

and gypsum<sup>2</sup> (or anhydrite). World stockpiles of sulfur exceed  $26 \times 10^6$  t with Saudi Arabia, Poland, and Iraq likely to increase the oversupply as new sulfur supplies are tapped there.

Over 90 percent of the sulfur used is converted to sulfuric acid, but other industrial uses abound. Some of these are: in the manufacture of wood pulp, carbon disulfide, insecticides, fungicides, bleaching agents, vulcanized rubber, detergents, pharmaceuticals, and dyestuffs. Among some new uses being studied are: (a) as an extender for paving asphalt, (b) sulfur concretes and mortars, (c) plant and soil treatment, (d) sulfur-alkali metal batteries, and (e) foamed sulfur insulation.<sup>3</sup>

## MINING AND MANUFACTURE OF SULFUR

Elemental sulfur ores were mined manually before the development of the Frasch process. The sulfur in these ores was then concentrated by burning part of the sulfur in piles to melt the remainder, drawing off the liquid, and casting it into molds. The development of the Frasch process made such mining impossibly expensive. Native sulfur deposits are mechanically mined in Eastern bloc countries, and to a lesser extent in other countries. Marketable sulfur is produced by heating in autoclaves, drawing off the liquid, and casting it into large blocks from which it is subsequently reclaimed as a solid. Some is converted to flowers of sulfur by distillation (sublimation).

Ores (from volcanic and similar deposits), without upgrading, can be roasted (burned) to make sulfur dioxide gas, which is used to produce sulfuric acid and for other purposes. Elemental sulfur is also produced by removing hydrogen sulfide from natural and refinery gases with absorbents such as mono- and/or diethanolamines. The hydrogen sulfide is then converted to elemental sulfur by the Claus or modified Claus process. This process is described under sulfur from fuel gases.

**FRASCH PROCESS.** The major tonnage of all the elemental sulfur of the world has been obtained from the sulfur-bearing porous limestones of the salt-dome caprocks of Texas, Louisiana, and Mexico by the Frasch process. As early as the late 1890s, Herman Frasch devised his ingenious method<sup>4</sup> of melting the sulfur underground or under the sea and then pumping it up to the surface. Ordinary oil-well equipment is used to bore holes to the bottom of the sulfur-bearing strata, a distance underground from 150 to 750 m. A nest of three concentric pipes, varying in size from 3 to 20 cm in diameter, passes through the sulfur-bearing stratum and rests on the upper portion of the barren anhydrite, as shown in Fig. 4.1. A 10-cm pipe passed through the 20-cm one so that an annular space exists between the two, extends nearly to the bottom of the sulfur-bearing rock, and rests on a collar that seals the annular space between the 20- and the 10-cm pipes. An air pipe, 3 cm in diameter, inside the others, reaches to a depth slightly above the collar mentioned above. The 20-cm pipe is perforated at two different levels, one above and the other below the annular collar. The upper set of perfora-

<sup>2</sup>Higson,  $\text{CaSO}_4$  as a Raw Material for Chemical Manufacture, *Chem. Eng. News* 29 (43) 4469 (1951); Hill, Schonand, and Zergiebal, *Ind. Eng. Chem.* 49 (8) 1204 (1957).

<sup>3</sup>Davis, Sulfur: New Uses Needed, *Chem. Eng.* 79 (17) 30 (1972).

<sup>4</sup>Sulfur Mining at Newgulf, *Chem. Eng.* 48 (3) 104 (1941); Haynes, *The Stone that Burns*. Van Nostrand, New York, 1970.

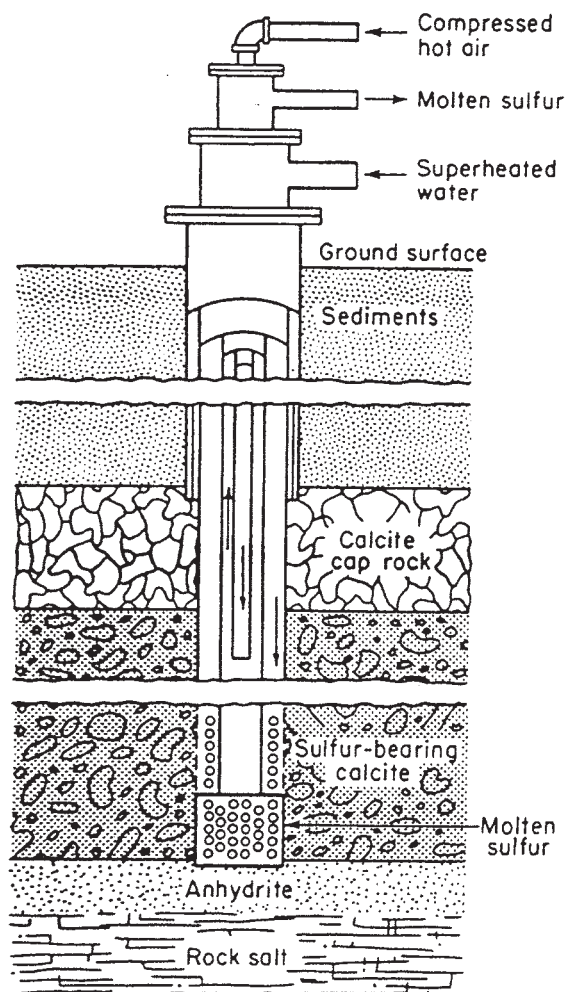


Fig. 4.1. Schematic diagram of the Frasch process for mining sulfur. (McGraw-Hill Encyclopedia of Science and Technology.)

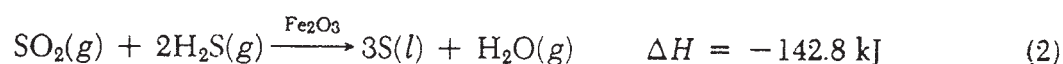
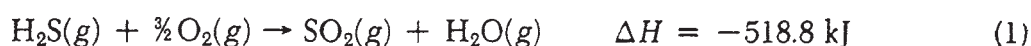
tions permits escape of the hot water, and molten sulfur enters the system through the lower perforations.

For operation of the well, hot water at about  $160^{\circ}\text{C}$  is passed down the annular space between the 20- and the 10-cm pipes. It discharges through the perforations into the porous formation near the foot of the well. The sulfur-bearing rock around the well through which this water circulates is raised to a temperature above the melting point of sulfur, about  $115^{\circ}\text{C}$ . Molten sulfur, being heavier than water, sinks and forms a pool around the base of the well, where it enters through the lower perforations and rises in the space between the 10- and the 3-cm pipes. The height to which the sulfur is forced by the pressure of the hot water is about halfway to the surface. Compressed air forced down the 3-cm pipe aerates and reduces the density of the liquid sulfur so that it will rise to the surface. The compressed air volume is regulated so that the production rate is equalized with the sulfur melting rate in order not to deplete the sulfur pool and cause the well to produce water. Water must be withdrawn from the formation at approximately the same rate as it is injected to prevent a buildup of pressure to the point where further injection would be impossible. Bleed wells for extracting water from the formation usually are located on the deeper flanks of the dome to withdraw the heavier cold water which accumulates there. Water heating capacities of existing power plants are as high as 38,000 t/day. The amount of water required to produce 1 t of sulfur depends on the richness of the deposit and other factors. Requirements may range from 4 to 50 t per metric ton of sulfur mined.

On the surface, the liquid sulfur moves through steam-heated lines to a separator where

the air is removed. The sulfur can be either solidified in large storage vats or kept liquid in steam-heated storage tanks. More than 95 percent of all U.S. sulfur is shipped as a liquid in insulated tank cars, tank trucks, and heated barges or ships. This reduces freight costs and gives the purchaser much purer sulfur.

**SULFUR FROM FUEL GASES.** Increasingly hydrogen sulfide is being removed<sup>5</sup> during the purification of sour natural gas, coke-oven gas, and from petroleum refinery gas by dissolving it in potassium carbonate solution or ethanolamine, followed by heating to regenerate it (see Chap. 6). The hydrogen sulfide thus produced is burned to give sulfur dioxide for sulfuric acid. However, the majority is converted to elemental sulfur by various modifications of the original Claus process, for which the reactions are:



The use of this process is illustrated in the flowchart of Fig. 19.2. Air pollution regulations require new plants to attain over 98 percent conversion, and the province of Alberta, Canada, is asking for 99.5 percent conversion.<sup>6</sup> To meet the new emission regulations, a number of processes have been developed for cleaning the residual sulfur values from the tail gases of recovery plants.<sup>7</sup> A process used to treat the tail gases is shown in Fig. 4.2. Approximately one-half of the world production of elemental sulfur is made by gas treatment.

Other existing or potential sources of sulfur include coke-oven gases and synthetic crude oils from tar sands or shale oil. Tar sands and shale oil plants are being operated in Canada and Brazil.<sup>8</sup> Very little sulfur is presently recovered from coal, but efforts to reduce sulfur dioxide emissions by developing clean fuels from coal could produce significant amounts in the future. Coal cleaning technology can remove about half of the sulfur in coal, but the organic sulfur can be removed only by gasification, liquefaction, and hydrogenation processes. Several such processes are in various stages of development.<sup>9</sup> Where sulfur-containing

<sup>5</sup>Brennan, Amine Treating of Sour Gas: Good Riddance to  $\text{H}_2\text{S}$ , *Chem. Eng.* 69 (22) 94 (1962); Heppenstall and Lowrison, The Manufacture of Sulfuric Acid, *Trans. Inst. Chem. Eng.* 31 389 (1953); Sulfur from  $\text{H}_2\text{S}$ , *Chem. Eng.* 59 (10) 210 (1952); Duecker and West, op. cit. chaps. 4, 5, and 9; Estep, McBride, and West, *Advances in Petroleum Chemistry and Refining*, vol. VI, chap. 7, Interscience, New York, 1962.

<sup>6</sup>Rowland, *Oil Week*, Oct. 23, 1974, p. 9.

<sup>7</sup>Aquitane Cleans Claus Tail Gas with Sulfreen Unit, *Oil Gas J.* 70 (26) 85 (1972); Davis, Add-on Process Stems  $\text{H}_2\text{S}$ , *Chem. Eng.* 79 (11) 66 (1972); Barry, Reduce Claus Sulfur Emission, *Hydrocarbon Process.* 51 (4) 102 (1972); Chalmers, Citrate Process Ideal for Claus Tail-gas Cleanup, *Hydrocarbon Process.* 53 (4) 75 (1974); Ludberg, "Removal of Hydrogen Sulfide from Coke Oven Gas by the Stretford Process," paper presented at the 64th annual meeting of the Air Pollution Control Association, Atlantic City, N.J., 1971.

<sup>8</sup>Pattison, Oil Begins to Flow from Canadian Tar Sands, *Chem. Eng.* 74 (24) 66 (1967); Franco, Brazil Tries New Shale Oil Process, *Oil Gas J.* 70 (37) 105 (1972).

<sup>9</sup>Chohey, Taking Coal's Sulfur Out, *Chem. Eng.* 79 (16) 86 (1972); *Environ. Sci. Technol.* 8 (6) 510 (1974).