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# Sulfur and Sulfuric Acid

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## Keywords

Sulfur • Sulfuric acid • Production • Consumption • Transportation • Storage

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## Sulfur

Sulfur is one of the few elements that is found in its elemental form in nature. Typical sulfur deposits occur in sedimentary limestone/gypsum formations, in limestone/anhydrite formations associated with salt domes, or in volcanic rock [1]. A yellow solid at room temperature, sulfur becomes progressively lighter in color at lower temperatures and is almost white at the temperature of liquid air. It melts at 114–119 °C (depending on crystalline form) to a yellow liquid which turns orange as the temperature is increased. The low viscosity of the liquid begins to rise sharply above 160 °C, peaking at 93 Pas at 188 °C, and then falling as the temperature continues to rise to its boiling point of 445 °C. This and other anomalous properties of the liquid state are due to equilibria between the various

molecular species of sulfur, which includes small chains and rings.

Sulfur is also found as sulfide minerals in combination with iron or base metals (e.g., pyrites) and as sulfates in combination with alkali metals (copper) and alkaline earths (e.g., gypsum). Hydrogen sulfide, with its “rotten egg” odor, and carbon dioxide are the principal “sour” components of sour gas. Crude oil and coal include a variety of complex organic species containing sulfur. Such compounds are removed from the liquid fuels by treatment with hydrogen to convert the sulfur component to hydrogen sulfide, which is removed from the fuel stream. Removal of sulfur from fuels for technical and environmental reasons represents the largest current source of elemental sulfur.

World elemental sulfur production in 2014 was about 69 million metric tons (Mt), slightly more than that of 2009. Other sources (pyrites roasting primarily in China and cleaning smelter gas effluent globally) have added about 7 Mt to the sulfur balance (Table 1).

Currently, a majority of all sulfur is derived from hydrocarbon processing. Minor quantities are still mined. Poland has a capacity of 700,000

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**Table 1** Elemental sulfur production in all forms (Million metric tons)

World sulfur production by type	1999	2009	2014
Mined/Frasch	3.0	0.3	0.6
<i>Recovered sulfur, of which</i>			
From metallurgy	11.4	13.2	12.5
From oil & gas	34.3	40.4	40.5
From other	4.0	0.8	8.4
Total	52.7	54.7	62.0
Other forms			
Pyrite			
Other			
Total	5.8	13.6	7.1
Grand total	58.5	68.3	69.1

Source: U.S. Geological Survey 2003, 2013, 2014

metric tons (t) with a long history in Frasch mining. In 2014, Devco USA began the process of rebuilding Iraq's Mishraq state sulfur mine, which at full capacity would produce 500,000 tons per year of sulfur [2]. Most sulfur mines are associated with oil deposits found in conjunction with geologic formations known as salt domes. In situ cross-contamination with hydrocarbons (as at the Mishraq mines) leads to the production of "dark" sulfur with technically and commercially unacceptable levels of carbon contamination. Volcanic sulfur deposits yield bright sulfur, but it is often contaminated with toxic metal oxides. Small quantities of several specialty sulfurs are produced for a variety of other applications, including fungicides, bleaching, fumigation, pharmaceuticals, rubber manufacture, and cutting oils. Applications of elemental sulfur as a fertilizer are growing globally. The Sulphur Institute ([www.sulphurinstitute.org](http://www.sulphurinstitute.org)) serves as a source of information for the sulfur industry worldwide. Additionally, a publication by the USGS entitled "Materials Flow of Sulfur" is available at <http://minerals.USGS.gov/minerals/pubs/commodity/sulfur/index.html>.

## Transportation and Storage

Although all sulfur is produced and most is consumed in a molten state, the majority of international commerce outside of North America and Europe uses solid sulfur. Vancouver British

Columbia, Canada, was once the world's leading sulfur exporting port. Volumes peaked at 6.3 Mt in 2004, declining to 2.4 Mt in 2014 [3]. West Asia (Abu Dhabi, Saudi Arabia, and Qatar) are expected to see increased sulfur production on the order of 60% by 2019 and Canada's "commercially available" sulfur output is likely to continue to decline [4].

Prior to bulk transport, solid sulfur is normally "formed" into a variety of shapes associated with individual solidification processes. These will be discussed in the following section. "Formed" solid sulfur is easily transported by truck, railcar, barge, or ocean vessel. It is classified as a non-hazardous "granular formed sulfur." Caution must be exercised in order to avoid fugitive dust and spillage. Sulfur dust is highly visible, will become corrosive, and under certain circumstances, can be explosive.

In the case of marine transport, which may last several weeks, the risk of corrosion during transit must be addressed. Vessel holds must be coated prior to loading, to prevent direct sulfur-steel contact. A new coat of paint covering all steel is good. However, nicks and scratches quickly expose steel. Various products and means of coating holds are employed by knowledgeable companies prior to loading. This preparation avoids a range of potentially severe consequences and cannot be bypassed without significant risk to cargo and vessel. Spraying water with surfactants, or aqueous foam, on sulfur as it is being loaded or unloaded is another key safety measure which mitigates dust dispersion. Water used in dust suppression as sulfur is loaded will move to the bottom of holds during transit. Daily pumping of this residue to sea is necessary to avoid the accumulation of up to several feet of standing water in the bottom of the hold. Prior to loading and following discharge, formed sulfur is often stored in the open air.

In contrast, domestically produced sulfur destined for internal use in the United States, Canada, and Europe is almost exclusively transported in liquid form. This has led to the establishment of an extensive sulfur infrastructure consisting of molten sulfur terminals, tanker

ships and barges, rail tank-cars, and tank-trucks. In the case of marine transport, vessels range from 9500 to 23,000 t and barges from 1000 to 2500 t. Overseas, molten shipments can be received in Morocco, Tunisia, and one port in India. Japan prohibits the marine transport of solid sulfur, even in the case of export activities. This has led to a fleet of coastal vessels, some as small as 1000 t, for exporting molten sulfur from Japan to users in China, Taiwan, and formerly, Republic of Korea.

Molten sulfur in ships is maintained in a liquid state using heating coils. When transported by rail tank car, at least a portion of the sulfur cools and solidifies during transit. It is reliquefied prior to discharge. The remelting process can take up to 3 days (for example, in the United States with sulfur coming from Canada during the winter). Remelt is accomplished by passing low pressure steam through coils located between the car's inner tank and outer skin. Care must be taken to use a low heating temperature to avoid turning sulfur into a viscous material. Trucks normally operate within distances which preclude cooling and solidification. Nevertheless, limited coiling allows for emergency steaming. In Tampa, FL, many sulfur truck trailers are designed for round trip carriage. An inner tank carries sulfur from the port and, depending on the design, phosphoric acid, solid fertilizers, or phosphate rock in an outer container on the return.

Some countries have regulations that require molten sulfur be treated (degassed) at the production point to reduce the hydrogen sulfide level below 10 ppm weight. Vancouver, British Columbia, Canada, requires formed sulfur transshipped at the port to test below 30 ppm weight. The United States and Canada do not have a national maximum hydrogen sulfide content standard for sulfur.

Storage of molten sulfur requires insulated tanks equipped with heating coils through which steam or glycol is constantly circulated. The tank's internal surfaces, particularly the roof, must be protected against corrosion and carefully monitored. Corrosion occurs most often when moisture enters through tank vents while it empties, condenses on the wall, and mixes with

vapors of sulfur and its compounds. In recent years, CSI Controls has developed an enhanced system to heat sulfur tanks externally to prevent sulfur from freezing on the walls. It also evaporates all moisture from the walls and roof. Tanks, pumps, and lines must also be properly insulated and heated. A means of injecting steam into the tank void must be provided for fire control. Finally, depending on environmental regulations, tank vents may require scrubbing systems. In the case of marine terminals, these must be sized to accommodate large volumes of air as vessels discharge. "Formed" solid sulfur, on the other hand, can be stored in a pile exposed to the open air. Runoff water containment and neutralization is required around such sites. Some localities may have maximum H<sub>2</sub>S content standards, protective walls, enclosed storage, windbreakers, and sprinkling systems to prevent blowing dust. Another means of storage, employed to minimize cost and maximize volume in any given area, is to "vat" or "block" the sulfur. In this case, a properly constructed impermeable "base pad" surface is prepared. This is then enclosed (surrounded by) with aluminum plates (forms) which are 50–75 cm high. A thin layer of molten sulfur is poured onto the pad and allowed to solidify. The process is repeated until the level of sulfur reaches the top of the aluminum forms wall. Another set of forms is then attached to the top edge of the solidified sulfur and the process is repeated. In this manner, sulfur "blocks" over 10 m high and several hundred meters long are created. Sulfur from blocks is reclaimed onsite, by melting, or by mechanical means followed by melting or shipment as the "crushed bulk" material. Despite its apparent simplicity, innumerable technical issues affect every aspect of the block construction, pouring, maintenance, and reclamation. Among these are insuring no liquid, dust, or gas effluent escapes from the site; corrosion; overcoming the effects of sun, rain, and freezing; insuring proper solidification of the sulfur being poured; wall degradation; and others. Companies experienced in creating sulfur blocks and providing equipment are Devco USA (<http://www.devcousa.com/>), Enersul Inc. (<http://www.enersul.com>), and

Hazco Environmental Services, Ltd. (<http://www.hazco.com>). Considerable information on these matters can be obtained from Sulfur, a BC [Insight.com](http://Insight.com) publication.

A key final consideration when storing solid sulfur is the inevitable presence of sulfuric acid. Sulfur can become contaminated naturally with sulfuric acid through the action of *thiobacilli thiooxidans* [5] or continuous exposure to direct sunlight [6] and the presence of moisture. Recent research has demonstrated the short-term effectiveness of certain bactericides in delaying bacterial colonization. Nevertheless, discrete pockets of weak (highly corrosive) sulfuric acid should always be presumed to exist within a sulfur storage pile. Hydrochloric acid may also be present when solid sulfur has been transported by ocean vessel [7]. Ocean deliveries of solid sulfur should be neutralized to avoid potentially disastrous corrosion of downstream equipment.

## Solidification and Melting

For many years, the standard industry practice was to ship solid sulfur as a “crushed bulk.” The words adequately describe its appearance and dustiness. Crushed bulk is the least acceptable type of solid sulfur. It is created when using earthmoving equipment to recover sulfur, which has been allowed to solidify in blocks, sheets, or vats. The product is extremely dusty. Very few producers (Russia, Kazakhstan, and Iran) still ship crushed bulk. Most consumers refuse to accept shiploads even at significant price discounts due to dustiness, related contamination, and product loss. “Lump and Crushed” sulfur is classified as a hazardous material by the International Maritime Organization (IMO).

*Slate*, another type of formed sulfur, was the sulfur industry’s first attempt at developing a type of solid sulfur which was less dusty than “crushed bulk.” Slate is produced by pouring a thin (usually up to 3 cm) layer of molten sulfur onto a moving belt while simultaneously cooling the belt’s underside. Solidified sulfur breaks off into irregular shapes when falling off the end of the belt, leading it to resemble pieces of “peanut

brittle.” Owing to its greater dustiness, slate sulfur is a less desirable form of formed sulfur and faces commercial resistance. Slate is classified as nonhazardous by the IMO.

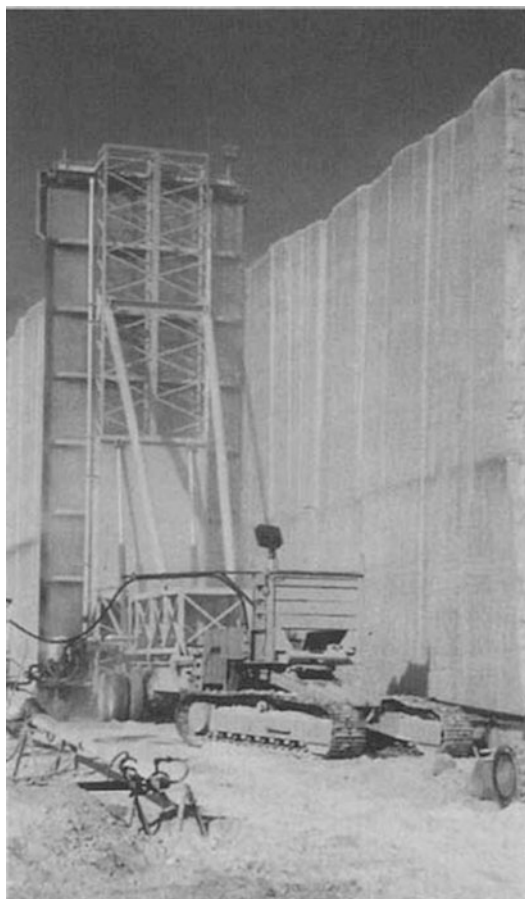
Best Available Current Technologies (BACT) for solidifying sulfur create a pelletized, prilled, or granular product. These types of “formed” sulfur were first developed in the late 1970s, and improvements continue. They minimize breakage and sharp edges, which create dust during handling. *Pelletized* sulfur is a pellet generated when a discrete amount of sulfur is deposited and cooled on a conveyor belt. It has the shape of an egg yolk on a plate. The most common processes are offered by “Sandvik” [8] and “Berndorf” [9], but other licensors exist. *Prilled* sulfur is created when sulfur droplets are cooled by a surrounding fluid, which may be air or water. *Air-prills* are created by spraying sulfur from the top of a tower into a strong updraft of cool air. It is an extremely smooth product. No air-prilling facilities have been built in almost three decades because the process emits sulfur dust to the environment. High volume air scrubbing systems to eliminate dust pollution have not been successful. In addition, the last two installations at Jubail, Saudi Arabia, were destroyed by a fire believed to have been ignited by static electricity. Wet-prills are created when sulfur droplets enter a cool water bath. They have a slightly irregular texture caused by water’s more rapid cooling action. Devco USA [10], Martin Sulphur [11], and Enersul L.P. [12] have fairly similar technologies and products. Current processes create a homogeneous product, which resembles small nuggets. All sulfur-forming operations in the United States produce wet-prill. *Granular* sulfur is created through the gradual buildup of successive layers of sulfur around a central core. As a result, the ultimate product size can be controlled. Enersul [12] possesses the most widespread granulation system, with installations in Canada, the Former Soviet Union, Europe, and the Middle East. Kaltenbach-Thuring SA [13] provides another type of granulation technology.

Despite developments in forming technology and dust suppressants, moisture remains the

primary tool for dust mitigation. To that end, a mixture of water and surfactant should be applied during all bulk transfer operations.

Melting block inventory is most often accomplished using a track-mounted Ellethorpe melter (Fig. 1). This resembles a rectangular ironing-board mounted on tracks. The “hot” portion is placed vertically against the block’s side. Sulfur melted by the rectangular surface is collected at the base and piped to filtration (if appropriate) and storage. Mechanical reclamation, normally from inside the block to minimize dust emissions, crushes sulfur and transfers the lumps to a static pit or above ground tank melter.

Melting or remelting solid sulfur that has been transported by vessel requires proper knowledge and equipment. Contaminants,



**Fig. 1** An Ellethorpe melter (Courtesy Con-Sul, Inc.)

including sand, dirt, rocks, and rusted metal, which can mix with solid sulfur during transit and storage must be removed. Sulfuric acid is another issue. Weak acid is almost always present in solid sulfur that has been stored for some time, and especially when sulfur is stored, transported by vessel, and then stored again. Although customers can require a specification below 100 ppm free acid at load-port, they may receive several times that level when measured at the destination melter. The currently accepted practice is to mix lime or a liquid oxidizer with the material being melted to neutralize all acids. Liming, in turn, requires a filtration stage—large installations use steam jacketed pressure leaf filters, containing a diatomaceous earth medium over a stainless steel mesh, to remove the lime/ash residue. An alternative is to allow ash to settle prior to transfer from an intermediate pit.

Carbon compound molecules contained within sulfur will be converted to an extremely hard (Car-Sul) material when solid sulfur is reliquefied. Car-Sul, which can be filtered, abrades sulfur burner spray nozzles [14]. Users of sulfur in the sulfuric acid industry therefore prefer receiving sulfur, which has never been solidified rather than incurring the foregoing operating costs and losses of sulfur in filtrate residue. Owing to the volume of production, legislation, and a developed liquid infrastructure, most sulfur consumed in North America, Europe, Japan, and Korea is never solidified.

## Development of the Sulfur Industry

Early mankind doubtlessly found elemental sulfur in volcanic craters, encrusting the edges of hot sulfur springs, and embedded in limestone formations. They discovered that it would burn and could be used for medicinal purposes and as a bleach, fumigant, colorant, and incense. These uses are mentioned in ancient writings. The Romans produced incendiary weapons from sulfur. In the thirteenth century, the Chinese invented gunpowder using sulfur, nitrate, and charcoal.

The earliest commercial sulfur came from limestone deposits. Those in Sicily and the Italian mainland developed world markets in the eighteenth and nineteenth centuries. Traditional mining methods were used to produce sulfur ore, which was burned slowly in a pile (Calcarone) to yield crude sulfur [15]. Steam smelting in autoclaves came into use in about 1859. In 1890, Robert Gill built a multichamber furnace to improve the process's production rate and efficiency. The Italian monopoly of sulfur markets continued until the early 1900s when the Frasch process brought previously unrecoverable sulfur deposits on the North American Gulf Coast into production. Oil exploration efforts in Texas and Louisiana in the late 1800s uncovered sulfur deposits in limestone at depths of 200–300 m, but mining was complicated by the intervening layers of quicksand and the presence of hydrogen sulfide gas. Numerous conventional mining attempts at Sulphur, Louisiana, failed.

In December 1894, Hermann Frasch demonstrated the hot water process for mining underground sulfur deposits. With its favorable economics, the Frasch process completely displaced the Italian sulfur industry. The ready availability of low-cost sulfur opened the way for commercial sulfuric acid production by burning sulfur. This eventually supplanted the long-standing iron pyrite combustion process for sulfuric acid production, which required extensive gas-cleaning operations.

In 1883, the Claus process for producing sulfur from hydrogen sulfide through partial combustion over an iron oxide catalyst was patented. It had limited success over the following 50 years as a method for producing sulfur and its primary use was to remove the sour component in gas processing.

The number of Claus installations grew during the second half of the twentieth century. An increase in sour gas and liquid petroleum feedstocks, processing and, more recently, environmental regulations led to greater quantities of sulfur being removed from hydrocarbon fuels. Sulfur extracted from oil and gas has increased dramatically since the 1970s when environmental

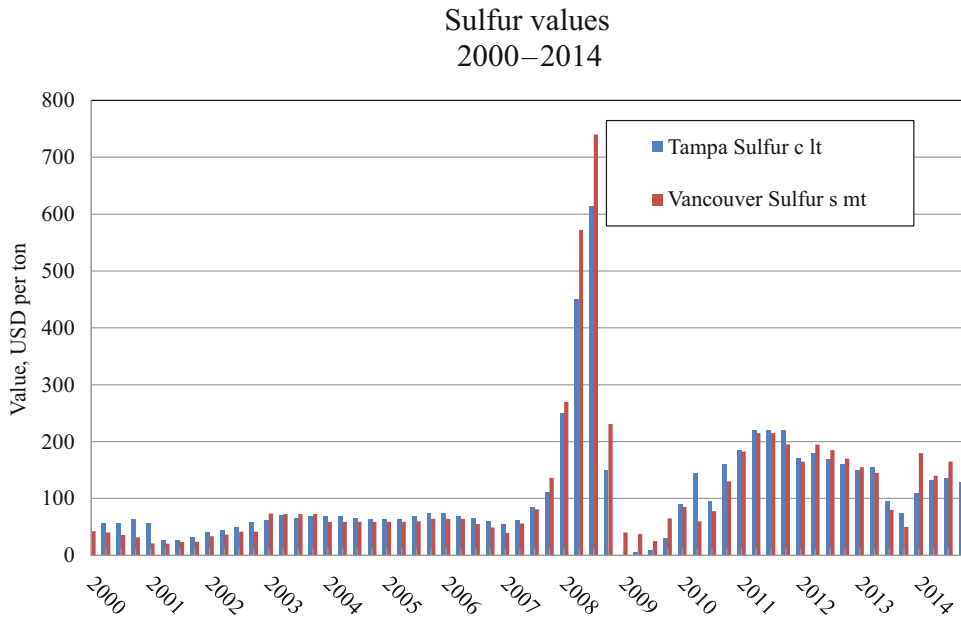
legislation took hold. In 1985, Frasch and recovered sulfur in the United States each accounted for about 5 Mt of production. By 1995, US Frasch output had declined to 3.2 Mt and recovered represented 7.3 Mt. In 2000, faced with oil companies' disposal of recovered sulfur at low prices and rising natural gas costs to heat mine-water, US Frasch mining ceased [16]. Frasch sulfur technology, with its colorful and inventive history, lasted just over 100 years in the United States. For the world, removing sulfur from hydrocarbons provided more than one-half of the 70 Mt of elemental sulfur produced during 2014 [17].

The cessation of US Frasch output at the end of the 1990s brought the demise of associated infrastructure and dissipated the industries' commercial focus. Since 2001, sulfur producers have been unable to effectively match supply with consumer demand through inventory management.

The consequence has been a series of value fluctuations (most notably declines in 2001, 2004, 2008–2009, and 2013) due to declines in phosphate fertilizer output, which led to a decrease, and in 2008–2009, a collapse of sulfur prices [18] (see Fig. 2).

Contrary to normal economic reasoning, fluctuations in price are not due to large imbalances between demand and commercially available supply. Rather, they are due to small imbalances, compared to the 70 Mt of annual output worldwide. Even small fluctuations cannot be accommodated in the industry's limited commercial storage facilities. Refineries and sour-gas processing plants must dispose of their sulfur output. Volumes in excess of the limited storage capacity available normally force refineries to cease operations due to environmental regulations. Therefore, any reduction in demand and a smooth outflow to consumers will lead to aggressive price discounting.

Although Frasch sulfur companies maintained a working storage capacity of approximately 7 Mt of solid sulfur at several locations in the early 1980s, total US solid block storage is currently below 600,000 t at present (2016). Such storage also helped reduce upward movements in



**Fig. 2** Sulfur values 2000–2014 (Courtesy Con-Sul, Inc.). Note: 1Q 2009 Tampa price \$0 c contract, s spot

price when weather or accidents restricted deliveries. As sulfur went through periods of low value, producers in more distant locations (Canada, Russia, Saudi Arabia, and Kazakhstan) have resorted to blocking the material (see section “Solidification and Melting”). This occurred during the late 1960s along the Alberta foothills area (East of the Rocky Mountains from the US border to well North of Edmonton, Canada).

In the late 1970s, the area contained upward of 22 Mt of elemental sulfur. Along with US stockpiles, it served as the world’s reserve. Over the past three decades, Alberta’s stockpiles have been as low as 4 Mt and as high as 16 Mt. In 2014, the figure was about 11 Mt: 3 Mt in the foothills and more than 8 Mt in the oil sands producing area. Sulfur produced and stored in the oil sands, as differentiated with the limited production and storage in the foothills, has only a limited commercial availability due to constraints in transportation infrastructure and costs. Changing these conditions requires capital investment and governmental approval. Neither is likely given the volatile nature of sulfur demand and prices. Therefore, Syncrude’s 9 Mt block of sulfur and parts of the 600,000 t

produced per year are commercially unavailable. In stark contrast, had production and inventory been located in the foothills and had reclamation and transportation existed, it could have been shipped to markets especially during periods of tight supplies.

Other areas where a significant volume of sulfur inventory accumulation has taken place when prices do not justify the cost of commercial disposal are Saudi Arabia (1970s to early 1980s and 2000–2009), Russia (depleted in 2011), and Kazakhstan (still with 6 Mt of inventory in 2016).

Sulfur industry practice when calculating an outlook of annual supply/demand balances uses total production less demand with no differentiation for “commercially available” or “commercially unavailable” supply sulfur. Similarly, no distinction is made for “commercially available sulfur” inventory at Alberta foothills locations and noncommercially available at Syncrude’s Oil Sands location.

One process for disposing of unwanted sulfur streams is reinjection of  $H_2S$  and  $CO_2$ . The process has long been used in Canada and the United States on a small scale. The largest project is

currently at ExxonMobil's La Barge, Wyoming, gas plant where up to 400,000 t per year of elemental sulfur has been removed from the market since 2005. Huge projects to reinject sulfur at the Kashagan field in Kazakhstan and at various Arab Gulf locations are underway or contemplated.

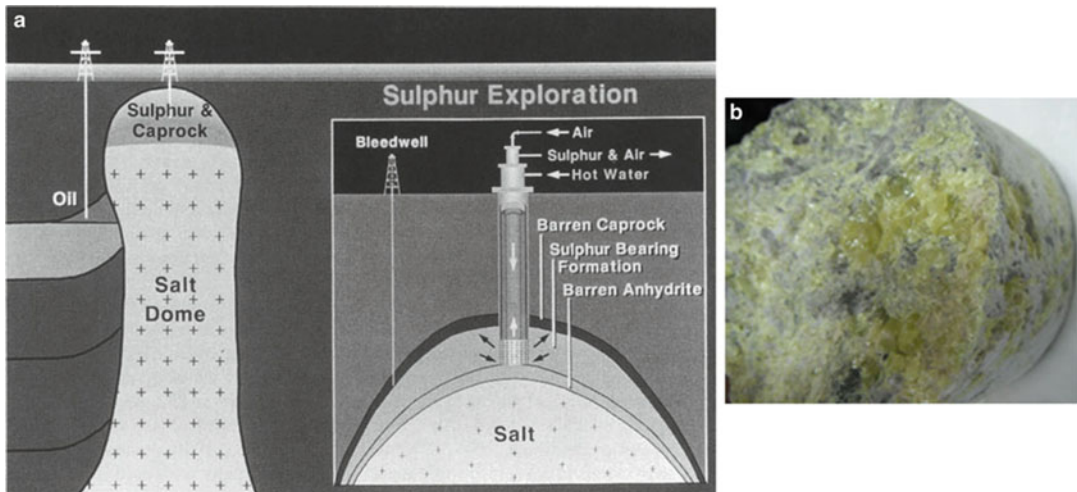
Sulfur (as sulfuric acid) is also produced from sulfide ores (pyrites) by thermal decomposition in the absence of air, by roasting/smelting under reducing conditions, or by reaction of the ore with  $\text{SO}_2$ . Hydrometallurgical processes have produced sulfur from metal pyrites as a by-product sulfuric acid.

Except for China, pyrites roasting no longer accounts for significant quantities of sulfur production. And even China has embarked on a rapid conversion to using elemental sulfur in former pyrites roasters in order to lower production costs and pollution. Canadian sulfur exporters initiated this trend with the development and introduction of innovative technology. The Canadian exports of sulfur to China rose from 31,000 t in 1995 to a peak of 3.9 Mt in 2005 [19]. Since then, the volume declined to less than 1.0 Mt starting in 2013.

## Sulfur Production Processes

Despite the economically driven closure of the Main Pass 299 sulfur mine (24 km east of the Mississippi River Delta, Louisiana) in 2000 (just 8 years after initial output), the Frasch process remains the most effective method for extracting sulfur from native deposits. Certain constraints on the geological formations required by the Frasch process limit its use to deposits along the Gulf of Mexico, Iraq, Mexico, Poland, and the former Soviet Union. Figure 3 shows the structure needed for Frasch mining from salt domes. The sulfur-bearing limestone must have sufficient porosity to allow sulfur to migrate upon melting. Both the caprock and the underlying anhydrite formation should be impervious to prevent the loss of the hot water pumped into the mine. These salt-dome deposits are typically lens-shaped and are 175 m thick with diameters of a few hundred meters up to several kilometers. Some horizontal deposits exist and have been exploited.

A sulfur well consists of a casing and three concentric pipes reaching into the sulfur-bearing strata. The outer 20–25 cm pipe carries 165 °C



**Fig. 3** (a) Frasch process for mining sulfur from salt-dome formations (Courtesy Freeport Sulphur Co.). (b) Sulfur-bearing limestone



water pumped into the formation to melt the sulfur. An inner cement-lined 8–15 cm pipe is used to transport the melted sulfur to the surface. Compressed air is passed through the 2.5 cm tube in the center to airlift the sulfur. Without the airlift, the molten sulfur would rise only part way in the middle pipe. The compressed air produces a low-density sulfur froth that rises to the surface. The superheated water melts the sulfur in the vicinity of the well, forming a molten sulfur pool at the bottom of the well. As production continues, the formation fills with water. To continue production, bleed wells are drilled at the periphery of the formation to allow for discharge of the cooled mine water. In some mine fields, sufficient mine water is lost to the geological formation to provide for continued production. To limit mine water loss and reduce water heating costs, mud or synthetic foam is sometimes pumped into the formation to seal major crevices.

Although most US Frasch mines were located inland, Freeport Sulfur Co. pioneered offshore sulfur mining in the 1960s [20]. The company utilized off shore oil drilling techniques to access several shallow water deposits. Developing a means to use saltwater to provide heated mine water presented the company with unique challenges in corrosion and scaling control. The now defunct Main Pass 299 facility located in 61 m of water 24 km from the Mississippi Delta commenced production in 1992 and closed in 2000.

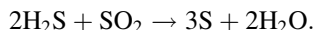
Sulfur produced from salt-dome structures can be quite pure, but it often contains up to 1% of bituminous residues, which render it dark and can make it unacceptable for sulfuric acid production. Some purification is obtained by filtering the dark sulfur through diatomaceous earth. Nevertheless, the most effective means of meeting maximum commercial specifications for carbon is through blending dark sulfur with bright recovered sulfur devoid of carbon. That practice was widely used by Louisiana Frasch producers. To improve filtration, carbonaceous material is converted into larger, filterable particles (Car-Sul) by treating the sulfur with heat or sulfuric acid. Freeport's submerged

combustion distillation process was used from 1966 until 1979 to purify Frasch sulfur with up to 2% carbonaceous material.

## Recovered Sulfur

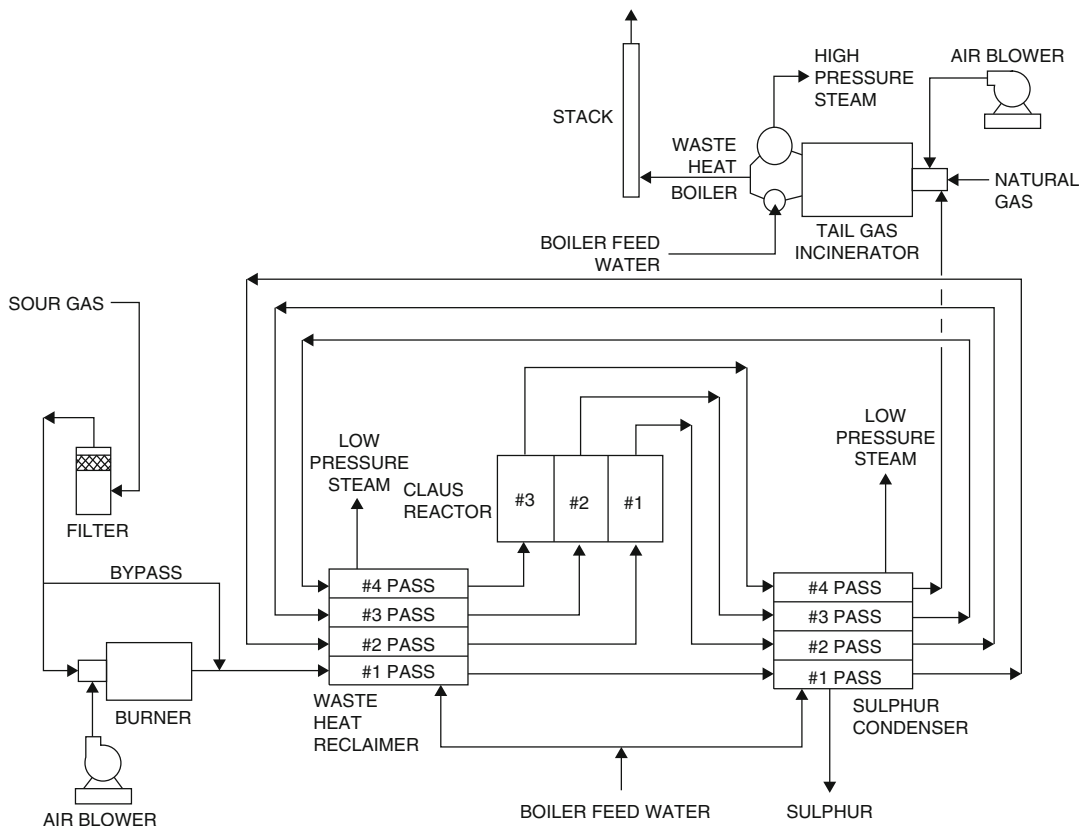
Hydrogen sulfide is recovered from natural gas or refinery gases by absorption in a solvent or by regenerative chemical absorption [21]. In either case, a concentrated hydrogen sulfide stream is produced that is treated further by the Claus process. A typical Claus plant has a feed stream of at least 45% H<sub>2</sub>S, but with modifications can handle streams containing as little as 5% H<sub>2</sub>S. For gas streams with low concentrations of hydrogen sulfide, direct conversion of the hydrogen sulfide to sulfur is accomplished in a solvent system, as in the Stretford or CrystaSulf processes.

The Claus process is based on the reaction of H<sub>2</sub>S with sulfur dioxide according to the highly exothermic reaction:



In practice, sulfur dioxide is produced in situ by partial oxidation of the hydrogen sulfide with air or oxygen in a furnace. In the split-flow arrangement, one-third of the H<sub>2</sub>S stream is burned and then recombined with the remaining two-thirds before entering the Claus reactor. In the straight-through version, the entire H<sub>2</sub>S stream is sent through the burner and the extent of H<sub>2</sub>S combustion is controlled by the air feed rate.

A flow diagram for a typical Claus process is shown in Fig. 4. The hydrogen sulfide is burned in a fuel-fired furnace (950–1250 °C) with air to produce sulfur and a gas stream containing H<sub>2</sub>S and SO<sub>2</sub>. Process controls maintain the H<sub>2</sub>S:SO<sub>2</sub> ratio near 2, in accordance with the stoichiometry. Heat is removed from the gas stream in a waste heat boiler to control the process gas temperature. The process gas is passed through one or more catalyst beds to convert the H<sub>2</sub>S and SO<sub>2</sub> to sulfur, which is then removed in condensers between each bed. A high temperature shifts the



**Fig. 4** Flow diagram for a typical Claus process

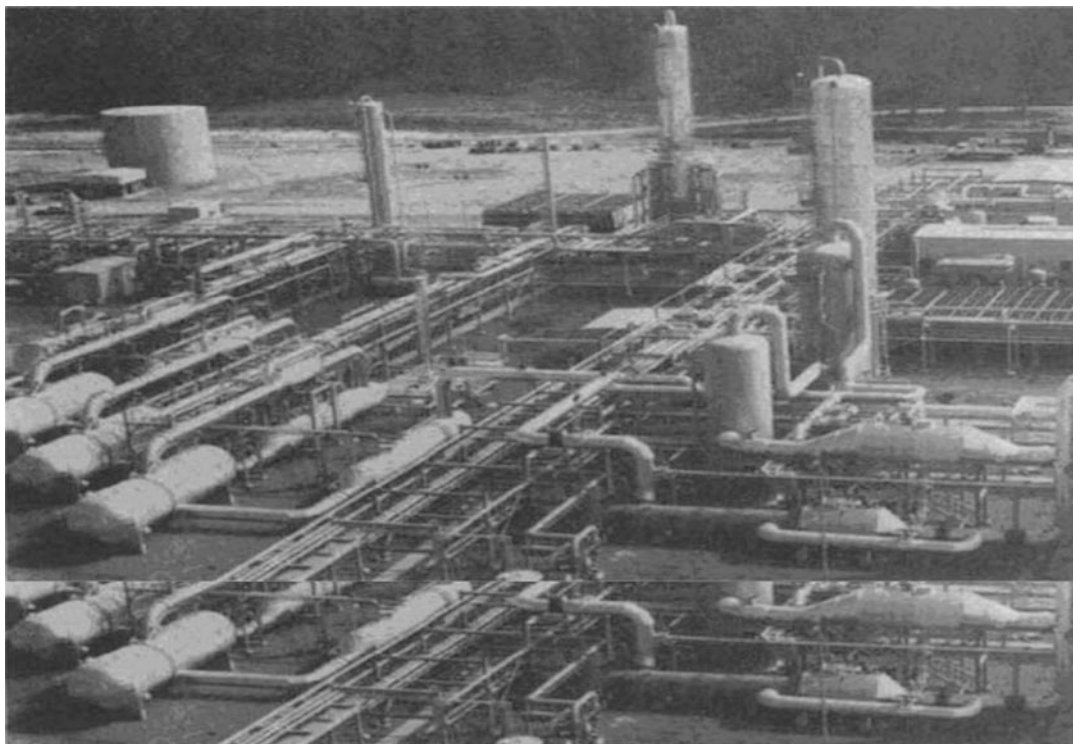
equilibria toward the reactants, whereas a low temperature causes sulfur condensation on the catalyst bed, leading to decreased catalyst activity, requiring bed switching/regeneration to achieve modern recovery standards. In practice, the temperature is controlled closely for each Claus reactor, with higher temperatures at the first reactor where compounds such as COS and CS<sub>2</sub> are converted to S. Much research and development into H<sub>2</sub>S conversion has occurred in the past decades. Three-state Claus units are now capable of achieving recoveries of >98%, a significant improvement over the 85–90% range of the late 1980s [22].

Figure 5 provides a photographic overview of a typical sulfur recovery plant based on the Claus process and a SCOT tailgas clean-up unit. The tail gas from the Claus reactors may be further processed to remove any remaining sulfur compounds. Combined H<sub>2</sub>S removal efficiencies

of 99.5–99.99% are achievable [23]. This may be done by low-temperature Claus-type solid-bed processes such as the Sulfreen process, wet-Claus absorption/oxidation processes such as the Clauspol 1500 process, or hydrogenation of the off-gas to form H<sub>2</sub>S for recycle such as the SCOT process. Residual sulfur compounds in the tail gas are then incinerated to SO<sub>2</sub>. The residual SO<sub>2</sub> in the oxidized tail gas may be scrubbed by any of several processes such as the Wellman-Lord process before being vented to the environment. It is feasible to bring the H<sub>2</sub>S content of the treated tail gas to as little as 150–10 ppm weight, depending on the solvent used [24].

## Production and Consumption of Sulfur

World production of sulfur in all forms reached 69.1 Mt in 2014—up from 58.5 Mt in 1999 [25].



**Fig. 5** Republic refining Co. 440

The lower growth rate than anticipated at the end of the 1990s and early 2000s arose principally from delays in implementing Caspian and Arabian Gulf sour oil and gas projects. Schedules slipped due to technical difficulties (Caspian—Kashagan field, Government issues at Tenghiz) and cost escalation/over-ambition and economic setbacks (Arab Gulf). Nonelemental sulfur output has seen a significant change in composition. Volumes arising from environmentally mandated stack-gas effluent recovery have increased. Within the mix, pyrites-derived sulfur production continues to decline, although only slightly with China being the main producer.

Table 1 summarizes the dramatic shifts in the sources of sulfur during this period. It shows the demise of Frasch and native sources of supply and a 9 Mt increase in recovered volume in 15 years. Added sulfuric acid and SO<sub>2</sub> recoveries from effluent gas added 8 Mt.

US output from 2000 to 2014 (see Table 2) shows a decline of elemental sulfur production of

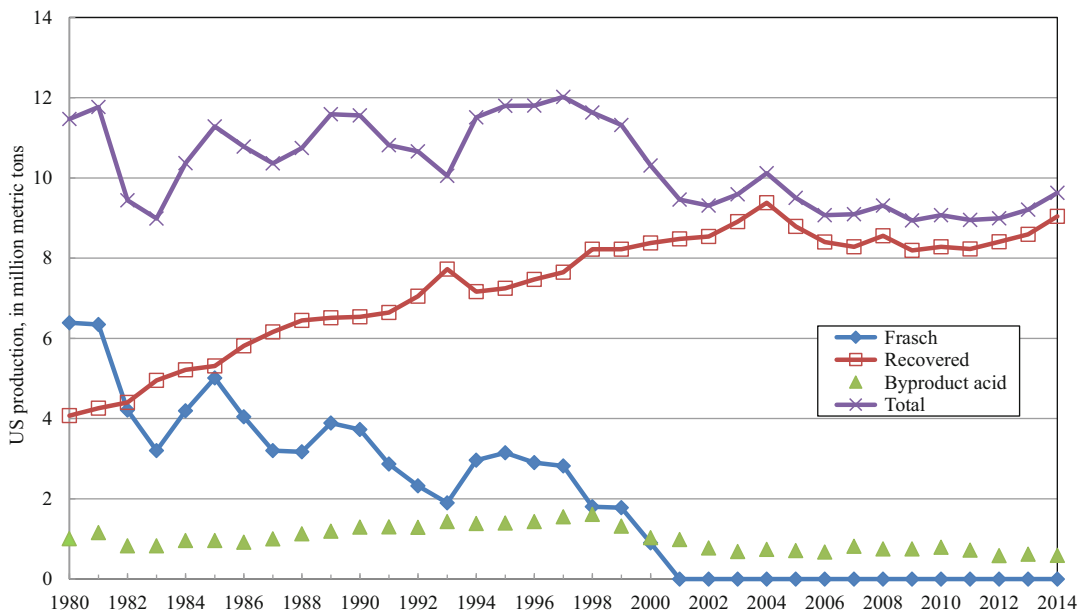
0.5 Mt. Figure 6 provides a historical perspective of changes from 1980 to 2014. Canada's sulfur production is concentrated in Alberta. Table 3 provides output data for the three western most provinces. Over the past 15 years, sulfur generated in the region declined by 3.3 Mt (39%) from 8.5 Mt in 1999 to 5.2 Mt in 2014. The primary causes were:

- Exhaustion of sour gas deposits, some under exploitation for more than 30 years.
- Failure of new sour gas deposits to yield the needed replacement output—the Caroline gas plant area being just one.
- Reduced gas prices resulting in lower gas production for export to the United States.
- Declining gas prices in the United States lead to sour gas exploration and exploitation ceasing.
- Delays in the development of oil sands upgrading facilities, which were expected to provide replacement volumes of sulfur.
- Wild cost inflation in the mid-2000s, inadequate

**Table 2** Estimated US sulfur supply/demand (Million metric tons)

	2000	2002	2006	2008	2010	2012	2014
<i>Production</i>							
Frasch	0.8						
<i>Recovered</i>							
Oil	6.4	6.5	7.0	6.9	7.1	7.4	8.0
Gas	2.3	2.0	1.4	1.1	1.1	1.0	1.0
Total	9.5	8.5	8.4	8.0	8.2	8.4	9.0
<i>Imports to US</i>							
Canada	1.51	1.10	2.03	2.18	2.30	2.32	1.90
Venezuela	0.16	0.16	0.41	0.36	0.02	0.09	0.07
Mexico	0.51	0.47	0.49	0.37	0.42	0.35	0.30
Other	0.03	0.03	0.00	0.10	0.40	0.00	0.05
Total	2.21	1.76	2.93	3.01	3.14	2.76	2.32
Exports	-0.80	-0.70	-1.10	-1.14	-1.40	-1.48	-1.80
Total supply	10.91	9.56	10.23	9.87	9.94	9.68	9.52
Consumption	11.19	9.56	10.12	10.00	10.22	9.61	9.30
Inventory change	-0.28	0.00	0.11	-0.13	-0.28	0.07	0.22

Source: North American Quarterly Review, January 15, 2016, Con-Sul, Inc.



**Fig. 6** Trends in the production of all forms of sulfur in the United States (Source: U.S. Geological Survey Minerals Yearbook and U.S. Bureau of Mines: Sulfur Annual Report)

physical, human, and regulatory resources, the financial bubble of 2007, and its subsequent collapse, all contributed to the delays.

From 1999 to 2003, production exceeded export shipments to the United States and overseas. As a result, inventories in the oil sands region of Alberta grew significantly. From 2004

**Table 3** Western Canada sulfur summary<sup>a</sup> (Million metric tons)

		1999	2000	2002	2004	2006	2008	2010	2012	2014
Production	8.5	8.4	7.9	8.0	7.6	6.6	5.8	5.2	5.2	
Shipments	7.3	7.0	7.3	8.5	8.0	7.3	6.2	5.8	5.1	

Source: North American Quarterly Review, January 15, 2016, Con-Sul, Inc.

<sup>a</sup>Note: Alberta, British Columbia, and Saskatchewan

**Table 4** Estimated annual export summary—total Canadian exports (Million metric tons)

		2000	2002	2004	2006	2008	2010	2012	2014
Vancouver	5.3	5.1	6.3	5.8	4.7	3.6	3.0	2.4	
US		1.5	1.9	2.0	2.0	2.2	2.3	2.3	1.9
Total		6.8	7.0	8.3	7.8	6.9	5.9	5.3	4.3

Source: North American Quarterly Review, January 15, 2016, Con-Sul, Inc.

forward, production was below export demand, leading to withdrawal of sulfur from inventory located in Alberta's foothills. Regional shipments and local use fell during the time frame from 7.3 Mt to 5.1 Mt. Canadian exports by rail, in liquid form, to the United States and overseas, as a solidified material, through the port of Vancouver also declined (Table 4).

Loss of the US Frasch companies' commercial structure affected North American markets dramatically. Recovered producers, devoid of storage capabilities and marketing experience, and needing to dispose of sulfur to avoid affecting refinery operating rates just had it removed from the refinery. Sulfur prices embarked on a decline, which culminated with spot sulfur prices falling to the \$10s per ton in Tampa, FL, and Vancouver by mid-2001. In contrast, prices during 1990 were \$140/t and \$108/t, respectively. A second collapse occurred in 2008–2009, leading to a Tampa price of zero during the first quarter of 2009 (see Fig. 2).

The United States remains the largest producer of sulfur. US production and consumption data are provided in Table 2. Fertilizers and agrochemicals represent the largest use for sulfur, 63%. In 2014, phosphatic fertilizers consumed 4.8 Mt of sulfur, in the form of sulfuric acid. Other agricultural chemicals accounted for 2.0 Mt, in the form of elemental sulfur. Sulfur represents the largest fungicide and pesticide product applied in the United States. Refining use, for alkylation, is the second largest segment

of consumption. It is also one of the most difficult segments to track accurately. This arises from refineries not reporting a portion of their production and using that material directly for internal use. Accordingly, a portion of actual sulfur output does not get reported within the scope of "production of sulfur," causing total uses to exceed production.

US production of elemental sulfur declined due to the cessation of Frasch mining operations. Output was 9.5 Mt in 2000, 8.4 Mt in 2006, only 8 Mt in 2008, and increased to 9.0 Mt in 2014.

## Sulfuric Acid

Sulfuric acid is the largest volume inorganic chemical manufactured in the world and its consumption is often cited as an indicator of the general state of the nation's economy [26]. About 30 Mt of sulfuric acid were produced in the United States in 2014, of which approximately 70% was used in fertilizer production. Its use extends to nearly every major chemical sector. This versatile acid is truly the "workhorse" of the chemical industry (Table 5).

Pure sulfuric acid is an oily, water-white, slightly viscous liquid with a melting point of 10 °C and a boiling point of 337 °C. It is infinitely miscible with water, forming sulfuric acid solutions characterized by their weight percent of H<sub>2</sub>SO<sub>4</sub>. Oleum may be formed by dissolving SO<sub>3</sub> in sulfuric acid to attain fuming sulfuric acid,

**Table 5** US sulfur and sulfuric acid sold or used (Thousand metric tons of sulfur content)

	Elemental S	Sulfuric acid	Total	Form
End use	2014	2014	2014	
Copper ores	–	251	251	H <sub>2</sub> SO <sub>4</sub>
Other ores	–	68	69	H <sub>2</sub> SO <sub>4</sub>
Pulp mills and paper products	–	129	129	H <sub>2</sub> SO <sub>4</sub>
Inorganic and other chemical products	–	132	132	S/H <sub>2</sub> SO <sub>4</sub>
Synthetic rubber and other plastic materials	–	6	6	S/H <sub>2</sub> SO <sub>4</sub>
Cellulosic fibers including rayon	–	–	–	S/H <sub>2</sub> SO <sub>4</sub>
Industrial organic chemicals	–	21	21	S/H <sub>2</sub> SO <sub>4</sub>
Nitrogenous fertilizers	–	175	175	–
Phosphatic fertilizers	–	4810	4810	–
Pesticides	–	8	8	S
Agricultural chemicals	1970	51	2020	S
Petroleum refining and other petroleum and other coal products	2120	1260	3380	S
Other chemical products	–	95	95	S
Metals leaching	–	11	11	H <sub>2</sub> SO <sub>4</sub>
Storage batteries (acid)	–	21	21	H <sub>2</sub> SO <sub>4</sub>
Exported sulfuric acid	–	77	77	H <sub>2</sub> SO <sub>4</sub>
Total identified	4090	7120	11,200	–
Unidentified	923	141	1060	
Grand total	5010	7260	12,300	S/H <sub>2</sub> SO <sub>4</sub>
As sulfuric acid	–	22,200	37,500	H <sub>2</sub> SO <sub>4</sub>

Source: U.S. Geological Survey Minerals Yearbook, Sulfur 2014

with concentrations nominally greater than 100% H<sub>2</sub>SO<sub>4</sub>. Historically, sulfuric acid concentrations were determined by measuring the solution density using hydrometers calibrated in degrees Baume (Be). This practice is waning, although some specifications and tables of properties still include this measurement (Table 6).

### Uses of Sulfuric Acid

The primary industrial uses of sulfuric acid are in phosphate fertilizer manufacture, petroleum refining, copper ore leaching, synthetic rubber and plastics, and pulp and paper mills [27]. It is used as a solvent, a dehydrating agent, a reagent in chemical reactions or processes, an acid, a catalyst, and an absorbent, and in many other applications. In spite of its wide usage, sulfuric acid rarely is contained in the final product. Sulfuric acid ends up as gypsum in phosphate fertilizer manufacture, for example. In many

other processes, the sulfuric acid is converted to a waste product that requires disposal or reuse. Because disposal of waste sulfuric acid and of sulfur compound air emissions are becoming increasingly unacceptable environmentally, the recycle and capture of sulfur values from waste sulfuric acid has become widespread.

Nearly, all sulfuric acid is manufactured by the contact process in which sulfur trioxide is absorbed into 93–98% H<sub>2</sub>SO<sub>4</sub>. The acid may be sold at various strengths, usually depending on the requirements of the consumer. It is generally marketed on a 100% basis, but normally is shipped as 93% H<sub>2</sub>SO<sub>4</sub> (66°Be), as 98% acid, or as 20–22% fuming oleum. Table 6 shows common acid strengths and end uses. Concentrated acid may be stored in mild steel tanks, but dilute acid must be contained in lead-lined or plastic tanks. Bulk shipments of concentrated acid are made in steel tanks on ships, tank barges, or railcars. Reagent grade acid is commonly sold in 5 L glass bottles.

**Table 6** Acid strengths and end uses

Percent Oleum				
Percent H <sub>2</sub> SO <sub>4</sub>	°Be	(% Free SO <sub>3</sub> )	Specific Gravity	Uses
35.67	30.8		1.2700	Storage batteries, electric utilities
62.18–9.65	50–55			Normal superphosphatic and other fertilizers
77.67	60.0		1.7059	Normal superphosphatic and other fertilizers; isopropyl and sec-butyl alcohols
80.00	61.3		1.7323	Copper leaching
93.19	66.0		1.8354	Phosphoric acid, titanium dioxide, steel pickling, regenerating ion exchange resins
98–99				Chlorine drying, alkylation, boric acid
104.50		20	1.9056	Surfactants, nitrations
106.75		30	1.9412	Hydrofluoric acid
109.00		40	1.9737	Explosives
111.24		50	1.9900	Reagent manufacture, organic
113.50		60	1.9919	Sulfonations, blending with
114.63		65	1.9842	Weaker acids

Source: Chemical Economics Handbook, SRI International, Dec 1990

## Development of the Sulfuric Acid Industry

Sulfuric acid is formed in nature by the oxidation and chemical decomposition of naturally occurring sulfur and sulfur-containing compounds. It is made by the action of bacteria (thiobacillus ferrooxidans and thiooxidans) on coal wastes or iron disulfide discarded on refuse dumps at coal and copper mines; it is produced in the atmosphere by the oxidation of sulfur dioxide emitted from the combustion of coal, oil, and other substances; and it also is formed by chemical decomposition resulting from geological changes.

Although there were vague references to “spirits” expelled from alum by Arabian alchemists in the tenth century and by Roman alchemists in the thirteenth century, the first distinct mention of sulfuric acid has been credited to Basil Valentine in late 1400s [28]. He burned sulfur with saltpeter in glass retorts or bell jars with a little water and also calcined copper as ferrous sulfate heptahydrate with silica, with both processes yielding sulfuric acid, although he took them to be different substances. These processes for making sulfuric acid continued until 1746 when John Roebuck constructed a lead chamber in England for sulfuric acid manufacture. This marked the beginning of the

“chamber process” for sulfuric acid, which was to continue in use for the next two centuries [29].

The first lead chamber was 1.8 m<sup>3</sup>, and 8:1 mixtures of sulfur and saltpeter in iron carts were rolled into it and burned with intermittent admission of air [30]. As in glass retorts, the sulfur trioxide that was formed combined with water to produce sulfuric acid, which condensed on the walls and collected in pans. Steam was introduced into the chambers in 1774, and continuous addition of air was begun in 1793. It then was recognized that the sulfurous acid from the burning of sulfur was oxidized by air and needed saltpeter only as a catalyst. In 1827, Gay-Lussac invented a tower for recovering the nitrogen oxides escaping from the chamber. The nitrogen oxides were condensed in sulfuric acid, but could not be economically recovered from the acid until the invention of the Glover denitrating tower in 1859. The introduction of these two towers completed the chamber process except for various refinements to reduce costs. The process could produce acid with up to 77% H<sub>2</sub>SO<sub>4</sub>, but generally yielded strengths in a 65–68% range. Higher-strength acid was produced by boiling chamber acid to remove water. A platinum still for producing concentrated sulfuric acid from chamber acid was first built for the Harrison Works in Philadelphia, PA, in 1814.

The developing markets for sulfuric acid in the late eighteenth century increased the demand for Sicilian sulfur. By 1832, sulfur prices had risen to \$80/t, and stocks rose; then in 1833, the market broke and the price declined to \$15/t. The Government of Sicily's attempts to stabilize sulfur at \$70/t failed, in part because of an 1833 discovery by a French chemist that sulfur dioxide could be obtained by roasting pyrites in a furnace. Process improvements in pyrite roasting made pyrites competitive with sulfur as a raw material by 1870. By 1880, with the single exception of the United States, the sulfuric acid industries had gone to a pyrites basis. By 1909, virtually all US sulfuric acid came from pyrites and as by-product acid from zinc and copper smelters. In the late 1890s, development of the Frasch process for sulfur mining resulted in lower prices for sulfur. This change, coupled with new developments in sulfur burners, led sulfuric acid manufacturers to resort back to sulfur as a raw material source. During World War I, gypsum was burned with coal to produce  $\text{SO}_2$  for sulfuric acid production. This process continued in Europe until the 1950s, with the last plant (in Great Britain) shutting down in 1975. Today, sulfuric acid production from pyrite roasting remains important in China, Finland, and Russia.

The contact process for sulfuric acid dates from 1831, when a Briton patented a method for converting sulfur dioxide to sulfur trioxide by passing the gas through a heated tube filled with finely divided platinum. The sulfur trioxide was adsorbed in chamber acid to produce concentrated and fuming sulfuric acids. Commercialization of the new process was delayed by lack of markets for the concentrated acid and poor understanding of the process parameters. About 1870, demand for fuming sulfuric acid spurred German development of the contact process. In 1901, BASF reported that the governing principles for the successful manufacture of contact acid were well understood. These included cleaning of the sulfur dioxide gas stream, use of excess oxygen, and temperature control of the catalyst bed. However, the reliance

of the contact process on feed acid produced by the chamber process limited its development until about 1930. It became known that the acid in the final  $\text{SO}_3$  absorption tower had to be kept in the range 98.5–99.0%  $\text{H}_2\text{SO}_4$  to be effective. Accurate dilution techniques to allow recycle of the absorber acid were developed in the late 1920s. The contact process then could continuously produce diluted acid and no longer required chamber acid. The development of effective vanadium catalysts for  $\text{SO}_2$  conversion allowed the use of smelter gases in the contact process. With its lower capital and operating costs, the contact process then supplanted the chamber process for sulfuric acid production. By 1940, the United States had equal numbers of chamber and contact process plants. In 2014, no commercial chamber plants were operating in the United States.

Since the 1940s, most developments in the contact process have focused on energy recovery and pollution abatement. The production of  $\text{SO}_2$ , its conversion to  $\text{SO}_3$ , and the dilution of  $\text{H}_2\text{SO}_4$  are exothermic processes that are exploited to reduce energy costs at sulfuric acid plants. Sulfur emissions have been sharply reduced by using two  $\text{SO}_3$  absorbers, although one absorber is the economic choice. Tail gas scrubbing processes have been developed to further reduce sulfur emissions from sulfuric acid plants. No single absorber plants has been built in the United States since the 1970s, although some were still in operation as recently as 2000. As of the early 1970s, U.S. Environmental Protection Agency (EPA) regulations limited new sulfur-burning sulfuric acid plant emissions to 2 kg of  $\text{SO}_2$  and 0.075 kg of acid mist per metric ton of  $\text{H}_2\text{SO}_4$  produced and metallurgical plants to 650 ppm by volume of  $\text{SO}_2$ . During the 1990s, some local requirements were more stringent than the EPA regulations and several plants were constructed with  $\text{SO}_2$  limited to 100 ppm of  $\text{SO}_2$  (about 0.5 kg of  $\text{SO}_2$  per metric ton of  $\text{H}_2\text{SO}_4$  produced). One double absorption plant followed by an ammonia-based DynaWave scrubber, built under Monsanto Enviro-Chem license in Ulsan, South Korea, started operation in 1999 with  $\text{SO}_2$  at 30 ppm.



## Manufacture of Sulfuric Acid by the Contact Process

The basic steps in the contact process are: (1) production of sulfur dioxide; (2) cooling and, for smelters, cleaning of the process gas; (3) conversion of the sulfur dioxide to sulfur trioxide; (4) cooling of the sulfur trioxide gas; and (5) absorption of the sulfur trioxide in sulfuric acid [31]. Figure 7a is a photograph of a contact process plant. A simplified diagram of a double absorption contact sulfuric acid process is shown in Fig. 7b. Because sulfur dioxide is produced by several processes, it is convenient to separate the discussion of sulfur dioxide production from its conversion to sulfuric acid.

### Sulfur Dioxide Production

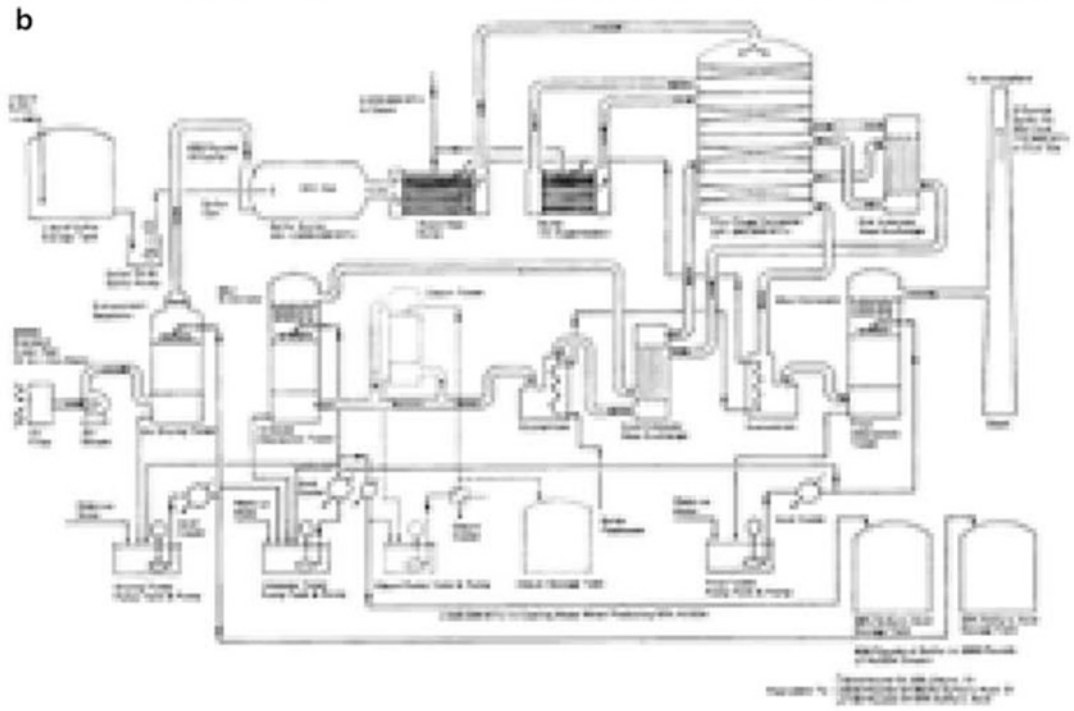
Sulfur is converted to sulfur dioxide by burning molten sulfur with dried air in a sulfur burner to yield a 1000–1200 °C gas stream containing 10–12% SO<sub>2</sub>. The burner is mounted at one end of a sulfur furnace, and the gas passes through a waste heat boiler at the other end. The gas temperature is reduced to 420–440 °C on residual oxygen level to limit the formation of nitrogen oxides, which otherwise would be very high at the combustion temperature of 1750 °C. The combustion gas then is cooled to 620–650 °C, and additional dried air is injected to burn the residual sulfur in an after burner. A second waste heat boiler cools the process gas to 420–440 °C before sending it to the converter.

Pyrites and other iron sulfides are roasted to produce an iron oxide cinder and an off-gas containing 7–14% SO<sub>2</sub>, which is contaminated with varying amounts of arsenic, lead, zinc, and other metal oxides. The off-gas must be cleaned before it is sent to the converter. Various types of pyrite roasting equipment have been used in the past, including shaft furnaces, multiple hearth roasters, rotary kilns, and dust roasters. Fluid-bed roasters have become widely used for their superior process technology, throughput rates, and economics. The roasting process must be controlled between 850 and 940 °C. At lower

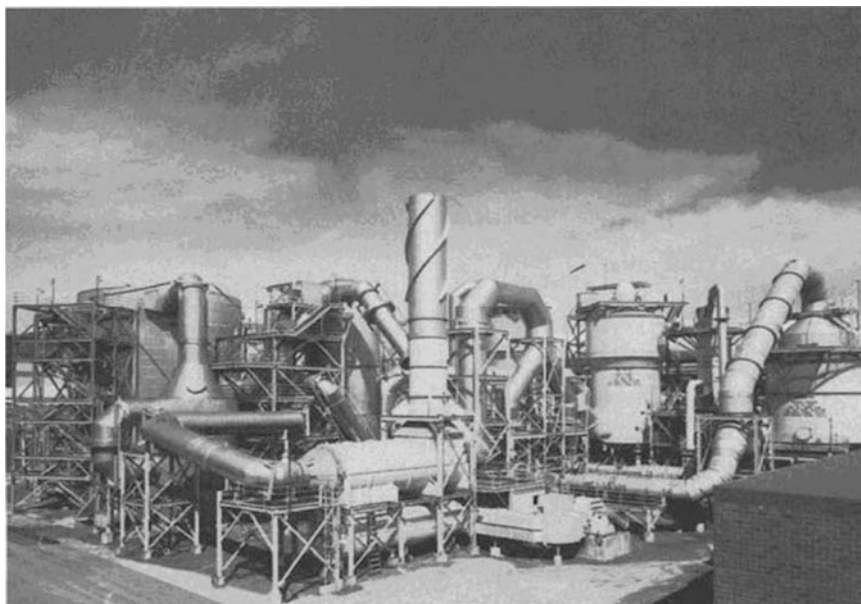
temperatures, the reaction is incomplete, whereas at higher temperatures, the iron oxides and sulfides form a eutectic melt that inhibits the reaction rate. Fluid-bed roasters surpass other types in temperature control and temperature uniformity throughout the bed. Fluid-bed technology for SO<sub>2</sub> production was introduced in the early 1950s by Dorr Oliver in the United States and by BASF in the Federal Republic of Germany.

Copper, lead, zinc, and other sulfide ores may be processed by roasting or smelting. Roasting or sintering of sulfide ore is essentially identical with pyrite roasting. Sulfur melting generally occurs at higher temperatures. Older reverberatory furnace smelters produce off-gas with only 1–2% SO<sub>2</sub>, too low for its economical recovery as acid. By using an oxygen-enriched air feed, the off-gas can be raised to 6–8% SO<sub>2</sub>. Bath smelters (Mitsubishi, Noranda), where the ore concentrates are heated and reacted in the slag/matte melt, produce an off-gas with 10–20% SO<sub>2</sub> [32]. Flash smelters (Vale, Outotec), which involve suspension and reaction of the concentrates in an oxidizing gas stream, operate at 1200–1300 °C and produce a waste gas with 10–15% SO<sub>2</sub>. Oxygen enrichment of the feed air can raise the SO<sub>2</sub> level in the off-gas to 30–80%. The Kivcet process smelts with pure oxygen and produces off-gas with 80–85% SO<sub>2</sub> [33]. Normally, strong gases are diluted with air to 14% SO<sub>2</sub> in order to limit outlet temperatures in the converter first pass to less than 640 °C and to provide sufficient oxygen to convert the SO<sub>2</sub>–SO<sub>3</sub>. In 1996, the original Olympic Dam sulfuric acid plant in South Australia was modified to operate with 18% equivalent SO<sub>2</sub> gas strength. This plant used a Monsanto preconverter and a cesium promoted catalyst [34]. Figure 8 is a photo of a metallurgical gas sulfuric acid plant.

Off-gas from roasting and smelting operations may contain arsenic, dust, halogens, mercury, NO<sub>x</sub>, SO<sub>3</sub>, and other toxic metal fumes [35, 36]. These components must be removed from the gas stream before it is sent to the converter. Although SO<sub>3</sub> is produced in the converter, its presence in the cooled gases upstream of the converter will cause excessive corrosion by forming sulfuric acid mists. The cleaning



**Fig. 7** (a) Modern double absorption sulfuric acid plant with view of sulfur furnace in foreground (Courtesy Monsanto Enviro-Chem). (b) Schematic flow diagram of absorption contact process for sulfuric acid manufacture



**Fig. 8** Modern metallurgical sulfuric acid plant with view of preheating furnace in foreground (Courtesy Kennecott, Monsanto Enviro-Chem, and Manly Prim Photography)

plant steps are: (1) hot-gas dedusting; (2) wet scrubbing; (3) gas cooling; (4) mist removal; and, if necessary, (5) mercury removal. The hot gases generally are passed first through a waste heat boiler to reduce the temperature to 250–400 °C. Cyclones followed by hot-gas electrostatic precipitators (50–90 kV) remove nearly all (99+%) of the dust. The gas then is contacted with weak (5–30%)  $\text{H}_2\text{SO}_4$  in an open spray tower which removes metal vapors and additional solids, cools the gas to 50–80 °C, and converts  $\text{SO}_3$  to acid mist for later removal. If higher levels of particulate removal are required, venturi, Swemco, or DynaWave scrubbers may be used. The saturated gas is next cooled in a packed tower or shell and tube heat exchanger to condense excess water. Shell and tube heat exchangers of graphite or alloy construction are generally used only in smaller size sulfuric acid plants or where the gas temperature has a tight approach to available cooling water. Silica packing is used in the towers, or sodium silicate is added to the weak acid circuits to remove fluorides as fluosilicic acid.

In cases where the fluoride levels are very high, additional liquid–gas contacting stages are

provided to reduce the gas phase concentration of fluorides. Acid mist is removed in wet electrostatic precipitators fitted with lead tubes and star wires or, more recently, with FRP or PVC tubes specially treated to maintain a conductive liquid film surface (Lurgi) [37] and composite wires fabricated with barbs to promote corona discharge [38]. If present, mercury is removed in an additional tower by scrubbing with mercury chloride solution (Boliden) [39], hydrochloric acid solution, or 70–85% sulfuric acid.

Waste sulfuric acid sludges from petroleum refineries are disposed of by conversion to  $\text{SO}_2$  for production of fresh sulfuric acid. The heavy organic components of the sludges can be decomposed thermally at 800–1300 °C (Lurgi, Monsanto Enviro-Chem) or reductively at 200–600 °C with coal in a rotary kiln (Chemico). Thermal decomposition is accomplished in a fuel-fired vertical or horizontal furnace. The acid sludge also can be injected into fluid-bed pyrite roasters as a means of disposing of the acid and reducing fossil fuel consumption. Dilute acid sludges must be concentrated to 60–75%  $\text{H}_2\text{SO}_4$  for economical conversion. This is generally done by using waste heat from the decomposition

process. The sulfur dioxide gas stream from these processes requires cleaning, as described above for roasting and smelting plants.

Calcium sulfate may be decomposed to cement clinker and sulfur dioxide gas in a coke-fired rotary kiln at 900–1400 °C (Miiller-Kiihne) [40]. However, the unfavorable economics of this process relegate it to countries that do not have other sources of sulfur. Phosphogypsum (gypsum produced by the acidulation of phosphate rock) may be decomposed in this way as a means of recycling the sulfur values in the large waste phosphogypsum piles at fertilizer plants (OWS-Krupp and FIPR/Davy McKee).

This process is hampered by the more extensive gas cleaning requirements for decomposing phosphogypsum as compared with natural gypsum. During the early 1980s, there was some interest in recycling phosphogypsum. Also, in the US, most phosphogypsum cannot be recycled because of radioactivity. By 2000, because of the high cost of these processes, there was little commercial interest. Environmental forces also are behind the recycling of ferrous sulfate from metals industry pickling liquors. This “green salt” is decomposed to sulfur dioxide and iron dioxide in pyrite roasters. Elemental sulfur, coal, or fuel oil may be used as supplementary fuels.

Refinery waste gases may be burned to eliminate hydrogen sulfide and other sulfur-containing contaminants. Streams containing small amounts of H<sub>2</sub>S or constituents unsuitable for Claus plants may require combustion to SO<sub>2</sub> as the means of disposing of the toxic gas. The resulting effluent gas usually is low in SO<sub>2</sub> and contains water vapor and carbon dioxide. Flue gases from fossil fuel power plants also fall into this category. Recovery of the sulfur values from these dilute gases usually is driven by environmental considerations rather than economics. In the United States, power plant flue gas often is scrubbed with lime to convert the SO<sub>2</sub> to gypsum sludge for use in gypsum board production or landfill disposal. Alternatively, the Bergbau Forschung process recovers sulfur dioxide by dry adsorption on activated coke at 130 °C.

The SO<sub>2</sub> is released by heating the coke to 600–650 °C. Sulfur dioxide can be absorbed in a sodium sulfite solution (Wellman-Lord process) to produce sodium bisulfite. Pure moist sulfur dioxide can be recovered by heating the sodium bisulfite.

### Single Versus Double Contact Process

The single absorption contact process for sulfuric acid is characterized by four main process steps: gas drying, catalytic conversion of SO<sub>2</sub> to SO<sub>3</sub>, absorption of SO<sub>3</sub>, and acid cooling. The maximum SO<sub>2</sub> conversion for a single absorption plant is about 97.5–98%. By adding a second SO<sub>3</sub> absorber with one or two catalyst beds between absorbers, the SO<sub>2</sub> conversion can be increased to 99.5–99.8% or even as high as 99.9% with a cesium promoted catalyst, resulting in lower SO<sub>2</sub> emissions. The double absorption process is now the industry standard.

If water vapor is present in the gas stream or the gas temperature or metal surface temperatures drop below the dew point, liquid acid is formed by condensation of H<sub>2</sub>SO<sub>4</sub> vapor rather than by absorption of SO<sub>3</sub>. Therefore, the SO<sub>2</sub> laden process gas sent to the converter must be dry to protect the downstream process equipment against corrosion. The drying generally is done in a packed tower with recirculating concentrated (93–98%) sulfuric acid kept at 50–60 °C by indirect cooling. The tower acid stream is heated by condensation of the water and by dilution of the acid. The tower temperature is used to control the moisture level of the gas sent to the converter. Acid from the drying tower is cross-flowed to the absorber or is sent to storage tanks for shipment. When sulfur is burned, the combustion air to the sulfur burner is dried because the combustion of sulfur does not produce water. Off-gases from pyrite roasters and metallurgical smelters are dried as part of the gas cleaning process. For roaster gases with low SO<sub>2</sub> concentrations, a predryer may be added upstream of the main dryer.

## Oxidation of SO<sub>2</sub>

Oxidation of SO<sub>2</sub> to SO<sub>3</sub> is accomplished in multi-stage, fixed-bed catalytic converters equipped with interstage boilers or heat exchangers to remove the heat of reaction. Typically, four stages are compartmented within a single vertical converter, which may be brick-lined, steel, or cast iron. Newer converters are stainless steel, and some have five stages for higher conversion. Isothermal tubular converters are no longer suited to modern high-capacity plants. The extruded cylindrical catalyst pellets are usually 4–9% V<sub>2</sub>O<sub>5</sub> with alkali metal sulfate promoters on a silica carrier (diatomaceous earth, silica gel, or zeolites). The reaction temperature for vanadium catalyst is generally 410–440 °C. In the late 1980s, a cesium-promoted catalyst became commercially available from Topsoe and Monsanto. These low-strike catalysts operate at 360–400 °C. Higher temperatures (~600 °C) reduce the SO<sub>2</sub> conversion and lead to structural damage of the catalyst. High-pressure drops across catalyst beds from catalyst dust formed during processing require periodic catalyst removal and screening to remove dust. Ring-shaped catalysts developed by Topsoe and others have lower dust pressure drops and have been widely accepted. Other catalyst shapes used are ribbed rings and cylinders. The usual catalyst loading per 1 t/day sulfuric acid capacity is 150–200 L in a double absorption plant and 200–260 L in a single absorption plant. Bayer developed and operated fluid-bed converters that utilize special 0.3–1 mm abrasion-resistant catalysts.

## Absorption of SO<sub>3</sub>

Sulfur trioxide from the converter is absorbed in 98% H<sub>2</sub>SO<sub>4</sub> recirculated counter currently through a packed tower maintained at 60–80 °C by indirect cooling. The optimum concentration of the absorber acid is near the H<sub>2</sub>O–H<sub>2</sub>SO<sub>4</sub> azeotrope, 98.3% H<sub>2</sub>SO<sub>4</sub>, where the SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and H<sub>2</sub>O vapor pressures are at their lowest values. Absorption efficiencies in excess

of 99.9% generally are obtained. On leaving the converter, the process gas is cooled first with feed gas in a gas–gas heat exchanger and then with boiler water in an economizer to 180–220 °C before it enters the absorber. An impingement separator, or Teflon or glass fiber mist eliminator, is placed in the top of the absorber to remove acid mists. If oleum, or fuming sulfuric acid, is produced at the plant, it is made in a separate oleum tower upstream of the absorber. A portion of the SO<sub>3</sub> stream to the absorber is diverted to the oleum tower where it is absorbed in a recirculating stream of oleum.

In double absorption plants, an intermediate absorber is placed between the second and third (or between the third and fourth) converter beds. By removing SO<sub>3</sub> from the gas stream at this intermediate point, higher SO<sub>2</sub> conversions are attained in the downstream converter beds, and the overall SO<sub>2</sub> conversion is increased. The cooled gas from the intermediate absorber is reheated by hot converter gas in gas–gas heat exchangers before returning to the converter. An oleum tower may be placed before the intermediate absorber.

## Acid Cooling

Absorption of SO<sub>3</sub> in concentrated sulfuric acid and the formation of H<sub>2</sub>SO<sub>4</sub> from SO<sub>3</sub> and H<sub>2</sub>O produce heat in the absorber, as does acid dilution from the addition of makeup water. Process control requires that the acid be cooled before it is recirculated to the dryer or absorber towers or sent to storage. Earlier acid coolers of parallel banks of stacked, irrigated, cast iron sections have been largely replaced by stainless steel shell and tube or plate exchangers, with or without anodic protection. Hastelloy, Sandvik SX, ZeCor, and Saramet alloys and Teflon linings are also used in acid piping and coolers [41–44].

Tail gas emissions are controlled by improving the SO<sub>2</sub> conversion efficiency and by scrubbing the tail gas. In a double absorption process plant, a five-bed converter has 0.3% unconverted SO<sub>2</sub>, as compared with 0.5% for a four-bed

converter. A Lurgi Peracidox scrubber may be used to remove up to 90% of the residual SO<sub>2</sub> in the tail gas from a double absorption plant. Hydrogen peroxide or electrolytically produced peroxymonosulfuric acid is used to convert the SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> in the Lurgi scrubber.

### Other Modifications to the Sulfuric Process [45]

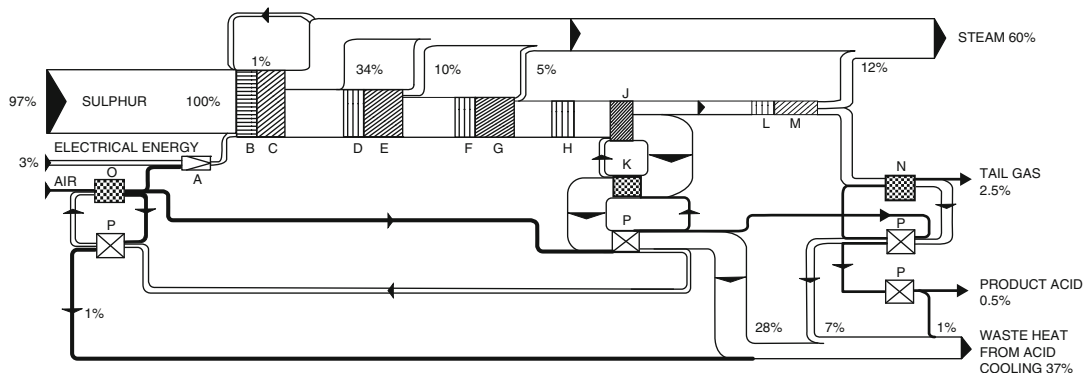
Tail gas from single absorption plants may be absorbed on activated carbon (Sulfacid) or scrubbed with ammonia (Monsanto AMMSOX) or sodium sulfite (Wellman Lord process). Metallurgical acid plants differ from sulfur-burning plants in that the cleaned SO<sub>2</sub> process gas must be heated before it is sent to the converter. Many of these plants have weak SO<sub>2</sub> streams that require large gas-gas heat exchangers for temperature control. Four plants in the Former Soviet Union processing 2–4% SO<sub>2</sub> use an unsteady-state oxidation process in which the cold (40–70 °C) SO<sub>2</sub> gas is reacted on hot catalyst beds without intervening heat exchangers [46, 47]. As the temperature front moves through the bed to the exit side, the flow is reversed. Cycle times are 30–120 min, and single-bed conversions of 80–90% are reported as compared with 55–60% for conventional processes at higher exit temperatures.

The thermal capacity of a 1000 t/day sulfuric acid plant is about 63 MW. This heat liberation must be controlled in a manner that maintains optimum gas temperatures in the converter system and optimum acid temperatures in the dryer and absorber circuits. Tail gas emissions also are affected by the energy balance. Figure 9 shows an energy flow diagram for a contemporary sulfur-burning sulfuric acid plant. About 97% of the total energy input derives from burning sulfur, and 3% comes from the electricity consumed to drive the gases through the plant. Most plants can recover 55–60% of the energy as high-pressure steam (40–60 bar, 400–480 °C), but about 40% is

lost as waste heat dissipated to the environment in the form of hot water from acid coolers.

During the late 1970s, acid plants were optimized to generate more steam. Steam can be produced at pressures up to 80 bar from high-temperature sulfur burners such as the Lurgi two-stage combustion system. The high-pressure steam is reduced to low pressure steam through a turbogenerator that cogenerates electricity. In double absorption plants, economizers were installed upstream or downstream of the heat exchanger servicing the intermediate absorber. Boiler feed water is preheated to 90–95 °C in this economizer to increase steam production. The energy production from acid plants was increased to 70% by installing low-gas temperature economizers, low pressure-drop catalysts, and suction drying towers, by increasing the SO<sub>2</sub> feed gas concentration and by preheating the boiler feed water with hot acid. Further energy recovery requires higher operating temperatures for the absorbers and acid coolers. Venturi concurrent absorbers operating at acid temperatures of 130–140 °C are installed in several plants. To recover acid heat directly as steam, it was necessary to increase the acid temperatures from 110 to 120 °C to about 200 °C.

As of 2005, Monsanto Enviro-Chem had built 21 Heat Recovery System (HRS) units since demonstrating the first HRS at Namhae Chemical in South Korea in 1987 [48, 49]. The process is based on 310 stainless steel, which resists corrosion in 98.5% H<sub>2</sub>SO<sub>4</sub> at temperatures up to 220 °C. The intermediate absorber at Namhae takes 194 °C gas from the converter third stage economizer and absorbs the SO<sub>3</sub> in 199 °C, 99% acid. Recirculated acid from the absorber is cooled from 220 °C in a 10-bar HRS boiler. The added energy recovery for this process is reported to increase the total recovery to 90%. Monsanto's proposed Monarch process combines HRS technology with the wet catalytic converter process (Lurgi) to increase heat recovery and shift it to high-pressure steam production for electric power generation [50].



**Fig. 9** Sankey energy flow diagram for a 1000 ton per day sulfur-burning double absorption sulfuric acid plant (feed gas 10% SO<sub>2</sub>). A blower, B sulfur furnace, C waste heat boiler, D catalyst bed 1, E steam superheater, F catalyst bed 2, G boiler, H catalyst bed

3, J intermediate heat exchangers, K intermediate absorber, L converter bed 4, M economizer, N final absorber, O air dryer, P acid coolers (Courtesy Lurgi GmbH, Frankfurt, Germany)

## Other Sources of Sulfuric Acid

Spent sulfuric acid usually is diluted in the process in which it is used: titanium dioxide pigment processing, plastics manufacture, and so on. The dilute acid may be used in processes requiring dilute acid or may be concentrated for reuse by a number of vacuum evaporation processes (Simonson-Mantius, Chemetics) [51] or by thin-film evaporation (DuPont, Bofors). In the submerged combustion distillation process, water is evaporated from the dilute acid by forcing hot flue gases from a fuel-fired burner below the acid surface (Chemico). The concentration of 75% acid to 95–98% H<sub>2</sub>SO<sub>4</sub> by the Pauling-Plinke process is done by feeding the 75% acid to a stripping column fitted with a stirred cast iron pot mounted in a furnace. The acid concentration in the pot must be kept above 80% to minimize corrosion.

Chemetics has developed a process for treating spent alkylation sulfuric acid with nitric acid to produce a sulfuric acid that can be used to acidulate phosphate rock, the major use for sulfuric acid. The organic contaminants are converted to carbon particles that are removed with the gypsum on filtration of the phosphoric acid. Special alloys are used in the fabrication of the acid reactor. Topsoe developed and, by 2005,

had built more than 45 wet sulfuric acid (WSA) process units. This process is especially suited for low-strength, less than 4%, SO<sub>2</sub> gas streams, which would not be auto-thermal or meet water balance conditions in the conventional dry sulfuric acid contact process. In the WSA process, wet SO<sub>2</sub> gases pass through converter beds where the SO<sub>2</sub> is oxidized to SO<sub>3</sub>. The SO<sub>3</sub> reacts with water vapor to form H<sub>2</sub>SO<sub>4</sub> in the gas phase. The acid is condensed in proprietary WSA condensers. Sulfuric acid is produced at concentrations around 98% [52, 53].

## Production and Consumption of Sulfuric Acid

Total world production of sulfuric acid (1999, 2009, and 2014) is given in Table 7, and total production from pyrites and other forms is given in Table 8. Production increased by about 77 Mt from 1999 to 2014. Output from elemental sulfur feedstock rose about 42%, while that from “other” sources increased by 62%. Increased recovery from smelters was a major contributor in the latter’s increase.

China represents the most dramatic change: 22.5 Mt of output in 1999 versus 79.5 Mt in 2014. Of that, only 5.0 Mt were produced using

**Table 7** World production of new sulfuric acid for 1999, 2009, and 2014 (Million metric tons 100% H<sub>2</sub>SO<sub>4</sub>)

End use	1999		2009		2014		Difference 1999–2014	
	From elemental sulfur	Total	From elemental sulfur	Total	From elemental sulfur	Total	From elemental sulfur	Total
Western Europe	8.5	17.5	5.8	12.1	6.9	14.2	−1.6	−3.3
France	1.4	2.2	0.4	0.6	0.4	0.7	−1.0	−1.5
Germany	1.2	3.0	1.3	3.0	1.5	3.1	0.3	0.1
Spain	0.3	2.8	0.2	1.9	0.1	1.9	−0.2	−0.9
Eastern Europe FSU	10.3	15.6	11.2	17.6	15.0	22.5	4.7	6.9
Poland	1.2	2.0	0.4	1.2	1.2	2.2		0.2
FSU	8.3	12.0	10.0	14.4	13.2	18.4	4.9	6.4
North America	37.6	46.3	29.3	34.4	32.3	39.5	−5.3	−6.8
Canada	1.6	4.8	1.2	3.0	1.2	4.2	−0.4	−0.6
US	33.2	37.2	25.5	27.5	27.9	30.4	−5.3	−6.8
Mexico	2.8	4.3	2.6	3.9	3.2	5.0	0.4	0.7
Asia	17.4	43.3	38.0	82.5	50.8	107.4	33.4	64.1
China	5.0	22.5	28.0	59.7	36.9	79.5	31.9	57.0
Japan	2.2	6.9	1.2	6.3	1.4	7.0	−0.8	0.1
India	5.2	6.1	4.4	7.8	6.4	10.4	1.2	4.3
World Total	103.5	159.6	116.0	190.0	145.0	236.3	41.5	76.7

Source: d'Aquin GE, Fell RC (2012), U.S. Geological Survey estimates

**Table 8** Sulfuric acid production from pyrites and other forms (Million metric tons 100% H<sub>2</sub>SO<sub>4</sub>)

	1999		2009		2014		Difference 1999–2014	
	Pyrites	SOF	Pyrites	SOF	Pyrites	SOF	Pyrites	SOF
Western Europe	2.1	6.9	0.6	5.7	0.8	6.6	−1.3	−0.3
Eastern Europe FSU	1.0	4.3	0.2	6.2		7.5	−1.0	3.2
North America		8.6		5.1		7.2		−1.4
Asia	12.8	13.1	14.0	30.6	19.6	37.1	6.8	24.0
World Total	16.5	40.0	15.0	59.0	20.6	70.8	4.1	30.8

Source: d'Aquin G.E. and Fell R.C., 2012, U.S. Geological Survey estimates

elemental sulfur in 1999 vs. 36.9 Mt in 2014. While China increased output from pyrites slightly, environmental recovery projects at smelters added a considerable volume.

Table 9 lists the sulfuric acid-consuming industries in the United States and shows the trends in their acid consumption rates from the 1980s to date. The largest US sulfuric acid-consuming industry is agriculture. Nearly all the sulfuric acid consumed in agriculture was reacted with phosphate rock (principally Ca<sub>9</sub>(PO<sub>4</sub>)<sub>6</sub>CaF<sub>2</sub>) to produce phosphoric acid. Granular phosphate fertilizers are produced by

ammoniating phosphoric acid to yield mono- and di-ammonium phosphates.

Petroleum refining is the largest nonfertilizer use for US sulfuric acid. The acid competes with hydrogen fluoride as a catalyst in petroleum alkylation reactions for gasoline production. Sulfuric acid acts as a catalyst in synthetic rubber and plastics manufacture. Copper ore leaching is carried out by distributing the acid over leach piles of the ore and collecting the copper-rich leachate for processing. Sulfuric acid from nearby smelters is normally used in copper ore leaching.



**Table 9** Sulfuric-acid-consuming industries in the United States (Million metric tons 100% H<sub>2</sub>SO<sub>4</sub>)

Consuming industries	1979	1989	1999	2009	2014
<i>Agriculture</i>					
Phosphatic fertilizers	23.2	26.4	23.8	16.6	14.7
Nitrogenous fertilizers	0.5	0.3	0.6	0.5	0.5
Pesticides	0.2	0.1			
Other agricultural chemicals	0.2	0.1	3.8	3.2	6.2
Total	24.1	26.9	28.2	20.3	21.4
<i>Other industries</i>					
Petroleum refining	2.4	2.1	5.8	8.1	10.4
Synthetic rubber and plastics	0.6	1.2		0.2	0.1
Rayon and cellulose	0.3	0.2			
Other chemical products	3.2	2.0	0.6	1.2	0.4
Copper ore processing	2.1	1.8	2.2	1.1	0.8
Uranium and other ore processing	0.4	0.1			
Iron and steel	0.9	0.2			
Other metals	0.1	0.2	0.3		0.2
Pulp and paper	0.8	1.0	0.4	0.6	0.4
Pigment and paint	0.6	0.4	0.8	0.9	0.2
Other	1.6	0.9	0.6	0.3	0.2
Total	13.0	10.1	10.7	12.4	12.7

Source: U.S. Geological Survey Minerals Yearbook and U.S. Bureau of Mines: Sulfur Annual Report

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