sim 274°C$. Its anhydride, SO_3 [7446-11-9], is also a liquid with a specific gravity of 1.857 and a normal boiling point of 44.8°C. Sulfuric acid is by far the largest volume chemical commodity produced and is sold or used commercially in a number of different concentrations including 78 wt% (60° Bé), 93 wt% (66° Bé), 96 wt%, 98–99 wt%, 100%, and as various oleums (fuming sulfuric acid, $H_2SO_4 + SO_3$) [8014-95-7]. Stabilized and unstabilized liquid SO_3 are items of commerce.

Sulfuric acid has many desirable properties that lead to its use in a wide variety of applications including production of basic chemicals, steel (qv), copper (qv), fertilizer (qv), fibers (qv), plastics, gasoline (see GASOLINE AND OTHER MOTOR FUELS), explosives (see EXPLOSIVES; PROPELLANTS), electronic chips, batteries (qv), and pharmaceuticals (qv). It typically is less costly than other acids; it can be readily handled in steel or common alloys at normal commercial concentrations. It is available and readily handled at concentrations >100 wt% (oleum). Sulfuric acid is a strong acid. It reacts readily with many organic compounds to produce useful products. Sulfuric acid forms a slightly soluble salt or precipitate with calcium oxide or hydroxide, the least expensive and most readily available base. This is a useful property when it comes to disposing of sulfuric acid. Concentrated sulfuric acid is also a good dehydrating agent and under some circumstances it functions as an oxidizing agent.

2. History

Sulfuric acid has been an important item of commerce since the early-to-mid-1700s. It has been known and used since the Middle Ages. In the eighteenth and nineteenth centuries, it was produced almost entirely by the chamber process, in which oxides of nitrogen (as nitrosyl compounds) are used as homogeneous catalysts for the oxidation of sulfur dioxide. The product made by this process is of rather low concentration (typically 60° Baumé, or 77–78 wt% H_2SO_4). This is not high enough for many of the commercial uses developed since the early 1900s. The chamber process is therefore considered obsolete for primary sulfuric acid production. However, more recently, modifications to the chamber process have been used to produce sulfuric acid from metallurgical off-gases in several European plants (1–3).

During the first part of the twentieth century, the chamber process was gradually replaced by the contact process. The primary impetus for development of the contact process came from a need for high strength acid and oleum to make synthetic dyes and organic chemicals. The contact process employing platinum catalysts began to be used on a large scale for this purpose late in the nineteenth century. Its development accelerated during World War I to provide concentrated mixtures of sulfuric and nitric acid for explosives production.

In 1875, a paper by Winkler awakened interest in the contact process, first patented in 1831. Winkler claimed that successful conversion of SO_2 to SO_3 could only be achieved with stoichiometric, undiluted ratios of SO_2 and O_2. Although erroneous, this belief was widely accepted for >20 years and was employed by a number of firms. Meanwhile, other German firms expended a tremendous amount of time and money on research. This culminated in 1901 with Knietsch's lecture before the German Chemical Society (4) revealing some of the investigations carried out by the Badische Anilin-und-Soda-Fabrik. This revealed the abandonment of Winkler's theory and further described principles necessary for successful application of the contact process.

In 1915, an effective vanadium catalyst for the contact process was developed and used by Badische in Germany. This type of catalyst was employed in the United States starting in 1926 and gradually replaced platinum catalysts over the next few decades. Vanadium catalysts have the advantages of exhibiting superior resistance to poisoning and of being relatively abundant and inexpensive compared to platinum. After World War II, the typical size of individual contact plants increased dramatically in the United States and around the world to supply the rapidly increasing demands of the phosphate fertilizer industry. The largest sulfur burning plant as of 2005 is ~ 4500 metric tons of acid/day. Plants using sulfur in other forms, especially SO_2 from smelting operations (metallurgical plants), have also increased in size. One metallurgical plant has been built to produce 3700 metric tons of acid/day (5).

Another significant change in the contact process occurred in 1963, when Bayer AG announced the first large-scale use of the double-contact (double-absorption) process and was granted several patents (6–9). In this process, SO_2 gas that has been partially converted to SO_3 by catalysis is cooled, passed through sulfuric acid to remove SO_3, reheated, and then passed through another one or two catalyst beds. Through these means, overall conversions can be increased from ~ 98 to $>99.7\%$, thereby reducing emissions of unconverted SO_2 to the atmosphere. Because of worldwide pressures to reduce SO_2 emissions, most plants as of 2005 utilize double-absorption. An early U.S. patent (10) disclosed the general concept, but apparently was not reduced to practice at that time.

3. Physical Properties

3.1. Sulfur Trioxide.

Pure sulfur trioxide [7446-11-9] at room temperature and atmospheric pressure is a colorless liquid that fumes in air. Sulfur trioxide can exist in both monomeric and polymeric forms. In the gaseous and liquid state, pure SO_3 is an equilibrium mixture of monomeric SO_3 and trimeric S_3O_9 (11), also called γ-SO_3.

$$3\,SO_3 \leftrightarrow S_3O_9$$

In the gaseous state, the equilibrium lies far to the left (12). In the liquid state, the amount of S_3O_9 is reported by some investigators to be $\sim 25\%$ (25°C)

(13). Others report that the liquid is primarily S_3O_9 (14). For both gas (12,15) and liquid (16–18), the degree of association increases with decreasing temperature.

If the SO_3 is pure, it freezes to γ-SO_3, also called ice-like SO_3, at 16.86°C (19). It is possible that some monomeric SO_3 may also be present in the crystal structure of the ice-like form (17,20–22).

Traces of moisture, ie, of H_2SO_4, as low as 10^{-3} mol% (17,23) cause liquid SO_3 to polymerize first to a low melting, asbestos-like form, β-SO_3. The β-SO_3 forms crystals with a silky luster. Additional reaction involves cross-linking of β-SO_3 to form a high melting asbestos-like form, α-SO_3. The α-SO_3 crystals resemble ice needles. An additional form has been mentioned in the literature as vaselinartiges (24), ie, vaseline-like, or gelatinous (25–27). This form, it has been speculated, is partially cross-linked β-SO_3. Both the alpha and beta forms melt to give γ-SO_3. The early literature used reversed nomenclature for α-, β-, and γ-SO_3; when α- was the ice-like form; β- was the low melting, asbestos-like form; and γ- was the high melting, asbestos-like form.

β-SO_3 consists of helical chain molecules (28) of unknown length (23). The α-SO_3 form is also a polymer similar to β-SO_3, but probably in a layered cross-linked structure (22,23). Melting points, or more precisely triple points, of 32.5 and 62.2°C have been given to beta and alpha polymers, respectively (22,29). The presence of these values persists in product literature, but they are rarely observed in industrial practice. The β-polymer melts only slowly a few degrees above its reported melting point (30). The α-polymer can best be melted by heating under pressure to 80°C (25,30). Without pressure, the polymer sublimes. Initial melting of the β-polymer often leaves behind a residue that is much more difficult to melt. This residue is probably a cross-linked β-polymer that may be a precursor to a pure α-polymer (26). Because of the slowness of melting and the lack of a distinct melting point, the melting process is believed to be a slow depolymerization rather than a general disintegration of the entire polymer molecule (31).

Even in the presence of considerable moisture, solid polymer never forms > 30°C (25). Below 30°C, liquid stability decreases with increasing moisture and decreasing temperature (25). The actual formation of solid polymer has been hypothesized to involve the formation in the liquid of high molecular weight polysulfuric acids, followed by precipitation.

In perfectly dry SO_3 no sulfuric acid molecules would exist. But in the presence of even a trace of water, it seems likely that high molecular weight polysulfuric acids exist. As the higher polyacids form, the increasing molecular weight would be expected to decrease their solubility, leading to precipitation. Owing to kinetic considerations, lower temperatures also favor the formation, and hence precipitation of higher polyacids (26). The formation of polyacids in solution may be relatively rapid and the rate of formation of solid β-polymer controlled by the rate of nucleation (26). Temperatures < 0°C do not appear to accelerate polymer formation as is sometimes believed. Instead, samples quickly cooled to -30 and -78°C, held, and then quickly rewarmed showed less polymer than SO_3 slowly cooled to 0°C, and then slowly rewarmed even though the cycle times for all samples were the same (26).

A study on the thermodynamic properties of the three SO_3 phases is given in Ref. 32. Table 1 presents a summary of thermodynamic properties of pure sulfur trioxide. A significantly lower value has been reported for the heat of fusion of γ-SO_3, 24.05 kJ/kg (5.75 kcal/kg) (33), as have slightly different critical temperature, pressure, and density values (34).

Figure 1 shows the density of sulfur trioxide as a function of temperature. This curve is a composite of data taken from the literature (44–48). The vapor pressures of sulfur trioxide's α-, β-, and γ- phases are presented in Fig. 2 (49). Different values of SO_3 vapor pressure for α-, β-, and γ- phases have been reported in Refs. 32 and 34 (see Table 2). Additional data is available (50).

The thermodynamic properties of sulfur trioxide, and of the oxidation reaction of sulfur dioxide are summarized in Tables 3 and 4, respectively. Thermodynamic data from Ref. 52 are believed to be more accurate than those of Ref. 51 at temperatures below $\sim 435°C$.

3.2. Sulfuric Acid. Sulfuric acid is a dense, colorless liquid at room temperature, having a specific gravity as shown in Fig. 3 (53). Historically, the concentration of sulfuric acid has been reported as specific gravity (sp gr) in degrees Baumé. In the United States, the Baumé scale is calculated by the following formula:

$$^{\circ}\text{Bé} = 145 - \left(\frac{145}{\text{sp gr}}\right)$$

In Germany and France, the Baumé scale is calculated using 144.3 as the constant. The Baumé scale only includes the sulfuric acid concentration range of 0−93.19% H_2SO_4. Higher concentrations are not included in the Baumé scale because density is not a unique function of concentration between 93 and 100% acid. The density of sulfuric acid versus temperature and concentration is shown in Fig. 4 (53).

Figures 5 and 6 present the electrical conductivity of sulfuric acid solutions (54,55). For sulfuric acid solutions in the 90−100% H_2SO_4 concentration range, the electrical conductivity measurements reported by Ref. 55 are believed to be the best values; other conductivity data are also available (56,57).

The viscosity of sulfuric acid solutions is plotted in Fig. 7 (58); other viscosity data may be found in Refs. 57–63. Surface tension of sulfuric acid solutions is presented in Fig. 8 (64). Surface tension of selected concentrations of sulfuric acid as a function of temperature up to the boiling point is given in Ref. 65; other data are also available (61,62,66–68).

The index of refraction of sulfuric acid solutions (65) and additional related data (69) along with solubility data for oxygen in sulfuric acid solutions (70), are available in the literature. The solubility of sulfur dioxide in concentrated sulfuric acid is shown in Fig. 9 (71); additional data is also available (72).

Data on chemical properties, such as self-dissociation constants for sulfuric and dideuterosulfuric acid (63,68,73,74), as well as an excellent graphical representation of physical property data of 100% H_2SO_4 (75) are available in the literature. Critical temperatures of sulfuric acid solutions are presented in Fig. 10 (76).

Boiling points of sulfuric acid are given in Fig. 11. There is some uncertainty in the data close to 100% H_2SO_4 (77). Freezing points also are not well established, in part because acid purity and cooling rates significantly affect the observed freezing points. Acid impurities lower the freezing point, and cooling rates may be such that subcooled liquid sulfuric acid is produced. Figure 12 shows the freezing points (78). Additional freezing point data (79), and discussions (62,80) are available.

At atmospheric pressure, sulfuric acid has a maximum boiling azeotrope at $\sim 98.48\%$ (81,82). At 25°C, the minimum vapor pressure occurs at 99.4% (81). Data and a discussion on the azeotropic composition of sulfuric acid as a function of pressure can also be found in these two references. The vapor pressure exerted by sulfuric acid solutions below the azeotrope is primarily from water vapor; above the azeotropic concentration SO_3 is the primary component of the vapor phase. The vapor of sulfuric acid solutions between 85% H_2SO_4 and 35% free SO_3 is a mixture of sulfuric acid, water, and sulfur trioxide vapors. At the boiling point, sulfuric acid solutions containing $<85\%$ H_2SO_4 evaporate water exclusively; those containing $>35\%$ free SO_3 (oleum) evaporate exclusively sulfur trioxide.

A tabulation of the partial pressures of sulfuric acid, water, and sulfur trioxide for sulfuric acid solutions can be found in Ref. 83 from data reported in Ref. 84. Figure 13 is a plot of total vapor pressures for 0–100% H_2SO_4 versus temperature. References 84–86 present thermodynamic modeling studies for the sulfuric acid–water system. Vapor pressure, enthalpy and dew point data are available (82).

Figure 14 shows the heat of mixing of sulfuric acid and water (87). Additional data are in Ref. 88.

3.3. Oleum. Oleum strengths are usually reported as weight percent free SO_3 or percent equivalent sulfuric acid. The formula for converting percent oleum to equivalent sulfuric acid is

$$\%H_2SO_4 = 100 + \%\,\mathrm{oleum}/4.444$$

Thus, 20% oleum is equivalent to 104.5% H_2SO_4.

Oleum is generally thought of as a mixture of sulfuric acid and free sulfur trioxide. In various strength, oleums the free SO_3 actually forms disulfuric acid, $H_2S_2O_7$, and trisulfuric acid, $H_2S_3O_{10}$ (89). Researchers have also argued for the existence of higher molecular weight polyacids although their presence in significant amount has been the subject of considerable controversy. An excellent review and discussion of the compositions of both the liquid and vapor phases of oleum, including a thermodynamic description of oleum with regard to the formation of $H_2S_2O_7$, is available (89).

The density of oleum at 20 (79) and at 25°C (42) has been reported. The boiling points of oleum are presented in Fig. 15 (90). Freezing points are shown in Fig. 16 (78,91). An excellent discussion on the crystallization points of oleum is available (72). The solubility of sulfur dioxide in oleum has been reported (71,72). Viscosity of oleum is summarized in Fig. 17 (58); additional viscosity data are available (79).

A composite curve of heat of infinite dilution of oleum from reported data (4,92–94) is presented in a compiled form in the literature (95), where heats of formation of oleums from liquid or gaseous SO_3 are also reported (Tables 5 and 6). Heat of vaporization data are also available (96). Oleum heat capacity data are presented in Fig. 18 (79); solubility data of SO_2 in oleum can be found in Ref. 72.

There are significant differences in various sets of published data for oleum vapor pressure. A review of existing vapor pressure data plus additional data from 10 to 8600 kPa (1.45 to 1247 psi) over the entire concentration range of oleum is available (97), including equations for vapor pressure versus temperature. Vapor pressure curves for oleum calculated from these equations are shown in Fig. 19. Additional vapor pressure data from 0.06 to 14 kPa (0.5 to 110 Torr) is given in the literature (96).

3.4. Manufacture. Sulfuric acid may be produced by the contact process from a wide range of sulfur-bearing raw materials by several different process variants, depending largely on the raw material used. In some cases, sulfuric acid is made as a by-product of other operations, primarily as an economical or convenient means of minimizing air pollution (qv) or disposing of unwanted by-products.

The contact process remained virtually unchanged from its introduction in the late 1800s until the 1960s when the double absorption process was introduced to reduce atmospheric SO_2 emissions. Double absorption did not, however, substantially change the nature of the process or the process equipment. In the 1970s and 1980s the increased value of energy, and production of sulfuric acid from a variety of waste products, including off-gases and spent sulfuric acid, led to a number of new process and equipment modifications (98,99).

The principal direct raw materials used to make sulfuric acid are elemental sulfur, spent (contaminated and diluted) sulfuric acid, and hydrogen sulfide. Elemental sulfur is by far the most widely used. In the past, iron pyrites or related compounds were often used. Pyrites plants are still found around the world, but as of 2005 are not common except in China (100). A large amount of sulfuric acid is also produced as a by-product of nonferrous metal smelting, ie, roasting sulfide ores of copper, lead, molybdenum, zinc, or others.

In all types of contact plants, the first steps in the process have the objective of producing a reasonably continuous, contaminant-free gas stream containing appreciable sulfur dioxide and some oxygen. The gas stream is preferably dry, but plants can be designed to handle wet gas directly, eg, from H_2S combustion. This requires careful design of equipment to minimize mist formation in the condensation–absorption portion of the plant. If the initial oxygen concentration of the process gas is low, additional air or oxygen must be added prior to or during catalytic oxidation to ensure that there is an excess over stoichiometric needs for conversion of SO_2 to SO_3.

The gas stream containing sulfur dioxide is either dried before passing to the catalytic oxidation step, or (in a wet gas process) is oxidized in the presence of water vapor with subsequent acid condensation and removal. When acid is produced from elemental sulfur, the air used for sulfur burning is dried. In almost all cases, typical plant designs use sulfuric acid from the process as a drying agent. “Wet” catalytic oxidation is becoming more common, especially for treating weak sulfurous gas streams. Some applications of Haldor Topsøe WSA-2 wet gas catalysis process are described in the literature (101).

The sulfur trioxide produced by catalytic oxidation is absorbed in a circulating stream of 98–99% H_2SO_4 that is cooled to $\sim$70–80°C. Water or weaker acid is added as needed to maintain acid concentration. Generally, sulfuric acid of $\sim$98.5% concentration is used because it is near the concentration with minimum total vapor pressure, ie, the sum of SO_3, H_2O, and H_2SO_4 partial pressures. At acid concentrations much $<$98.5% H_2SO_4, relatively intractable aerosols of sulfuric acid mist particles are formed by vapor-phase reaction of SO_3 and H_2O. At much higher acid concentrations, the partial pressure of SO_3 becomes significant. Both factors lead to unacceptable, visible atmospheric emissions of sulfuric acid mist.

The catalytic oxidation of SO_2 to SO_3 is highly exothermic and, as expected, equilibrium becomes increasingly unfavorable for SO_3 formation as temperature increases $>$410–430°C. Unfortunately, this is about the minimum temperature level required for typical commercial catalysts to function. Consequently, plant catalytic reactors (converters) are typically designed as multistage adiabatic units with gas cooling between each stage. Sulfur dioxide concentrations in the gas stream range from 4 to 14 vol%; lower or higher concentrations occasionally being handled by special process or plant modifications.

In early years, the contact process frequently employed only two or three catalyst stages (passes) to obtain overall SO_2 conversions of $\sim$95–96%. Later, four pass converters were commonly used to obtain conversions of from 97 to slightly $>$98%. For sulfur burning plants, this typically resulted in SO_2 stack emissions of 1500–2000 parts per million (ppm) by volume. With catalyst improvements, particularly the use of cesium promoted catalyst, conversions near 99% have been achieved.

In the early 1970s, air pollution requirements led to the adoption of the double contact or double absorption process, which provides overall conversions of $>$99.7%. The double absorption process employs the principle of intermediate removal of the reaction product, ie, SO_3, to obtain favorable equilibria and kinetics in later stages of the reaction. A few single absorption plants are still being built in some areas of the world, or where special circumstances exist, but most industrialized nations now have emission standards that cannot be achieved without double absorption or tail-gas scrubbers. A discussion of sulfuric acid plant air emissions, control measures and emissions calculations can be found in Ref. 102.

Plants producing oleum or liquid SO_3 typically have one or two additional packed towers irrigated with oleum ahead of the normal SO_3 absorption towers. Partial absorption of SO_3 occurs in these towers, and sulfuric acid is added to maintain desired oleum concentrations. Normally, oleum up to $\sim$35 wt% free SO_3 content can be made in a single tower; two towers are used for 40 wt% SO_3. Liquid SO_3 is produced by heating oleum in a boiler to generate SO_3 gas, which is then condensed. Oleums containing $SO_3 >$40 wt% are usually produced by mixing SO_3 with low concentration oleum.

Where elemental sulfur or hydrogen sulfide is used as raw material, considerable heat is evolved during the initial combustion. Additional heat is generated by catalytic oxidation to SO_3 and by the reaction of SO_3 and H_2O to form H_2SO_4. In such plants, much of the heat is typically used to produce steam, which can be utilized either for heating requirements in other processes or to generate power via turbines. In many cases, large plants of this type are essentially coproducers of steam or power and sulfuric acid; both products have significant economic value. Where spent acid is used as raw material, it usually is decomposed in furnaces fired by gas, oil, or other fuels (sometimes H_2S or sulfur), and the high temperature gas from such furnaces can also generate steam or power (see POWER GENERATION).

In general, plants using SO_2 gas derived from metallic sulfides, spent acids, or gypsum anhydrite purify the gas stream before drying it by cold, ie, wet, gas purification. Various equipment combinations including humidification towers, reverse jet scrubbers, packed gas cooling towers, impingement tray columns and electrostatic precipitators are used to clean the gas.

Plants that burn good quality elemental sulfur or H_2S gas generally have no facilities for purifying SO_2. Before the advent of relatively pure Frasch or recovered sulfur, however, hot gas purification was frequently used in which the SO_2 gas stream was passed through beds of granular solids to filter out fine dust particles just prior to entering the converter.

Sulfur shipped as a solid frequently becomes contaminated with dirt and scale during shipping and handling. In areas of the world where solid sulfur is still handled, molten sulfur is frequently filtered prior to use as an alternative to, or in combination with, hot gas purification. Since the early 1970s, most sulfur used in the United States and Europe has been shipped and handled as a liquid containing very low ash concentrations, typically $<0.005\%$. Using this type of raw material, neither sulfur filtration nor hot gas purification are essential, and are rarely used.

Tail gas scrubbers are sometimes used on single absorption plants to meet SO_2 emission requirements, most frequently as an add-on to an existing plant, rather than on a new plant. Ammonia (qv) scrubbing has been popular, but to achieve good economics the ammonia value must be recovered as a usable product, typically ammonium sulfate for fertilizer use. A number of other tail gas scrubbing processes have been used, including use of hydrogen peroxide, sodium hydroxide, lime and soda ash, and the absorption and subsequent release of SO_2 from a sodium bisulfite solution (the Wellman-Lord process).

Other regenerative scrubbing processes have also been introduced. These include CANSOLV, Labsorb, and Solinox/ClausMaster (103–107). [The Solinox process (Linde AG, Höllriegelskreuth, Germany) is now licensed to (formerly Monsanto Enviro-Chem Systems) MECS, Inc. (St. Louis) and is marketed under the trade name ClausMaster.] These processes absorb SO_2 from gas stream and regenerate it as concentrated SO_2. The SO_2 can be recycled back to the front end of the acid plant or used elsewhere. All three processes have been commercialized. Though not economically justified, some tail gas scrubbers can reduce emissions beyond that achievable by dual absorption alone. These processes have also been proposed as alternatives to dual absorption for new plants.

Small amounts of sulfuric acid mist or aerosol are always formed in sulfuric acid plants whenever gas streams are cooled, or SO_3 and H_2O react, below the sulfuric acid dew point. The dew point varies with gas composition and pressure, but typically is 80–170°C. Higher and lower dew point temperatures are possible depending on the SO_3 concentration and moisture content of the gas. Such mists are objectionable because of both corrosion in the process and stack emissions.

Since the 1960s, sulfuric acid mists have been satisfactorily controlled by passing gas streams through equipment containing beds or mats of small diameter glass or Teflon fibers. Such units are called mist eliminators (see AIR POLLUTION CONTROL METHODS). Use of this type of equipment has been a significant factor in reducing stack emissions of acid mist to acceptable levels. Packed fiber mist eliminators are considered BACT for mist removal.

3.5. Generation of Sulfur Dioxide Gas. *Sulfur Burning.* With the trend to very large single train plants, current practice is to use horizontal, brick-lined combustion chambers with dried air and atomized molten sulfur introduced at one end. Atomization typically is accomplished either by pressure spray nozzles, with or without atomization air, or by mechanically driven spinning cups. Because the degree of atomization is a key factor in producing efficient combustion, sulfur nozzle pressures are typically 2.76 MPa (150 psi) or higher. Sulfur furnaces are typically designed as proprietary items by companies specializing in acid plant design and construction. Some designs contain baffles or secondary air inlets to promote mixing and effective combustion.

In any process involving the handling of molten sulfur, the lines and spray nozzles must be steam jacketed and steam pressure must hold the molten sulfur within the range of 135–155°C, where its viscosity is at a minimum. Above 160°C the viscosity rises sharply and at 190°C its viscosity is 13,000 times that at 150°C.

The self-sustaining ignition temperature of pure sulfur is ~260°C, but may be slightly higher for dark sulfur, ie, sulfur-containing organic impurities. Consequently, a source of ignition is not required if the combustion chamber is preheated to ~400–425°C before sulfur is admitted. When burning sulfur in air, SO_2 concentrations in the range of ~3–14 vol% can be produced by the burners described. Special burners capable of producing higher SO_2 concentrations are also available (see SULFUR COMPOUNDS).

The temperature of gas leaving the sulfur furnace is a good indication of SO_2 concentration, even though thermocouples employed for temperature measurement (qv) frequently read somewhat lower than the true temperatures because of radiation and convection errors. At a combustion air temperature of 55°C, a temperature of 955°C corresponds to ~10.0 vol% SO_2, 1034°C–11.0 vol% SO_2, 1112°C–12.0 vol% SO_2. Other temperatures and concentrations are in similar proportion.

At high flame temperatures, small amounts of nitrogen will react with oxygen to form nitrogen oxides, NO_x, primarily nitric oxide, NO. The chemistry of these nitrogen oxides is complex. Ultimately, however, some form nitrosylsulfuric acid, which ends up either as trace amounts in product acids or, in considerably higher concentrations, as condensed acid collected in mist eliminators.

Sulfur burners are normally operated at moderate pressures, in the range of 135.8–170.3 kPa (5–10 psig), using air supplied by the main blower for the plant.

Spent Acid or H_2S Burning. Burners for spent acid or hydrogen sulfide are generally similar to those used for sulfur with a few critical differences. Special types of nozzles are required both for H_2S, a gaseous fuel, and for the corrosive and viscous spent acids. In a few cases, spent acids may be so viscous that only a spinning cup can satisfactorily atomize them. Because combustion of H_2S is highly exothermic, careful design is necessary to avoid excessive temperatures.

Spent acid burning is actually a misnomer, for such acids are decomposed to SO_2 and H_2O at high temperatures in an endothermic reaction. Excess water in the acid is also vaporized. Acid decomposition and water vaporization require considerable heat. Any organic compounds present in the spent acid will oxidize to produce some of the required heat. To supply the additional heat required, auxiliary fuels, eg, oil or gas, must be burned. When available, sulfur and H_2S are excellent auxiliary fuels.

Relatively high (typically 980–1200°C) temperatures are required to decompose spent acids at reasonable burner retention times. Temperatures depend on the type of spent acid. A wide variety of spent acids can be processed in this way, but costs escalate rapidly when the sulfuric acid concentration in spent acid (impurity free basis) falls below ~ 75%. A few relatively uncontaminated spent acids can be reused without decomposition by evaporating the excess water in concentrators, or by mixing in fresh sulfuric acid of high concentration. Weak spent acids are frequently concentrated by evaporation prior to decomposition.

Because large amounts of water vapor are produced by combustion of H_2S or spent acids, ambient, not dried air, is supplied to the burners. In some cases, burners are operated at pressures slightly below atmospheric pressure to pull in outside air; in other cases, preheated combustion air at low pressure may be supplied by ducts.

Ore Roasting, Sintering, or Smelting. Generation of SO_2 at nonferrous metal smelters is determined primarily by the needs of the various metallurgical processes and only incidentally by requirements of the sulfuric acid process. Traditionally, sulfur recovery from copper (qv), nickel, lead (qv), and zinc (qv), smelters has been limited to treatment of gases from roasters, sintering machines, and converters. Roasters and sintering machines operate continuously and produce a fairly uniform, but low concentration off-gas. Traditional converters, which operate as batch reactors, produce gases having varying concentrations of SO_2. Moreover, there is considerable time when the furnaces are off-line for charging and transferring metals. Treatment of these cyclical and low grade gases is costly and involves technical problems that make efficient acid production difficult.

More recently, intensive smelting processes have been developed that use highly oxygen-enriched air or even technically pure oxygen to minimize fuel consumption. The resulting gases are high (25–75%) in SO_2, but generally low in oxygen. These smelting processes are often followed by traditional batch converting and the combined gas flow to the acid plant is more uniform and higher strength than when treating converting gases alone.

The most modern smelters (~ 2005) now use continuous smelting and converting processes that utilize high levels of oxygen-enriched air to produce a uniform flow of high strength process gas. This allows efficient acid plant design including high levels of energy recovery that was formerly only possible in sulfur-burning acid plants.

4. Process Details and Flow Sheets

The stoichiometric relation between reactants and products for the contact process may be represented as follows:

$$SO_2 + 0.5\,O_2 \leftrightarrow SO_3 \tag{1}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{2}$$

There are three important characteristics of the first of these equations. It is exothermic, reversible, and shows a decrease in molar volume on the right-hand side, ie, in the direction of the desired product. To improve equilibrium or driving force for the reaction, the sulfuric acid industry has attempted one or a combination of the following process design modifications: increasing concentration of SO_2 in the process gas stream; increasing concentration of O_2 in the process gas stream by air dilution or oxygen enrichment; increasing the number of catalyst beds; removing the SO_3 product by interpass absorption, known as the double absorption process; lowering catalytic converter inlet operating temperatures, ie, using better catalysts; and increasing the catalytic converter operating pressure (pressure plants).

4.1. Sulfur Burning Plants.

Single absorption sulfuric acid plants were standard in the industry for many years. These used either relatively low strength (~8 vol%) SO_2 gas without air dilution, or air dilution designs and higher (~10 vol%) inlet gas strength. Air dilution was a common design option using additional dry air, instead of heat exchangers, to cool the process gas entering the last one or two converter passes. The additional air improved conversion at the final converter pass by increasing oxygen concentration and reducing equivalent sulfur dioxide concentration of the process gas. Its chief advantage was reduced investment over designs with heat exchangers for interpass cooling.

In the single absorption plant, SO_2 was oxidized to SO_3 in a multipass converter. Gas leaving the converter passed through a single SO_3 absorption tower (hence the term "single absorption") then passed to the atmosphere. Even with current improved catalysts, equilibrium considerations in a single absorption plant limit overall SO_2 conversion to 98–99%. This is equivalent to emissions of 12–27 lb_m SO_2/ton of acid.

In the United States, New Source Performance Standards (NSPS) limit SO_2 stack emissions for new sulfuric acid plants to limit to 2 kg of SO_2 per metric ton of 100% acid produced (4 lb_m/short ton), which is equivalent to a sulfur dioxide conversion efficiency of 99.7%. (In practice, permitting agencies may require limits considerably below 4 lb_m/ton for plants in areas with poor air quality. This requires very aggressive use of catalyst, tail gas scrubbers or both.) Acid plants used as pollution control devices, eg, those associated with smelters, may have different regulations. To achieve this high conversion efficiency producers normally use the double absorption process.

Typical double absorption plant design uses intermediate SO_3 absorption after the second or, more commonly, the third converter pass ($3 + 1$ configuration). Plants with five passes in a $3 + 2$ configuration have also been built.

Figure 20 shows a typical flow sheet for a $3 + 1$, double absorption sulfur burning plant. Plants of this design burn sulfur to generate a process gas stream of about 10.0–12.0% SO_2. The scheme shown produces 66° Bé and 98.5% acid. If oleum is desired, an oleum tower and associated pump and cooler would be installed ahead of the interpass absorption tower. If 66° Bé acid product is not needed, a common pump tank is usually used for both the drying and absorbing towers.

Typical converter operating conditions are shown in Table 7.

Process air in sulfur burning plants is dried by contacting it with 93–98 wt% sulfuric acid in a countercurrent packed tower. Dry process air is used to minimize sulfuric acid mist formation in downstream equipment, thus reducing corrosion problems and stack mist emissions.

Most of the heat of combustion from the sulfur furnace is removed in a boiler, which reduces the process gas temperature to the desired converter inlet temperature. Typically, the inlet temperature (Table 7) to the first converter pass is dictated by catalyst performance, catalyst bed depth, and process gas strength. Standard, ie, sodium- or potassium-promoted, vanadium catalysts do not have sustained catalytic activity at temperatures <400–410°C, although fresh catalyst may have an initial reaction ignition temperature as low as 385°C. Such low ignition temperatures cannot be sustained by conventional catalysts. (The catalyst ignition temperature is the temperature below which substantial catalytic conversion (approaching equilibrium) cannot be sustained in any given bed or pass.) Catalysts promoted with cesium, have a considerably lower sustainable ignition temperature (~ 390°C) and have proved useful in special situations (108).

Sulfur dioxide gas is catalytically oxidized to SO_3 in a fixed-bed reactor (converter) that operates adiabatically in each catalyst pass. The heat of reaction raises the process gas temperature in the first pass to ~ 600°C (see Table 7). The temperature of hot gas exiting the first pass is then lowered to the desired second pass inlet temperature (430–450°C) by removing the heat of reaction in a steam superheater or second boiler.

In converter passes downstream of the first pass, exit temperatures are limited by thermodynamic equilibrium to ~ 500°C or less. To obtain optimum conversion, the heat of reaction from succeeding converter passes is removed by superheaters or gas to gas heat exchangers. The temperature rise of the process gas is almost directly proportional to the SO_2 converted in each pass, even though SO_2 and O_2 concentrations can vary widely.

Gas leaving the converter is normally cooled to 165–230°C using boiler feedwater in an “economizer”. This increases overall plant energy recovery and improves SO_3 absorption by lowering the process gas temperature entering the absorption tower. The process gas is not cooled to a lower temperature to avoid the possibility of corrosion from condensing sulfuric acid originating from trace water in the gas stream. In some cases, a gas cooler is used instead of an economizer.

Gas leaving the economizer flows to a packed tower, called the interpass absorption tower, where SO_3 is absorbed. Concentrated sulfuric acid circulates in the tower and cools the gas to within a few degrees of the acid inlet temperature. The typical acid inlet temperature for 98.5% sulfuric acid absorption towers is ~ 75–80°C. The irrigation rate in the tower is designed so that the sulfuric acid exits the absorption tower at 100–125°C. Acid temperature rise within the tower comes from the heat of hydration of sulfur trioxide and sensible heat of the process gas. The hot product acid leaving the tower is cooled in heat exchangers before being recirculated or pumped into storage tanks. If oleum is desired, SO_3 is absorbed in an oleum tower ahead of the interpass absorption tower.

Acid circulated over SO_3 absorbing towers is maintained at ~ 98.5% to minimize its vapor pressure. Where lower concentration product acid is desired, it is made either in separate dilution facilities, or in drying towers operated at 93–96% H_2SO_4.

The conversion efficiency of any sulfuric acid plant can be presented as an equilibrium-stage process. Figure 21 presents the equilibrium-stage diagram of a single absorption sulfur-burning plant using 8% SO_2 burner gas. The slopes of the adiabatic temperature rise lines are directly proportional to the specific heat capacity of the process gas, which is reasonably constant for any degree of conversion.

The curve in Fig. 21 represents SO_2 equilibrium conversions versus temperature for the initial SO_2 and O_2 gas concentrations. Each initial SO_2 gas concentration has its own characteristic equilibrium curve. For a given gas composition, the adiabatic temperature rise lines can approach the equilibrium curve, but never cross it. The equilibrium curve limits conversion in a single absorption plant to ~ 99%, even with aggressive catalyst use. The double absorption process removes this limitation by removing the SO_3 from the gas stream, thereby altering the equilibrium curve. With appropriate loadings of newer catalysts, new dual absorption plants can achieve an overall conversion of ~ 99.9%. This is equivalent to an emission rate of 0.65 kg SO_2/metric ton of 100% acid produced (1.3 lb_m/short ton). A typical equilibrium curve after the SO_3 has been absorbed and the operating line for the final catalyst pass are shown in Fig. 22.

With the SO_3 removed from the process gas, the gas is reheated to 390–430°C, depending on the catalyst used, and sent to the final converter pass where nearly all the remaining SO_2 is converted to SO_3. Reheating the process gas is accomplished in gas-to-gas heat exchangers (see Fig. 20), using some of the heat from the initial converter passes.

Approximately 93–97% of total sulfur dioxide is converted to sulfur trioxide in the first three converter passes, and is absorbed in the interpass absorption tower; the sulfur trioxide produced in final converter pass is absorbed in the final absorbing tower. The smaller amount of sulfur trioxide absorbed in the final absorption tower of double absorption plants typically raises its acid temperature to only 105°C or less. Interpass and final absorbing towers are very similar in size since tower diameter is dependent on total gas throughput, not sulfur trioxide concentration.

4.2. Non-Sulfur Burning Plants. Acid plants having a SO_2 source other than sulfur burning, eg, from metallurgical plants or spent acid decomposition, usually receive cold process gas that must be heated to the reaction temperature of ~ 425°C before entering the converter. Reheating can be done by burning additional sulfur and adding the hot gas from the sulfur furnace to the main gas stream, or using gas-to-gas heat exchangers, using heat from the converter as the heat source. In a dual absorption plant without additional sulfur burning, a high percentage of the heat of reaction in the converter is needed for heating and reheating the process gas.

4.3. Oleum Manufacture. To produce fuming sulfuric acid (oleum), SO_3 is absorbed in one or more special absorption towers irrigated by recirculated oleum. Because of oleum vapor pressure limitations the amount of SO_3 absorbed from the process gas is typically limited to $< 70\%$. Because absorption of SO_3 is incomplete, gas leaving the oleum tower must be processed in a nonfuming absorption tower.

The absorption of SO_3 for oleum production is carried out over a relatively narrow temperature range. The upper temperature is set to provide a reasonable partial pressure driving force for the oleum concentration used. The lower practical temperature limit is the freezing point of oleums, which is high enough to be a problem in shipping and handling as well. For some oleum uses, it is practical to add small amounts of HNO_3 as an antifreeze (109).

4.4. Sulfur Trioxide. The anhydride of sulfuric acid, SO_3, is a strong organic sulfonating and dehydrating agent that has some specialized uses (see SULFONATION AND SULFATION). Its principal applications are in production of detergents and as a raw material for chlorosulfuric acid and 65% oleum. More recently, SO_3 gas has been added to cooled combustion gases at many coal burning power plants to improve dust removal in electrostatic precipitators (see AIR POLLUTION CONTROL METHODS).

Liquid SO_3 is a difficult material to handle because of its relatively low (44.8°C) boiling point, its tendency to form solid polymers $< 30°C$, plus high reactivity with almost all organic substances and water. It reacts explosively with water because of a very high heat of reaction. In addition, trace amounts of water (sulfuric acid) act as polymerization catalysts for liquid SO_3 and produce a series of high molecular weight polymers with elevated melting points. When polymerization occurs, attempts to melt the solids can cause piping or equipment failures because high (exceeding atmospheric pressure) vapor pressures develop before melting occurs. Polymerization is promoted by cooling the liquid $< 30°C$. It can be inhibited by adding small amounts of various patented stabilizers to the liquid, such as 0.3% dimethyl sulfate with 0.005% boric oxide (30). Stabilized liquid SO_3 is an item of commerce, and instructions for its storage and use are available from suppliers.

Liquid SO_3 is usually produced by distilling SO_3 vapor from oleum and condensing it. This operation is normally carried out at a sulfuric acid plant where the stripped oleum can be readily refortified or reused. Eliminating all traces of sulfuric acid from the SO_3 vapor stream is important to minimize polymerization of the liquid condensate. When this is done, it is frequently possible to utilize unstabilized liquid SO_3 if precautions are taken to prevent its freezing before use. At some plants, gaseous 100% SO_3 is utilized directly instead of producing liquid.

5. Equipment

5.1. Absorption and Drying Towers. Towers are typically carbon steel vessels lined with acid proof brick and mortar and packed with ceramic saddles (see ABSORPTION). Structured packing has also been used. Beginning in the early 1990s, all metal towers (with no brick lining) have been built from high silicon stainless steel alloys such as SX, Saramet, or ZeCor.

Various acid distributors have been used, including perforated pipes and trough and downcomer designs. Some designs are prone to plugging from packing chips and sulfates, and thus strainers are frequently used in acid lines. Distributors were formerly made out of cast iron and were limited in the number of distribution points per square foot that could be achieved. Designs using stainless steel alloys can provide up to four distribution points per square foot (43/m^2).

Well-designed absorption or drying towers operate at absorption efficiencies $>$99.5%, typically 99.8 to $>$99.9%. Drying towers are typically designed using special glass fiber mesh pads at the gas exit to remove acid spray and large mist particles. Sometimes, and especially when the main blower is downstream from the drying tower, more efficient packed bed fiber mist eliminators are installed. Glass or Teflon packed fiber bed mist eliminators are standard in interpass and final absorption towers, where high efficiency collection of acid mist is more critical.

5.2. Acid Coolers. Cast iron trombone coolers (110), once the industry standard, are considered obsolete. In 1970, anodically passivated stainless steel shell and tube acid coolers became commercially available. Because these proved to have significant maintenance savings and other advantages, this type of cooler became widely used. Anodic passivation uses an impressed voltage from an external electrical power source to reduce metal corrosion. Anodic passivation and its application to sulfuric acid equipment, such as shell and tube coolers and carbon steel storage tanks, is discussed in the literature (111–113). More recently, shell and tube coolers made from SX, Saramet, or ZeCor have been installed in several acid plants. These materials do not require anodic protection.

Plate and frame coolers using Hastelloy C-276, Hastelloy D205, and SMO-254 plates have been used successfully. Anodically protected plate coolers are available, as well as plate coolers with plates welded together to minimize gasketing. Because of the close clearance between plates cooling water for plate coolers must be relatively clean.

Impervious (impregnated) graphite coolers are utilized in acid service in which the sulfuric acid concentration is 90–93% or less. When operated properly, graphite coolers provide excellent service in weak acids. They are not recommended for acid services $>$93% concentration. Although graphite is relatively inert, the graphite impregnating agent is attacked by concentrated sulfuric acid. The main disadvantage of graphite coolers is brittleness. They are subject to damage by mechanical or hydraulic shocks. Though it predates a few of the newer alloys, Ref. 114 is a good discussion of acid plant coolers. A brief discussion of the evolution of acid coolers is included.

5.3. Catalysts. Commercial sulfuric acid catalysts typically consist of vanadium and potassium salts supported on silica, usually diatomaceous earth (see DIATOMITE). Catalyst is available in various formulations, shapes, and sizes depending on the manufacturer and the particular converter pass in which they are to be used. A detailed discussion of oxidation catalysts for sulfuric acid production is available (115).

Formerly, most catalysts were supplied as solid cylindrical extrudates or pellets ranging from 4 to 10 mm diameter. Ring-shaped catalysts or variations, including rings with longitudinal ribs, are used almost exclusively as of 2005, primarily as a means of saving energy via reduced gas pressure drop. The various ring-shaped catalysts also have greater resistance to dust fouling. Ring catalysts also have somewhat higher activity per unit volume than pellet catalysts.

Increased catalyst-bed pressure drop caused by dust fouling reduces production of acid and significantly increases energy consumption by the plant's blower. To avoid these problems, first converter pass catalyst is screened at every major turnaround, typically every 12–36 months. Second pass catalyst is screened less frequently because the first converter pass catalyst bed acts as a filter for the rest of the converter. Typical screening losses range from 10 to 15% of the catalyst bed per screening. Screening losses depend on screen mesh size and catalyst hardness as well as on screening rate.

Under normal operating conditions, vanadium catalysts in first and second pass service slowly lose catalytic activity over time. Catalyst aging is a combination of a loss of catalytically active material from the catalyst pellets and irreversible changes within the catalyst. It is well documented that at operating temperatures the active catalytic ingredient is a molten salt that migrates from catalyst into adjacent dust. Catalyst aging is accelerated by increasing temperatures and temperature cycling. Exposure to moisture above the dew point is not detrimental to sulfuric acid catalyst. However, exposure to moisture at temperatures below the dew point produces irreversible damage. Prolonged exposure to moisture reduces the vanadium to the +3 oxidation state, which is very difficult to reoxidize under converter conditions. Moisture also damages the binders that hold together the silica support. This reduces catalyst hardness resulting in higher than normal screening losses.

5.4. Catalytic Converters. Converters vary in design with different engineering firms. Stainless steel converters are generally preferred, although carbon steel converters are also still used. Stainless steel offers better corrosion resistance and significantly higher strength at operating temperatures than carbon steel. In plants having high temperatures and high NO_x content, significant scaling has been observed in stainless steel converters, although significant metal loss has not been found. This problem appears to be more closely linked to high NO_x content than high temperature and, so far, has not been sufficiently serious to result in abandonment of stainless steel designs.

Stainless steel designs generally use all welded interior construction, with stainless screens for catalyst supports. Traditional carbon steel converter designs use steel shells, sometimes partly or wholly brick lined, with cast iron and alloy internals. In the high temperature converter passes, carbon steel is protected from hot gases by brick lining or a sprayed aluminum coating. Both carbon and stainless steel converters are insulated to reduce heat losses. Essentially all designs use horizontal catalyst beds arranged one over another with gas flowing down through the catalyst.

One innovation in stainless steel converter design is to use "structurally shaped" support grids and division plates (116). Two advantages are claimed for the structural shape of the support grids and division plates: improved resistance to temperature differentials during startup and a higher strength design requiring less metal.

5.5. Gas–Gas Heat Exchangers. Gas–gas heat exchangers in double absorption plants are built of carbon steel or stainless steel. Typical tube diameters range from 37.5 to 100 mm, and the tubes run vertically in a typical shell and tube arrangement. To reduce corrosion and scaling, carbon steel tubes in high temperature service are Alonized, which is a proprietary aluminum alloy coating vapor diffused into the metal surface. Alonizing significantly increases the life of carbon steel with the added benefit of no loss of heat transfer from accumulation of corrosion scale.

5.6. Mist Eliminators. Most modern mist eliminators use fiber beds enclosed or supported by stainless steel or alloy-20 wire mesh or the like. Fibers are generally glass or in some cases Teflon. Mist eliminator design, ie, fiber diameter, packing density, bed depth, etc, is determined by particle size and loading, which is in turn determined largely by the application.

Acid mist eliminators use three aerosol collection mechanisms: inertial impaction, interception, and Brownian motion. Inertial impaction works well for aerosols with particle diameters $> 3\,\mu\text{m}$; Brownian motion and interception work well with aerosols having smaller particle diameters.

In drying towers of sulfur-burning plants, mesh pads, or inertial impaction-type mist eliminators are usually adequate. High efficiency mist eliminators are usually used ahead of drying towers of spent acid plants. Metallurgical plants may require wet electrostatic precipitators ahead of drying towers, followed by a mesh pad in the drying tower exit.

Packed fiber-bed mist eliminators can be designed to operate at various particle collection efficiencies, depending on allowable pressure drop and cost. A good discussion of sulfuric acid mist generation, control, and mist eliminator design is available (117,118).

5.7. Oleum Equipment and Piping. The traditional material of construction for oleum is carbon steel. Relatively low oleum velocities must be used in steel piping to prevent excessive corrosion. The corrosiveness of oleum decreases with increasing SO_3 concentration. For oleum concentrations $< 5\%$ SO_3, carbon steel is not recommended because of excessive corrosion. Steel is borderline from 5% to $\sim 15\%$ SO_3, depending on temperature.

Gray cast iron is not a recommended construction material for oleum. It is well documented that gray cast iron fails catastrophically by cracking in oleum service. The mechanism or the cause of cracking is not well understood, but it is agreed that the failures are due to a buildup of internal stresses within the cast iron. One notable exception is process iron, a proprietary cast iron of Chas. S. Lewis Co., (St. Louis, Missouri). Process iron has been used successfully in oleum service.

Standard stainless steels have significantly greater corrosion resistance to oleum than carbon steel, but their higher price may make these materials less economical, except for special services, such as valves, liquid distributors, oleum, and boilers.

5.8. Spent Acid Regeneration Gas Cleaning Equipment. Process gas leaving the spent acid regeneration furnace and waste heat boiler must be cleaned prior to entering the drying tower. Except where spent gases make up only a small portion of the total SO_2 stream, it is also necessary to remove as much water as possible from the spent gas to avoid water balance problems in the absorption portion of the plant. For many years, spent gas purification equipment consisted of brick and lead-lined spray humidification towers, electrostatic precipitators, Karbate cooler/condensers, packed cooling towers, and impingement tray towers. Venturi scrubbers and cyclone separators were sometimes used to remove acid mist and spray instead of electrostatic precipitators.

In the late 1980s, a new type of gas cleaning technology, based on patented DuPont froth scrubbing technology, was successfully introduced by MECS (St. Louis, Missouri) (119). Trademarked DynaWave, the main application of this technology for sulfuric acid plants is the Reverse Jet Scrubber in which a jet of scrubbing liquid is sprayed into the gas stream so as to balance the liquid and gas momentums. This produces a highly turbulent froth zone that efficiently cools and scrubs gas leaving the spent boiler. Temperatures entering the primary reverse jet scrubber are typically $\sim 325^\circ C$, but may be as high as $800^\circ C$.

DynaWave equipment is typically smaller than conventional equipment and is usually made of fiberglass reinforced plastic (FRP) at considerable capital savings over conventional materials. DynaWave is now in use at a number of plants worldwide.

5.9. Sulfuric Acid Piping. The traditional material of construction for handling concentrated sulfuric acid (>70 wt%) for most of the past century has been gray cast iron. Gray cast iron was the preferred material because of its low price and availability, plus tolerable corrosion. The expected service life of gray cast iron pipe is $\sim 7-15$ years, depending on the temperature, concentration, and velocity of the acid. Gray cast iron pipe and fittings should not be utilized immediately adjacent to anodically protected coolers. Gray iron pipe and fittings within 3–4 m of anodically protected acid coolers will fail catastrophically in 3 months to 1 year by spontaneous cracking similar to that observed in oleum service. Owing to its brittle nature, the ultimate failure of gray iron pipe may be catastrophic if thinning is not properly monitored.

In 1977, the U.S. water supply industry and the centrifugally cast iron pipe foundries made a change from gray cast iron to ductile cast iron pipe as the preferred material. In contrast to gray cast iron, ductile iron does not suffer from spontaneous catastrophic cracking in acid service near anodically protected equipment, or from catastrophic, brittle failure at the end of its useful life. Tests have shown that the expected life of ductile iron pipe in concentrated sulfuric acid service is about the same as gray cast iron pipe, with the possible exception of high velocity (>2.5 m/s) or other special services. Ductile iron pipe is available only in diameters of ≥ 75 mm. Small (<75 mm) diameter pipe is typically stainless steel or alloy 20, depending on concentration and temperature. Ductile iron used in acid service should have thicker walls for added corrosion allowance. Mondi is sold as a special piping specification and material specifically for acid service. Mondi ductile iron has increased Si and Cu for reported lower corrosion rates in acid service.

A few plants have been built using SX, Saramet, Zecor, or anodically protected 304 or 316 stainless steel piping. These options offer potentially higher reliability and lower iron content in product acid than ductile iron. The economics of these options versus ductile iron or other alloys are highly dependent on piping diameter and expected piping life. Impurities and acid velocities also are important in choosing the optimum piping material.

In the gas cleaning sections of spent acid or metallurgical sulfuric acid plants, the weak acid scrubbing circuit is typically handled by plastic or glass fiber reinforced plastic (FRP) pipe. The contaminants in weak acid usually vary too greatly to allow use of an economical alloy that will give adequate service.

Carbon steel is not normally a suitable piping material for concentrated sulfuric acid because of high corrosion rates in flowing acid. However, where temperatures and flow rates are low, heavy wall steel pipe is sometimes used for transferring product acid.

5.10. Sulfuric Acid and Oleum Storage Tanks. Carbon steel is used in concentrated sulfuric acid storage tanks because in quiescent and low temperature conditions its corrosion rate is acceptable. Carbon steel is not suitable for handling sulfuric acid in concentrations between 80 and 90% or $<68\%$ even under quiescent conditions, unless passivating agents are present. Failures of sulfuric acid storage tanks have occurred owing to the corrosive nature of the acid and the peculiarities of the corrosion phenomenon (120). Rigorous design, fabrication, and inspection is required for safe operation. Excellent guidelines exist (121). Where product contamination or low corrosion rates are important, either linings or the use of anodic protection are both well proven.

6. Materials of Construction

Resistance of alloys to concentrated sulfuric acid corrosion increases with increasing chromium, molybdenum, and silicon content. The corrosiveness of sulfuric acid solutions is highly dependent on concentration, temperature, acid velocity, and acid impurities. An excellent summary is available (122). Good general discussions of materials of construction used in modern sulfuric acid plants may be found in Refs. 123 and 124. More detailed discussions are also available (125–130). For nickel containing alloys in particular, Reference 131 is appropriate. An excellent compilation of the relatively scarce literature data on corrosion of alloys in liquid sulfur trioxide and oleum may be found in Ref. 131.

One of the more resistant, versatile, and economical alloys available in wrought form is alloy 20, which is designated as CN-7M or Durimet 20 in cast form. Alloy 20 and similar alloys, eg, alloy 20-Cb3, can handle sulfuric acid at ambient and slightly elevated temperatures throughout the concentration range, including oleum. Alloy 20 type alloys have suffered inconsistent and variable corrosion performance at moderate temperatures. This is probably due the allowable variations in metal chemistry and sensitivity to oxidizing or reducing agents impurities. Alloy 20 offers no advantage over Type 304 and 316 stainless alloys, where high concentrations of acid ($>98\%$) or oleum service is assured. High nickel/chrome–moly alloys, eg, alloy C-276, alloy C-22, and alloy 59, will also handle sulfuric acid at all concentrations. Resistance of these alloys is extended to higher temperatures than the alloy 20 type alloys for certain concentrations, especially $<93\%$ (132). At the high temperatures and concentrations found in contact plant absorbing towers the Lewmet 55 (cast) and Lewmet 66 (wrought) alloys (Chas. S. Lewis Co., St. Louis, Missouri) are used for velocity-sensitive components, such as orifice plates pump parts, nozzles, and screens (131,133).

Since the mid-1980s the high (5–6% Si) silicon stainless steels have made inroads as materials of construction for pipe and equipment handling contact plant acid in the 93–99% concentration ranges at operating temperatures. These include SX, Saramet, and ZeCor. These materials are, however, generally unacceptable in acid service below ~ 90% or in areas where localized oleum may be present. In the mid-1980s, MECS discovered an operating window at very high (~ 170–200°C) temperatures and 99% concentration where high chromium stainless steels, eg, type 310, can be used (134,135). Haynes has more recently developed a wrought, easily formable high (5–6%) silicon nickel base alloy designated alloy D-205, which is being used for plate and frame heat exchanger plates to cool 93 and 99% acid in contact plants.

Reference 127 is an excellent compilation of isocorrosion diagrams for metals in sulfuric acid service. Special precautions should be observed when utilizing isocorrosion charts as guidelines for alloy selection. Metal skin temperature, not bulk acid temperature, should be used as the criterion of selection because metal skin temperatures may be significantly higher or lower than bulk acid temperatures. This is particularly important when designing heat-transfer equipment: Heating coils have failed catastrophically because alloy selection was based on acid bulk temperatures instead of the higher metal skin temperature of the heating coil. In the case of acid cooling, an unnecessarily more expensive higher alloy may be chosen on the basis of bulk acid temperature.

Oxidizing contaminants, eg, nitric acid and ferric ions, may significantly alter the performance of alloys in sulfuric acid. For example, Hastelloy B-2 performs extremely well in concentrated sulfuric acid, but corrodes rapidly in the presence of ferric ions, nitric acid, or free SO_3 in sulfuric acid. For this reason, Hastelloy B-2 is not recommended for oleum service.

Tantalum has excellent corrosion resistance to concentrated sulfuric acid at high temperatures, but very poor corrosion resistance to oleum. Tantalum's high price prevents it from becoming a common material of construction in concentrated sulfuric acid service. Zirconium has excellent corrosion resistance to sulfuric acid solutions up to the boiling point in the concentration range of 0–65 wt% H_2SO_4. Duriron, a cast high silicon iron, has excellent corrosion resistance to sulfuric acid at all concentrations up to the boiling point. It is, however, very brittle and use is limited because of its propensity to fracture when subjected to thermal or mechanical shock.

In the past, lead was widely used as a material of construction for sulfuric acid concentrations less than ~ 80 wt% and occasionally for concentrations up to 93 wt%, at temperatures <45°C. Because of lead's low physical strength and loss of strength at high temperatures, extensive external supports are normally required. Consequently, modern practice uses various acid-resisting polymeric materials instead of lead whenever practical. Many plastics do not resist acid above 50–60 wt% H_2SO_4. The resistance and properties of polymers can vary widely depending on exact composition, degree of polymerization, etc. Hence, specific data or information should be obtained from the manufacturer or a materials consultant. Tetrafluoroethylene (TFE), fluorinated ethylene propylene (FEP), and perfluoroalkoxy polymer (PFA) materials, eg, Teflon, are the only common plastics that resist all acid concentrations (with temperature limitations). Poly(vinylidene fluoride) (PVDF), poly(ethylene-chlorotrifluorethylene) (ECTFE), and various proprietary baked phenolic resins are reasonably effective up to 94–95 wt% H_2SO_4 at temperatures near ambient.

In the gas cleaning sections of metallurgical and spent acid regeneration plants, extensive use is made of polyproplyene for tower packings and lined pipe, and of FRP for vessels, gas duct and piping. Butyl rubber, Hypalon and ethylene–propylene diene monomer (EPDM) have useful resistance in these systems where elastomers are needed, eg, gaskets and tank linings. Specific impurities or operating conditions may have major impact on resistance.

7. Special Plant Designs

7.1. Wet Gas Process. Use of sulfur compounds in flue gases and sulfurous off-gases for sulfuric acid production is problematic for conventional acid plants. The concentration of SO_2 (or other sulfur compounds) is frequently too weak to sustain “auto-thermal” conditions in the converter. Even if flue gases come to the acid plant hot, they often have a high moisture content and may be very dirty. Cleaning and drying operations produce a cold gas exacerbating the auto-thermal issue.

In the early 1980s, Haldor Topsøe A/S (Lyngby, Denmark) developed the Wet gas Sulfuric Acid (WSA) process, capable of processing weak, wet gas streams directly (136). The uniqueness of the WSA process is the direct production of sulfuric acid by vapor-phase reaction of SO_3 and water, and the use of a glass-tube falling film condenser to condense the product acid from the process gas. This eliminates traditional absorption towers, but limits product acid concentration to the sulfuric acid azeotrope.

Using available process heat (including hydrolysis of SO_3, heat of condensation and sensible heat in the process exit gas) to heat the incoming gas, the WSA process can treat very low gas compositions without supplemental heat (see Table 8).

By using supplemental heat, the WSA process can treat SO_2 and H_2S gases with concentrations down to 500 ppm volume (136).

References 137–139 describe some applications of the WSA process. To date, $>$ 40 WSA plants have been build worldwide treating process gases from a wide range of sources including the petroleum, metallurgical, and power industries (140).

7.2. Energy Efficient Plants. During the 1970s and 1980s a dramatic increase in energy cost, plus governmental regulation regarding cogeneration of electric power, led to significant modifications and variations in plant design. Many of these changes became standard by the 1990s. More recently, the need for additional electric generating capacity in many regions of the country has become a force in the development of energy recovery (see ENERGY MANAGEMENT; PROCESS ENERGY CONSERVATION).

Design changes have included increased gas strength (up to 12% for sulfur plants and 18% SO_2 for metallurgical plants); increased (up to 6.2 MPa, 900 psi, and 480°C) steam pressure and superheat; low temperature economizers; suction side dry towers, ie, dry towers placed on the suction side of the main compressor; reduced plant pressure drop via new catalyst shapes, low pressure equipment design, and improved tower packing; and installation of turbogenerators to convert steam to electricity. These changes allowed sulfur-burning plants to recover $\sim 70\%$ of the available energy.

A significant development occurred in the mid-1980s with the introduction of the heat recovery system (HRS) developed by MECS (141,142). In the HRS process, absorbing towers operate at temperatures as high as 220°C, recovering the sensible heat of the gas stream and the heat of reaction as steam with pressures up to 1140 kPa (150 psig). This achieves thermal efficiencies of 90–95% compared with $\sim 55\%$ for plants in the early 1970s. A number of HRS plants have been built or retrofitted, including at least two in excess of 4500 metric tons/day. The HRS process uses conventional stainless alloys and was made possible by the discovery that $> 99\%$ acid, a number of alloys have very low corrosion rates at temperatures as high as 200°C. The HRS process requires extremely careful control of acid concentration. Catastrophic corrosion rates will result if tower concentrations are significantly outside of the prescribed range. This requires rapid and proper response to boiler or other leaks that can introduce water to the process.

Good general discussions on the sources of heat and the energy balance within a sulfuric acid plant are available (143,144).

7.3. Cement Plants. Calcium sulfate in the form of anhydrite, gypsum, $CaSO_4{\cdot}2H_2O$; or by-product gypsum from phosphate fertilizers is occasionally used to produce sulfuric acid and cement (qv). Approximately 1 kg of Portland cement is produced for each kilogram of sulfuric acid. Because the capital requirement for such installations is approximately six to eight times the cost of an elemental sulfur burning plant, they are uneconomical except under special circumstances.

7.4. Oxygen-Enriched Processes. Typically, the cost of obtaining oxygen (qv) at high concentrations makes its use uneconomical at sulfuric acid plants unless special circumstances exist. Although proposed processes for oxygen enrichment have been published, perhaps only one plant of this type operated commercially for a sustained period. That plant, remodeled by Consolidated Mining and Smelting Co. (Cominco) to use 25 vol% SO_2, 30 vol% O_2, balance, nitrogen (145,146) is no longer in existence.

Oxygen or oxygen-enriched air is sometimes used in spent acid decomposition furnaces to increase furnace capacity. This reduces the amount of inerts in the gas stream in the furnace and gas purification equipment. This permits higher SO_2 throughput and helps both the heat and water balance in the conversion and absorption sections of the plant (147).

Increased use of oxygen in smelters is becoming very common and leads to much more concentrated and reactive gases being fed to metallurgical acid plants with reduced sizes, operating conditions and operating costs.

7.5. Sulfuric Acid Concentrators. Concentrators for increasing the strength of dilute sulfuric acid by removing water have been used since the early days of the industry. A two-volume text on this subject was published in 1924 (148); more recent discussions of the subject are also available (34,149–154).

The need for acid concentrators exists because many uses of sulfuric acid do not lead to its consumption. Instead, the acid is diluted and partially degraded or contaminated. In the past, large amounts of acid were disposed of either by using it in the phosphate fertilizer industry to dissolve phosphate rock or by neutralization and discharge to waterways.

Concern over contaminants entering the food chain through fertilizer removed the first option. Increased cost and regulation has all but removed the second. This has made concentration, or recycling, more attractive and in many cases even a necessity.

Modern concentrators frequently not only concentrate the acid, but may purify it as well, removing both organic and inorganic materials. Examples of some options available are discussed in Ref. 153. Vacuum evaporation is widely used. Its main advantage is the ability to produce relatively high product acid concentrations at low operating temperatures, thus reducing corrosion. Flash evaporation is sometimes employed as an initial purification step (153,155). In addition, small amounts of organic contaminants are frequently partially oxidized and sometimes can be largely removed by treating with small amounts of hydrogen peroxide or nitric acid to accelerate oxidation (156) (see EVAPORATION).

8. Economic Aspects

Historically, consumption of sulfuric acid was a good measure of a country's degree of industrialization and also a good barometer of general business conditions. This statement is far less valid in 2005, because of heavy sulfuric acid usage by the phosphate fertilizer industry. Of total U.S. sulfuric acid consumption in 2001 of 37.5×10^6 metric tons, $> 74\%$ went into phosphate fertilizers (157) as compared to 45% in 1970 and 64% in 1980. This trend is expected to continue. In the United States, use in the production of alkylate for gasoline has grown, while all other major uses are growing only slightly or declining. Worldwide, the demand for sulfuric acid for fertilizer and for leaching ores, notably copper and nickel, is growing. Demand for production of fertilizer in the United States is expected to decline as capacity is added in China and elsewhere.

Other uses of sulfuric acid are as a pickling agent for iron and steel, as a component of lead storage batteries, in water treatment, and in the production of textile fibers, explosives, pulp and paper, detergents, inorganic pigments, and other chemicals. Sulfur trioxide, either as liquid or from oleum, finds significant use as a sulfonating or sulfating agent for surfactants, plastics, and other products.

In the United States, the elimination of MTBE (methyl tertiary-butyl ether) and the increased use of ethanol for gasoline production are increasing the demand for petroleum alkylate. Alkylate producers have a choice of either a hydrofluoric acid or sulfuric acid process. Both processes are widely used today. However, concerns over the safety or potential regulation of hydrofluoric acid are likely to result in most of the growth being for the sulfuric acid process.

Outside the United States, MTBE is not likely to be eliminated, but the overall growth in gasoline demand and the elimination of the last uses of tetraethyl lead are fostering growth in alkylate production.

Additional areas for growth in the United States are expected to be in copper leaching, caprolactam, pulp and paper, methyl methacrylate, and batteries (157).

As of 1997–2001, $>$ 70% of U.S. production was not sold as such, but used directly by producers to make other materials. At almost all large fertilizer plants, sulfuric acid is made on site, and by-product steam from these sulfur burning plants is generally used to support the phosphate process and often to produce electicity. In the production of phosphate fertilizers, the primary role of sulfuric acid is to convert phosphate rock to phosphoric acid and solid calcium sulfates, which are removed by filtration. Most of the U.S. fertilizer plants are located in Florida, Idaho, Wyoming, Louisiana, and North Carolina.

Production and consumption trends in the United States are shown in Tables 9 and 10.

Since $\sim$ 1995 (through 2005) several factors have had a significant impact on the U.S. sulfuric acid industry. First is the continuing growth of oil refining, the increasing need to remove sulfur from products produced from oil, and the trend toward increasingly sour feedstocks (see SULFUR REMOVAL AND RECOVERY). The sulfur supply will continue to grow in the next decade with the further development of high sulfur bitumen production from Alberta. In addition, the amount of sulfur gas emissions from refineries and other sources, eg, smelters, has been reduced through more stringent regulations. These together have produced more nondiscretionary sulfur in North America than can be used, resulting in the elimination of all Frasch operations and a growing need to export sulfur. Second is the rapid growth outside the United States, particularly in China, which has created a large demand for sulfur offshore. Third is the growth of the fertilizer industry in China and elsewhere, trending toward the eventual reduction in U.S. phosphate fertilizer exports. Finally, the oil refining industry underwent a divesting phase followed by acquisition so that a few major refining entities are responsible for most of the sulfur produced. Overall these have resulted in a more than ample supply of sulfur, the need and means to export sulfur, excess sulfuric acid capacity and a decreased demand for sulfuric acid.

Sulfuric acid prices are usually quoted per ton of equivalent 100% H_2SO_4, even though actual assays may be less or more than 100%. In mid-1995, prices ranged \$61–83/t (\$55–75/short ton) depending on location within the United States. By 2001, facing strong imports of nondiscretionary smelter acid, prices had fallen to \$11–55/t (\$10–50/short ton). As of 2005, they had recovered to \$50–77/t (\$45–70/short ton). Projected total commercial value of U.S. production was \$$2.1 \times 10^9$ for 2005. Prices for oleum are typically higher than for nonfuming acid and increase substantially for concentrations $>$ 30% free SO_3. For all acid grades, small acid shipments or spot orders typically command a premium vs quoted contract prices in bulk.

The cost and price of sulfuric acid depend in large part on raw material cost and on freight costs. In many areas, the delivered cost of sulfur is the most important factor affecting sulfuric acid pricing. By-product raw material, ie, SO_2, costs at smelters are essentially zero, but the remote locations of many smelters make freight costs significant. Nevertheless, the nondiscretionary nature of smelter acid means that it must be sold if the smelter is to operate. The presence of smelter based acid in a given market can seriously affect the price of acid.

Worldwide sulfuric acid production figures are shown in Table 11. For Western Europe, supply has declined. It continues to grow in the Middle East and in Africa, particularly North Africa, which has extensive phosphate rock deposits. Strong growth is expected in Chile and Peru with the expansion of smelters as well as implementation of stricter environmental controls on existing smelters. China has undergone explosive growth from $\sim 30 \times 10^6$ metric tons in 2002 to $> 45 \times 10^6$ metric tons in 2005, and is projected to continue growing to $> 50 \times 10^6$ metric tons before 2010. Much of this is for increased fertilizer production that will result in a decrease in U.S. exports as discussed previously.

Other potential areas for growth include the Middle East and North Africa, Eastern Europe and former Soviet Union. Worldwide, as third world economies improve, production of nondiscretionary acid is expected to increase, owing to increased emphasis on protecting the environment.

9. Analysis and Specifications

Specifications for sulfuric acid vary rather widely between different producers and consumers and for different grades of acid. Exceptions include Federal specifications for “Sulfuric Acid, Technical” and “Sulfuric Acid, Electrolyte (for storage batteries)” and the *Food Chemicals Codex* specification for sulfuric acid, frequently called food-grade acid (although industry-wide, “food-grade” is nonspecific). Very little has been done to establish industry-wide analytical standards in the United States, except for development of the ASTM analytical methods, designated as E223-88 and summarized in Table 12.

Typical specifications for several common types or grades of acid are shown in Table 13. Similar limits are generally used for other sulfuric acid concentrations, with the exception of turbidity values for high strength acids (and oleum) and SO_2 and niter values in oleums. Because iron sulfate is relatively insoluble in concentrated acids, the turbidities of 98–99% H_2SO_4 and oleum may be higher than shown, even at acceptable total iron concentrations.

Sulfur dioxide concentrations in oleum are rarely specified or measured, but typical values are considerably higher than in acids of ≤ 99 wt% concentrations. This occurs because oleum is produced at relatively low temperatures in the presence of appreciable SO_2 in the gas phase, thus leading to high solubility. It is not possible to strip SO_2 from oleums by air blowing, a technique that is frequently applied to product acids of $\leq 99\%$ concentration.

Measurement and specification of nitrates and other nitrogen oxide compounds in sulfuric acid is a complex subject. The difficulty occurs because nitrogen oxides are usually present as nitrosylsulfuric acid, which decomposes to both nitrous and nitric compounds. Hence analytical procedures specific for nitrates only do not give a complete analysis.

A procedure to measure both types of nitrogen oxide compounds at the same time involves development of a pink color by mixing $FeSO_4$ with sulfuric acid, followed by measurement or comparison of color intensity. This general type of procedure and possible alternatives are discussed in Refs. 162–164.

Although color and turbidity of acid products are important properties, there is little standardization in such measurements. A frequently used procedure is to determine color and turbidity by comparison with standards originally developed by the APHA for examination of water (165).

A number of different grades of acid are produced for specialized uses, eg, reagent grade, food grade, and electronic grade. In addition, some producers offer special premium priced grades that contain little or no turbidity and color, or in some cases a maximum iron concentration of 10 ppm. Certain objectionable elements such as arsenic, lead, mercury, and selenium are not commonly specified for technical grade acid, but some producers attempt to hold each of these at <1 or $<2-5$ ppm in the case of lead, to minimize possible problems. Selenium is not usually present except at a few metallurgical-type plants or at plants using volcanic sulfur as raw material.

Metallurgical (smelter) plants and spent acid decomposition plants usually produce acid of good (low) color because their SO_2 feed gases are extensively purified prior to use. In some cases, however, and particularly at lead smelters, sufficient amounts of organic flotation agents are volatilized from sulfide ores to form brown or black acid. Such acid can be used in many applications, particularly for fertilizer production, without significant problems arising.

Descriptions of sulfuric acid analytical procedures not specified by ASTM are available (34,166). Federal specifications also describe the required method of analysis. Concentrations of 78 and 93 wt% H_2SO_4 are commonly measured indirectly by determining specific gravity. Higher acid concentrations are normally determined by titration with a base, or by sonic velocity or other physical property, for plant control. Sonic velocity has been found to be quite accurate for strength analysis of both fuming and nonfuming acid.

10. Health and Safety

10.1. Shipping and Handling. Sulfuric acid is injurious to the skin, mucosa, and eyes. Moreover, dangerous amounts of hydrogen may develop in reactions between weakened acid and metals. Sulfuric acid at high concentrations reacts vigorously with water, organic compounds, and reducing agents. Oleums and liquid SO_3 frequently react with explosive violence, particularly with water.

Those engaged in handling sulfuric acid should obtain detailed information on safe handling practices. Material Safety Data Sheets (MSDS) are available from the U.S. and European manufactures.

The *Code of Federal Regulations* (CFR) includes detailed rules for packaging and shipping. Pertinent sections are 49 CFR 171.15-171.17, hazardous material incidents and discharges; 49 CFR 172.101-172.102, hazardous material tables; and the following references for specific materials:

Sulfuric acid	49 CFR 173.202 and 173.242	Corrosive label
Oleum ($<30\%$)	49 CFR 173.201 and 173.243	Corrosive label
Oleum ($\geq 30\%$)	49 CFR 173.227 and 173.244 Poison Inhalation Hazard - Zone B	Corrosive and Poison labels
Sulfur trioxide	49 CFR 173.227 and 173.244 Poison Inhalation Hazard - Zone B	Corrosive and Poison labels

Requirements for transport in ships or barges are outlined in Section 46 of the CFR.

Steel tank cars, often lined to minimize iron contamination, are usually employed for high concentrations of sulfuric acid. Bottom outlets or valves are not allowed, nor are internal steam coils. Tank contents must be unloaded via standpipe. Using air pressure to unload is not recommended for safety reasons, but if air pressure is used, gauge pressures should be held at <0.21 MPa (30 psi).

The following general handling precautions should be observed:

General handling precautions should be observed. Sulfuric acid must not come in contact with eyes, skin, or clothing. When handling containers or operating equipment containing sulfuric acid, equipment appropriate for exposure conditions should be worn. This may include chemical splash goggles, face shield and chemical splash goggle combination (not face shield alone), rubber acid proof gloves, and a full acid proof suit, hood, and boots. Personnel must avoid breathing mist or vapors. The acid should be handled only in areas having sufficient ventilation to prevent irritation. Alternatively, an appropriate NIOSH/MSHA approved respirator should be worn.

Acid containers must be kept closed. Water must not enter containers. When diluting, always add the acid slowly with agitation to the surface of the aqueous solution to avoid violent spattering, boiling and eruption. Never add the solution to the concentrated acid.

Handling containers and pipelines also requires that special precautions be observed. An emptied container retains vapor and product residue. Thus, all labeled safeguards must be observed until the container is cleaned, reconditioned or destroyed. Drums, if not self-venting, should be periodically vented to prevent accumulations of hydrogen. To avoid hydrogen explosions when welding, any vessel that has contained sulfuric acid must be thoroughly purged and tested for explosive conditions before welding commences. In dismantling lines and equipment, it should always be assumed that a spray of acid may occur, and suitable precautions taken. Iron or other solid sulfates may plug lines or retain pockets of acid. Tightening flange bolts on pipes filled with acid is dangerous because of the possibility of mechanical failures.

In case of physical contact with sulfuric acid, immediately flush eyes or skin with plenty of water for at least 15 min while removing contaminated clothing and shoes. Call a physician. Wash clothing before reuse and destroy contaminated shoes.

In case of inhalation, remove the individual to fresh air. If necessary, give artificial respiration, preferably mouth to mouth. If breathing is labored, give oxygen. Call a physician.

In case of spill or leak, keep people away and upwind of the spill. If it is necessary to enter the spill area, wear self-contained breathing apparatus and full protective clothing, including boots. The area should be diked using sand or earth to contain the spill, the acid removed by vacuum truck, and the spill area flushed with water. Washings should be neutralize with lime or soda ash and pollution control authorities notified of any runoff into streams or sewers and of any air pollution incidents. Safety showers with deluge heads, protected against freezing, should be readily available at appropriate locations in any plant producing or using sulfuric acid.

10.2. Sulfuric Acid Toxicity. Sulfur trioxide does not exist in the atmosphere except in trace amounts because of its affinity for water. It rapidly combines with moisture in air to form sulfuric acid mist. Sulfuric acid aerosol or mist is a significantly more powerful pulmonary irritant than sulfur dioxide on a sulfur-equivalent basis (167–169).

Physiological responses to sulfuric acid mist inhalation are highly dependent on the particle size of the aerosol (167,169–171). For a constant sulfuric acid aerosol concentration, the irritant action of the aerosol increases with aerosol particle size. Other factors affecting the physiological response of inhaling sulfuric acid mist are humidity, temperature, and previous exposure. Studies of prolonged exposure to sulfuric acid fumes have been performed on workers in plants manufacturing lead acid batteries. Prolonged exposure to mineral acid fumes causes the teeth of the exposed subject to deteriorate (172–174). Overexposure to sulfuric acid aerosols results in pulmonary edema, chronic pulmonary fibrosis, residual bronchiectasis, and pulmonary emphysema. Additional toxicological information may be found in the literature (175,176).

The International Agency for Research on Cancer (IARC) has classified “occupational exposure to strong inorganic acid mists, containing sulfuric acid,” as a Category 1 carcinogen, ie, a substance that is carcinogenic to humans (177). The American Conference of Governmental Hygienists (ACGIH) has classified “sulfuric acid containing strong inorganic mists” as a Suspected Human Carcinogen. (category A2) (178). These classifications are for mists only and do not apply to sulfuric acid or sulfuric acid solutions. These classifications are highly controversial. The overall weight of evidence from all human studies has been evaluated (179). This study concluded, “Thus, the current epidemioligic data alone do not warrant classifying MSA (mists containing sulfuric acid) as a definite human carcinogen.” The overall weight of evidence from animal studies has been evaluated (180). This study concluded, “No evidence of carcinogenic potential was found in these studies, although investigations were compromised due to inadequate design and reporting.”

The OSHA Permissible Exposure Level (PEL) and the NIOSH Recommended Exposure Limit (REL) for human exposure to sulfuric acid mist are 1 mg/m^3 of air (181,182). The ACGIH Threshold Limit Value (TLV) for sulfuric acid mist is 0.2 mg/m^3. Sulfuric acid aerosols below the TLV are commonly not detected by odor, taste, or irritation. A TLV of 0.2 mg/m^3 is recommended by the ACGIH to prevent pulmonary irritation at particle sizes likely to occur in industrial situations (178). The following data summarizes human response to various levels of concentration of sulfuric acid aerosols:

Concentration, mg H_2SO_4/m^3 of air	Response
0.5–2.0	barely noticeable irritation
3.0–4.0	coughing, easily noticeable
6.0–8.0	decidedly unpleasant, marked alterations in respiration

The American Industrial Hygiene Association lists the following Emergency Response Planning Guidelines (ERPGs) for sulfuric acid, oleum and sulfur trioxide (183): ERPG-1, 2 mg/m^3; ERPG-2, 10 mg/m^3; ERPG-3, 30 mg/m^3. The ERPG-1 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 h without experiencing other than mild transient adverse health effects or perceiving a clearly defined objectionable odor. The ERPG-2 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 h without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action. The ERPG-3 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 h without experiencing or developing life-threatening health effects.

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Table 1. **Properties of Sulfur Trioxide**

Property	Value	References
critical temperature, °C	217.8	35
critical pressure, kPa[a]	8208	35
critical density, g/cm^3	0.630	35
triple point temperature (γ-phase), °C	16.8	32
triple point pressure (γ-phase), kPa[a]	21.13	29
normal boiling point temperature, °C	44.8	29
melting point (γ-phase), °C	16.8	29
transition temperature, °C	−183.0	32
liquid density (γ-phase at 20°C), g/cm^3	1.9224	34
solid density (γ-phase at −10°C), g/cm^3 liquid	2.29	36
coefficient of thermal expansion (at 18°C), per °C	0.002005	37
liquid heat capacity (at 30°C), kJ/(kg-°C)[b]	3.222	34,38
heat of formation of gas (at 25°C), (MJ-kg)/mol[b]	−395.76	39
free energy of formation of gas (at 25°C), (MJ-kg)/mol[b]	−371.07	39
entropy of gas (at 25°C), (MJ-kg)/(mol-°C)[b]	0.25666	39
heat of dilution, MJ/kg[b]	2.109	34
heat of fusion, kJ/kg[b]		
(α)	324.0	34
(β)	151.6	34
(γ)	94.07	34
heat of sublimation, MJ/kg[b]		
(α)	0.8518	32
(β)	0.7269	32
(γ)	0.7029	32
heat of vaporization (g liquid), MJ/kg	0.5843	32
diffusion in air (at 80°C), m/s	0.000013	40
liquid dielectric constant (at 18°C)	3.11	41
electric conductivity	negligible	42,43

[a] To convert kPa to psi, multiply by 0.145.

[b] To convert J to cal, divide by 4.184.

Table 2. **Vapor Pressure of SO_3, α-, β-, and γ-Phases**[a]

Temperature, °C	Vapor pressure, Pa[b] α	β	γ
0	773	4,266	5,999
25	9,732	45,860	57,730
50	86,660	126,700	126,700
75	400,000	400,000	400,000

[a] Ref. 34.

[b] To convert Pa to psi, divide by 6895.

Table 3. **Thermodynamic Properties of Sulfur Trioxide**[a]

Temperature, K	$\Delta H_f{}^\circ$, kJ/mol[b]	$\Delta F_f{}^\circ$, kJ/mol[b]
600	−460.2	−359.9
700	−459.6	−343.3
800	−458.9	−326.7
900	−457.9	−310.2
1000	−456.7	−293.9
1100	−455.5	−277.7
1200	−454.1	−261.5

[a] Ref. 51.

[b] To convert J to cal, divide by 4.148.

Table 4. **Thermodynamic Properties of $SO_2 + 0.5\ O_2 \rightarrow SO_3$**[a]

Temperature, K	ΔH_T, kJ/mol[b]	ΔF_T, kJ/mol[b]	K_p, $Pa^{-1/2}$[c]
600	−97.99	−41.59	13.13
700	−97.36	−32.30	0.7445
800	−96.57	−23.05	0.1006
900	−95.69	−13.97	0.02033
1000	−94.60	−4.94	0.005686
1100	−93.51	4.02	0.002025
1200	−92.30	12.84	0.000867

[a] Ref. 51.

[b] To convert J to cal, divide by 4.148.

[c] To convert $Pa^{-1/2}$ to $atm^{-1/2}$, multiply by 318.32.

Table 5. **Heat of Formation of Oleums by the Reaction:- $H_2O(liq) + xSO_3(liq) \rightarrow H_2SO_4 \cdot (1-x)SO_3(liq)$**[a]

	Liquid phase	
Free SO_3, %	SO_3, MJ/kg[b]	H_2O, MJ/kg[b]
0	1.107	4.919
10	1.009	5.086
20	0.9067	5.260
30	0.8022	5.434
40	0.6978	5.632
50	0.5905	5.841
60	0.4808	6.061
70	0.3684	6.317
80	0.2535	6.654
90	0.1333	7.106
100	0	

[a] Ref. 95, $x =$ mol total SO_3/mol H_2O.

[b] To convert J to cal, multiply by 4.184.

Table 6. **Heat of Formation of Oleums by the Reaction:- $H_2O(liq) + xSO_3(gas) \rightarrow H_2SO_4 \cdot (1-x)SO_3(liq)$**[a]

	Liquid phase	
Free SO_3, %	SO_3, MJ/kg[b]	H_2O, MJ/kg[b]
0	1.645	7.311
10	1.547	7.803
20	1.445	8.384
30	1.340	9.080
40	1.236	9.986
50	1.129	11.17
60	1.019	12.84
70	0.9067	15.56
80	0.7918	20.79
90	0.6716	35.83
100	0.5383	

[a] Ref. 95, $x =$ mol total SO_3/mol H_2O.

[b] To convert J to cal, multiply by 4.184.

Table 7. **Typical Converter Conditions for a 3 + 1 Double Absorption Plant with 11.5% SO_2 Inlet Gas**

Converter pass	1	2	3	4
inlet, °C	415–420	430–445	430–445	390–430
outlet, °C	625	530	470	450
ΔT, °C	185	90	30	20

Table 8. **Typical Gas Compositions Treated by WSA Without Supplemental Heat**[a]

	Range, vol%	Required inlet temp, °C
SO_2	1–1.5	220
SO_2	2–2.5	25
H_2S	≥ 1	25

[a] Ref. 136.

Table 9. **U.S. Sulfuric Acid (100% H_2SO_4) Production by Sulfur Source,**[a] **1000 metric tons**

Sulfur source	1997	1999	2001
elemental sulfur	35,423	32,670	30,073
copper smelter gas	4,195	3,457	1,835
zinc smelter gas	361	379	337
lead and molybdenum smelter gas	202	214	144
recycled acid	4,331	3,415	3,559
other	742	467	384
total	*45,255*	*40,602*	*36,332*

[a] Ref. 157.

Table 10. **U.S. Consumption of Sulfuric Acid (100% H_2SO_4),[a] 1000 metric tons**

Use	1997	1999	2001
phosphoric acid	32,216	32,333	27,372
other fertilizers	497	537	478
copper leaching	2,336	2,221	1,910
uranium and vanadium ore processing	15	24	6
other ore processing	334	229	140
petroleum alkylation	1,439	1,444	1,536
methyl methacrylate	976	998	1,047
caprolactam	933	918	811
aluminum sulfate	547	580	528
hydrofluoric acid	455	484	454
pulp and paper	1,023	422	420
titanium dioxide	333	350	345
cellulosic fibers and plastics	175	131	115
all other	5,814	1,144	2,374
total	*47,093*	*41,815*	*37,536*

[a] Ref. 157.

Table 11. **World Production of Sulfuric Acid (100% H_2SO_4), 10^6 metric tons**

Location	1993[a]	1997[b]	2001[b]
North America	41.3	49.5	40.6
Central and South America	6.2	13.4	15.1
Western Europe	17.0	18.7	16.1
Eastern Europe	19.6	4.0	3.7
Asia	33.5	24.0	67.3
Africa	16.4	17.6	18.1
Oceania	1.3	2.3	3.9
total world	*135.3*	*157.6*	*164.8*

[a] Ref. 158.

[b] Ref. 157.

Table 12. **ASTM Analytical Methods for Sulfuric Acid**[a]

Section No. (see references)	Properties	Principle
1–7	general, reagents	
8–16	total acidity	NaOH titration using phenophthalein
17–26	Baumé gravity	hydrometer measurement
27–33	nonvolatile matter	evaporation and weighing
34–43	iron	reduce, measure colorimetrically as *o*-phenanthroline complex
44–51	sulfur dioxide	remove by air sweep, absorb in alkali, add excess iodine, titrate
52–61	arsenic	evolve as arsine, absorb in pyridine and diethylthiocarbamate, measure color

[a] Ref. 159.

Table 13. **Typical Sulfuric Acid Specifications**[a]

	Acid type			
	Electrolyte[b] (Fed. Spec. O-S-801E)	Technical (Fed. Spec. O-S-809E)	Food Chemicals Codex[e]	Technical (industry typical)
Property	Class 1[c]	Class 1[d]		66°Bé (93%)
% H_2SO_4	93.2	93.0		93.2
sp gr, 15.5/15.5°C	1.8354	1.8347		1.835–1.837
nonvolatiles (max), %	0.03	0.025		0.02–0.03
As (max), ppm	1.0	2.5	3	
SO_2 (max), ppm	40		40[f]	40–80
iron (max), ppm	50		200	50–100
heavy metals (max) ppm			20	
nitrate (max), ppm	5.0		10	5–20
color (max)	per test			100–200 APHA[g]

[a] Ref. 160.

[b] Limits are also specified for platinum, organics, copper, zinc, antimony, selenium, nickel, manganese, ammonium, and chloride.

[c] Three other classes of lower strength acids are included.

[d] One other class of lower strength acid is included.

[e] Ref. 161.

[f] Reducing substances (as SO_2).

[g] APHA = American Public Health Association.

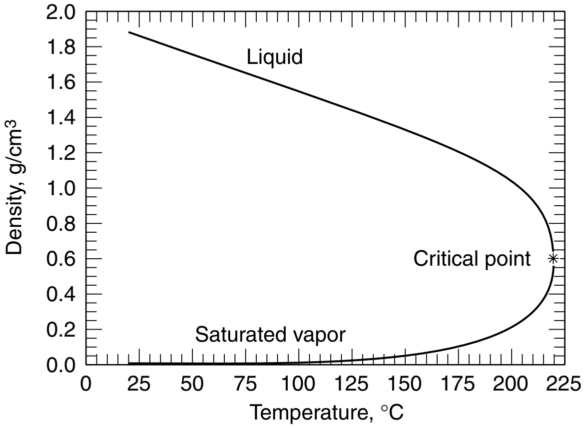

Fig. 1. Density of sulfur trioxide, where * represents the critical point (44–48).

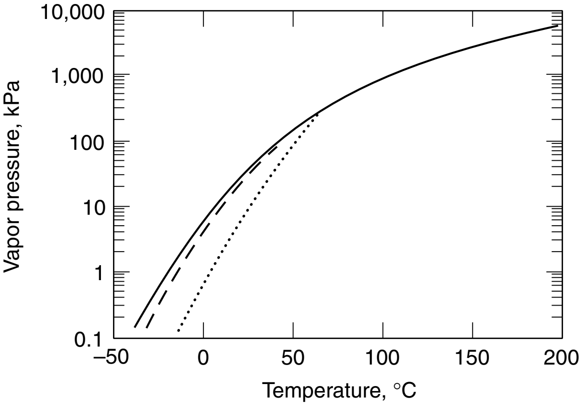

Fig. 2. Vapor pressure of sulfur trioxide: (—), γ-SO_3; (– – –). β-SO_3; (·········), α-SO_3 (49). (To convert kPa to psi, multiply by 0.145.)

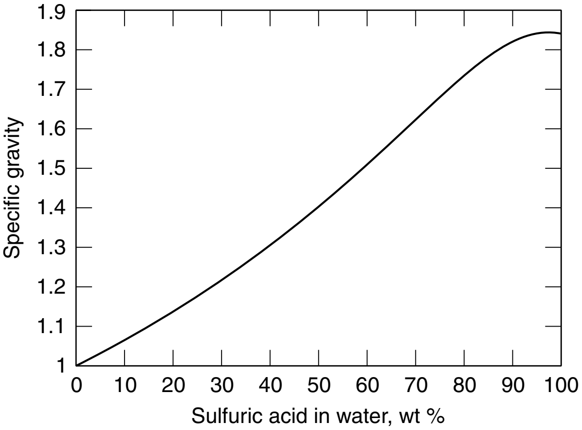

Fig. 3. Specific gravity of sulfuric acid, 15/4°C (53).

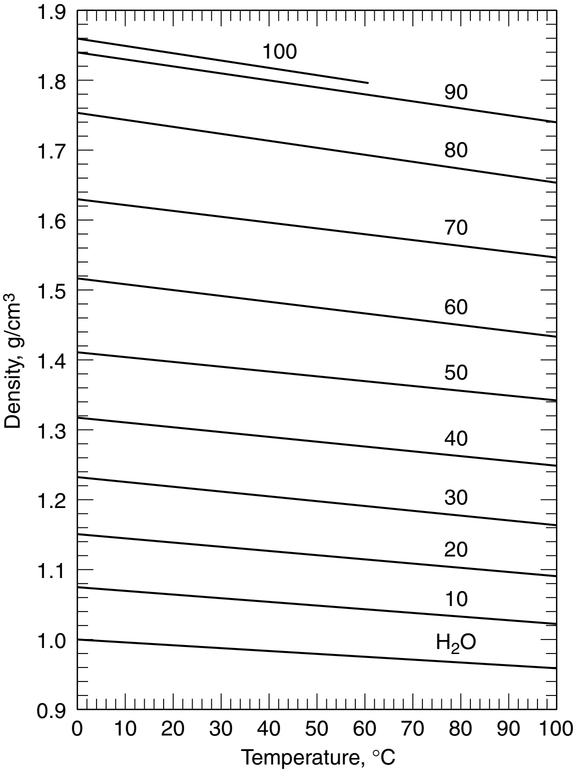

Fig. 4. Density of sulfuric acid, where the numbers represent wt% of H_2SO_4 in H_2O (53).

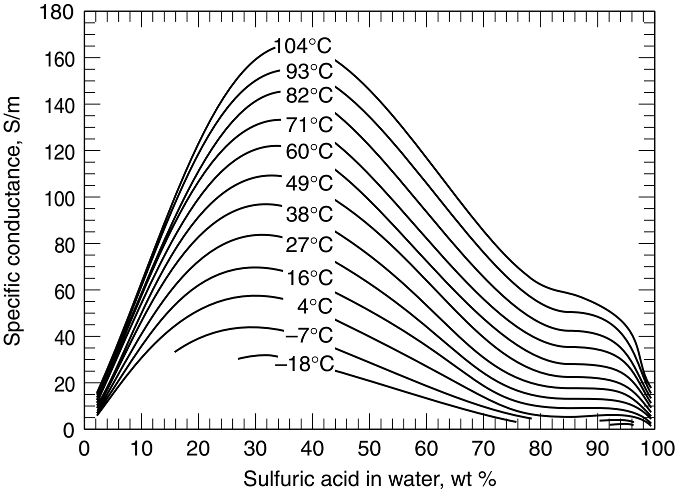

Fig. 5. Specific conductance of sulfuric acid (54).

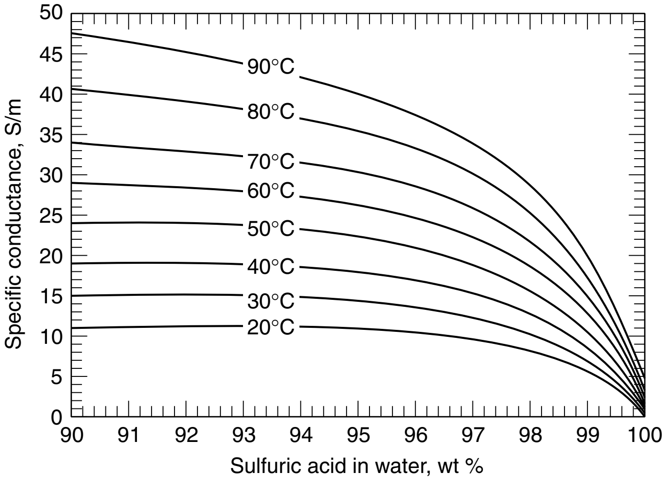

Fig. 6. Specific conductance of sulfuric acid (55).

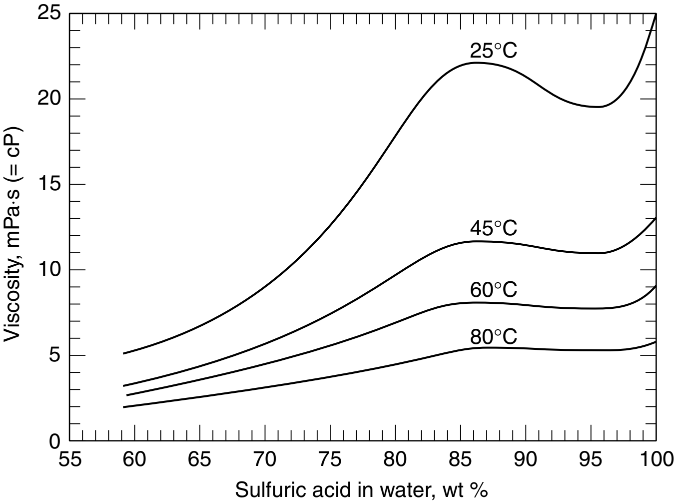

Fig. 7. Viscosity of sulfuric acid (58).

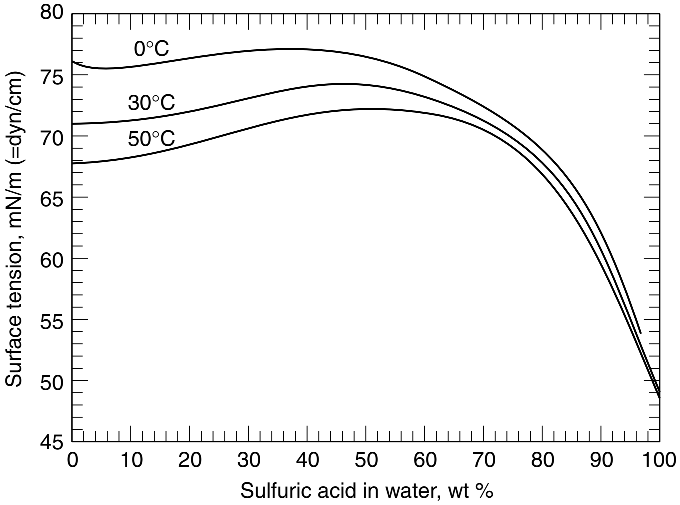

Fig. 8. Surface tension of sulfuric acid (64).

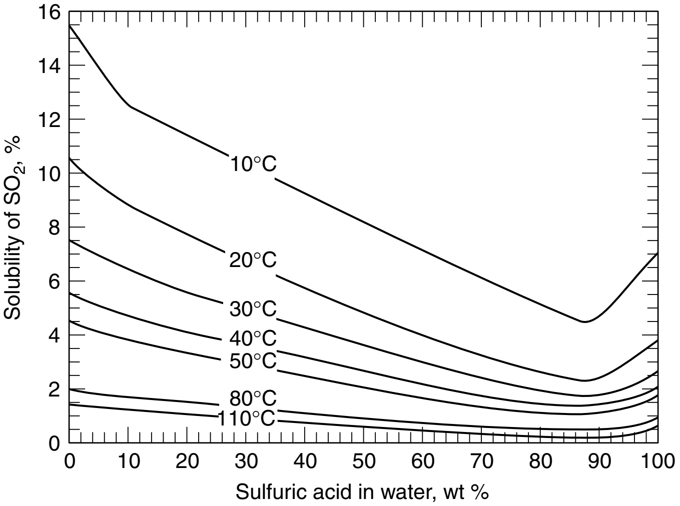

Fig. 9. Solubility of SO_2 in sulfuric acid at SO_2 pressure of 101.3 kPa (1 atm) (71).

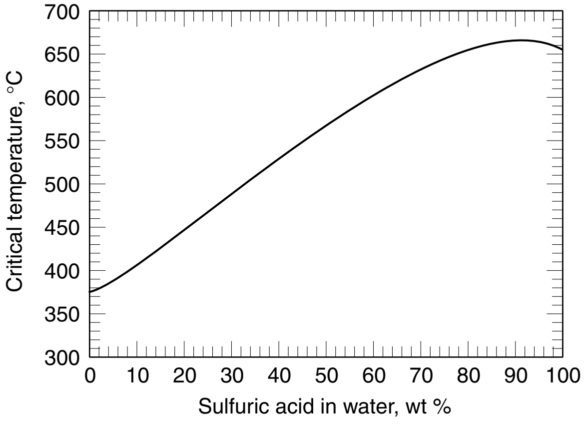

Fig. 10. Critical temperatures of sulfuric acid solutions (76).

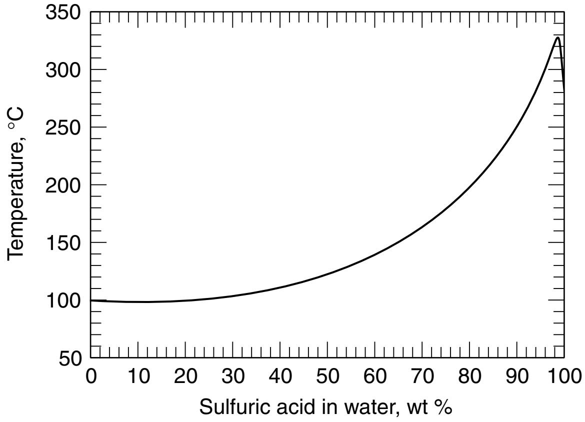

Fig. 11. Normal boiling point of sulfuric acid (77).

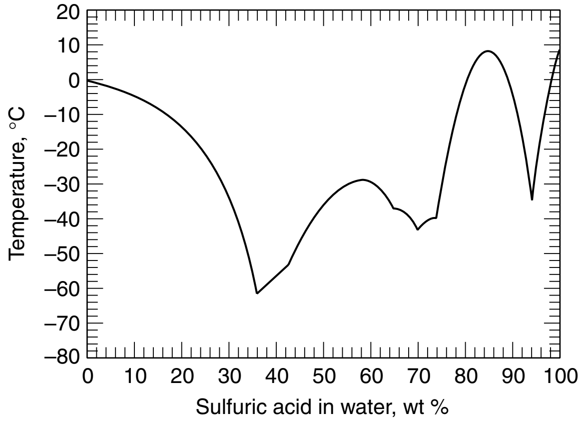

Fig. 12. Melting points of sulfuric acid (78).

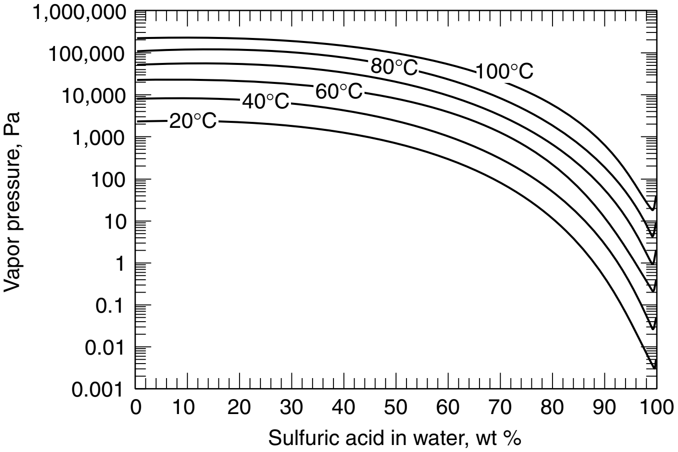

Fig. 13. Vapor pressure of sulfuric acid (84). To convert Pa to mmHg, multiply by 0.0075.

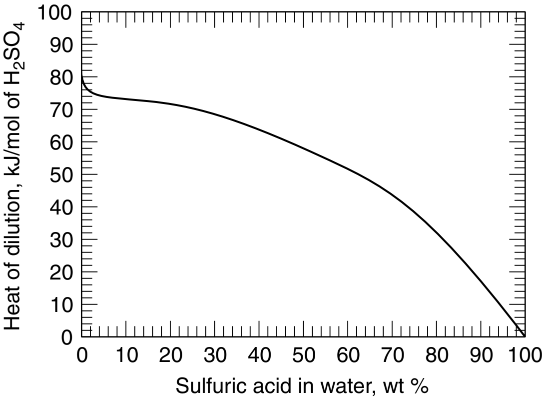

Fig. 14. Heat of mixing of sulfuric acid from H_2O and H_2SO_4 at 25°C (87). To convert J to cal, divide by 4.184.

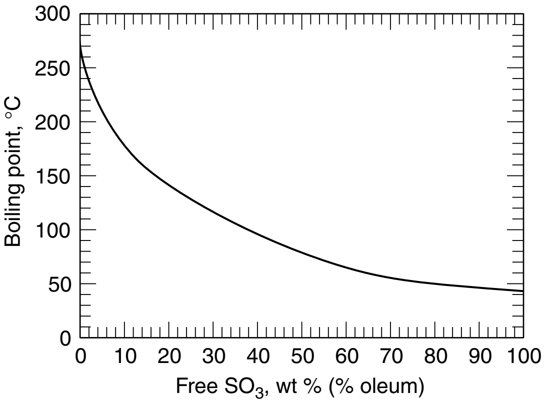

Fig. 15. Normal boiling points of oleum (90).

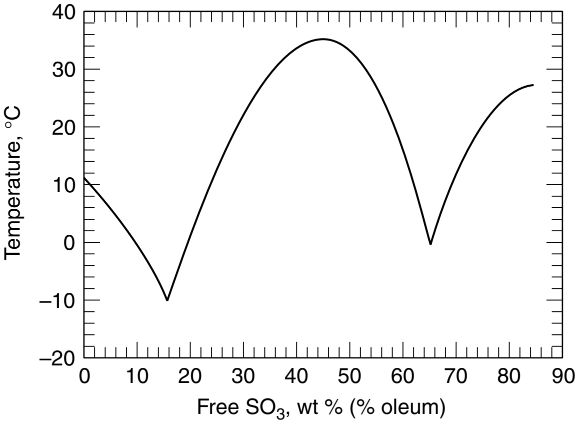

Fig. 16. Melting points of oleum. References 78 (<65%) and 91 (>65%).

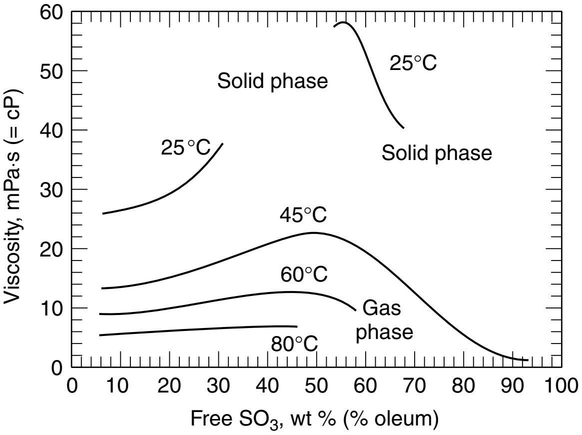

Fig. 17. Viscosity of oleum (58).

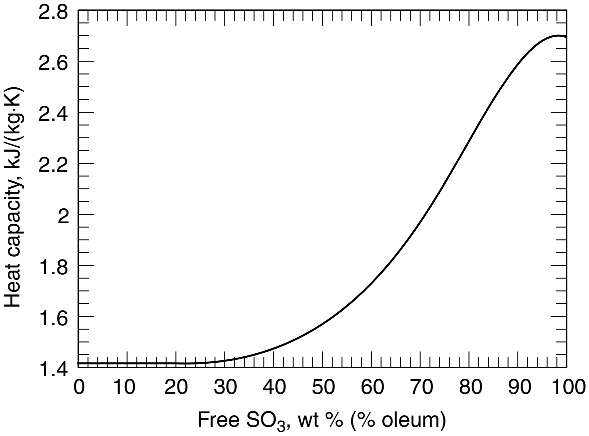

Fig. 18. Heat capacity of oleum at 20°C (79). To convert J to cal, divide by 4.184.

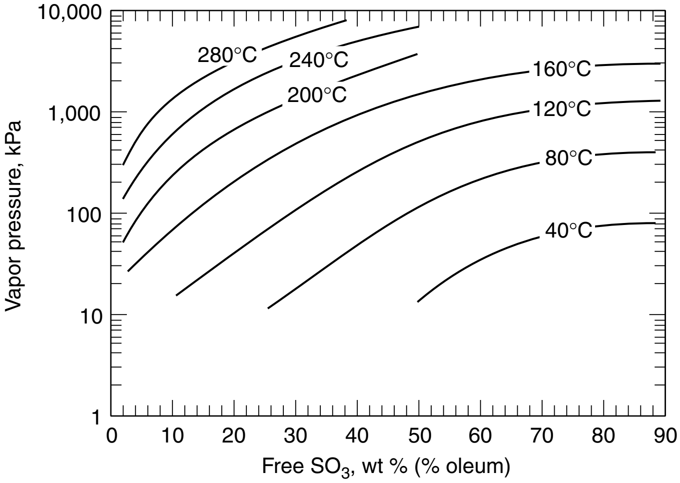

Fig. 19. Vapor pressure of oleum (97). To convert kPa to psi, multiply by 0.145.

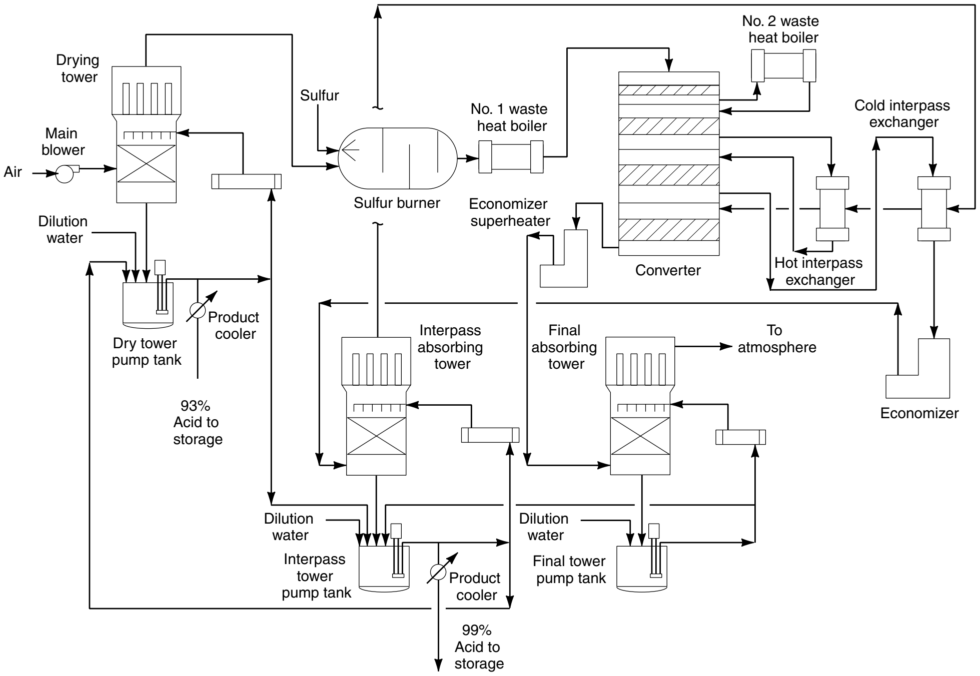

Fig. 20. Flow sheet for a 3 + 1 double absorption sulfur burning plant.

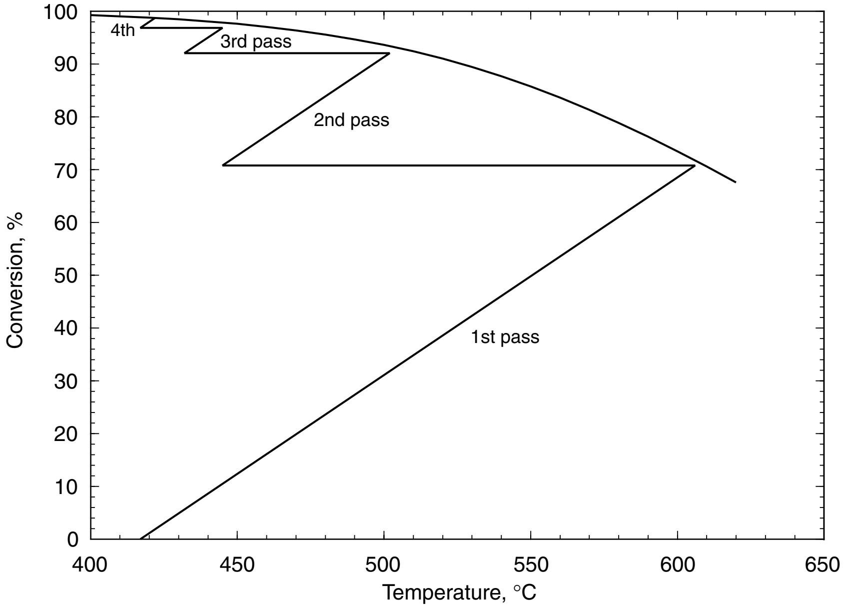

Fig. 21. Single absorption equilibrium-stage diagram, where the equilibrium curve is for 8% SO_2, 12.9% O_2; the diagonal lines represent the adiabatic temperature rise of the process gas within each converter pass; the horizontal lines represent gas cooling between passes, where no appreciable conversion occurs.

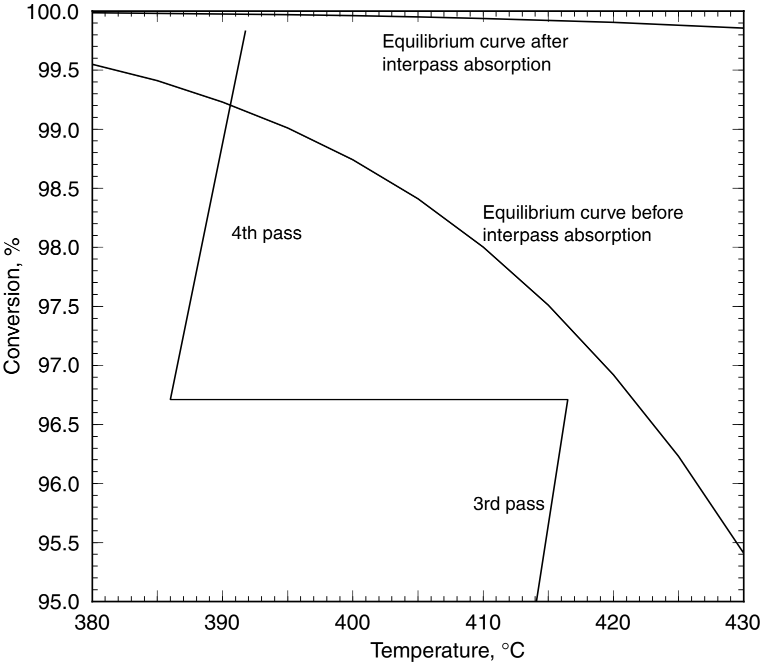

Fig. 22. Equilibrium stage diagram the final pass of a 3 + 1 dual absorption acid plant.