Sulfur and Sulfuric Acid

Robin W. Strickland, Ph.D.*

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. A yellow solid at normal temperatures, sulfur becomes progressively lighter in color at lower temperatures and is almost white at the temperature of liquid air. It melts at 114 to 119°C (depending on crystalline form) to a transparent light yellow liquid, becoming deep orange as the temperature is increased. The low viscosity of the liquid begins to rise sharply above 160°C, peaking at 93 Pa·s 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 include small rings and chains.

Sulfur also is found as sulfide minerals in combination with iron or base metals (e.g., pyrites) and as sulfates in combination with alkali metals and alkaline earths (e.g., gypsum). Hydrogen sulfide with its “rotten egg” odor is the primary sour component of sour gas. Crude oil and coal contain a variety of complex sulfur-containing organic species. These sulfur compounds are removed from the liquid fuels by treatment with hydrogen to convert the sulfur to hydrogen sulfide, which is taken off in the gas stream. The recovery of sulfur values from sour fuels for environmental reasons is the largest source of sulfur today.

World sulfur production in 1989 was 40 million tons. Over 99 percent of the sulfur that is marketed is sold as crude sulfur. The two primary grades are “bright,” which is bright yellow and at least 99.5 percent (typically 99.9+ %) pure, and “dark,” which can contain upwards of 0.25 percent carbonaceous material. Recovered sulfur generally is bright, whereas mined sulfur often is dark owing to traces of crude oil, which is associated with salt-dome sulfur deposits. Volcanic sulfur deposits yield bright sulfur, but it often is contaminated with toxic metal oxides. Sulfuric acid production accounts for 93 percent of the elemental sulfur production.
used in the United States. Small quantities of several specialty sulfurs are produced for a wide variety of other applications, including fumigation, bleaching, pharmaceuticals, pyrotechnics, rubber making, and cutting oils.

For many years, the standard industry practice was to ship sulfur as a crushed bulk solid. The shipment of dry bulk sulfur, however, is prone to introduce contamination and to generate sulfur dust during handling. The dust presents a potential environmental hazard and can result in dust explosions if proper preventive measures are not taken. In order to minimize these problems, the modern trend in handling solid sulfur is first to form it into slate, prills, pellets, or granules. Canada is a major shipper of formed solid sulfur, and such sulfur is used by many industries in Europe and Asia. In the United States, over 95 percent of crude sulfur is shipped molten in specially designed railcars, tank barges, tank trucks, and ships. Liquid sulfur shipment and storage also is practiced in Europe. Molten sulfur generally is preferred by the sulfuric acid industry, primarily because there is no need for remelting prior to use.

**Development of the Sulfur Industry**

Early humans doubtless 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 used it for medicinal purposes, as a bleach, as a fumigant, as a colorant, and as incense. Its use for these purposes is 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, of which 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. Steam smelting in autoclaves came into use about 1859. In 1890 Gill built a multichamber furnace to improve the process's production rate and efficiency. Italian monopoly of the 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 to 300 meters. Mining was complicated by intervening layers of quicksand and the presence of hydrogen sulfide gas. Numerous conventional mining attempts at Sulphur, LA, proved disastrous. Finally, 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. Ready availability of low-cost sulfur opened the way for commercial sulfuric acid production by burning sulfur. This process largely supplanted the long-standing iron pyrite combustion process for sulfuric acid production by eliminating its extensive gas-cleaning operations.

In 1883 C. F. Claus patented a process for producing sulfur from hydrogen sulfide through partial combustion over an iron oxide catalyst. A number of improvements on the Claus process were made over the next 50 years, but it enjoyed limited success as a method for producing sulfur. Its primary driving force was, and remains, the need for a means to remove the sour component of sour gas for processing reasons and for environmental compatibility. Since the 1950s the demand for larger quantities of cleaner natural gas to meet increasingly more stringent environmental standards has caused a proliferation of the family of Claus processes. The processing of sour gases has increased to the extent that the production of recovered sulfur now exceeds that of mined sulfur.

Sulfur has been 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 SO₂. Hydrometallurgical processes have produced sulfur from metal pyrites as a by-product. These processes do not contribute significant quantities of sulfur to the world markets. The reduction of sulfate ores (e.g.,