

US EPA ARCHIVE DOCUMENT

SULFUR

A. Commodity Summary

The United States is the world's foremost producer and consumer of sulfur and sulfuric acid, with production from Frasch, recovered, and byproduct sources. According to the U.S. Bureau of Mines, sulfur (in all forms) was produced at 169 operations in 30 states, Puerto Rico, and the U.S. Virgin Islands for a total shipment value of nearly \$500 million in 1994. Texas and Louisiana accounted for nearly 50% of domestic production. Agricultural chemicals (fertilizers) accounted for 61% of sulfur demand; organic and inorganic chemicals accounted for 10%; metal mining accounted for 5%; and petroleum refining accounted for 7%. Other miscellaneous uses, accounting for 17% of demand, were widespread because many products produced by industry require sulfur in one form or another during some stage of their manufacture.¹

Sulfur is a non-metallic element widely used in industry both as elemental sulfur (brimstone) and as sulfuric acid. Sulfur production is from three sources: combined sulfur, recovered sulfur, and formed sulfur. Combined sulfur occurs in natural compounds such as iron pyrite, copper sulfides, and gypsum. Recovered sulfur is produced as a byproduct of other processes such as oil refining or air pollution control. Formed sulfur is elemental sulfur cast or pressed into particular shapes to enhance handling and to suppress dust generation and moisture retention.²

In 1994, recovered elemental sulfur was produced by 59 companies at 150 plants in 26 states, one plant in Puerto Rico, and one plant in the U.S. Virgin Islands. Byproduct sulfuric acid was produced by 16 facilities in 1994.³ The three companies listed in Exhibit 1 produce the bulk of mined sulfur in the United States. These three companies accounted for 32% of the U.S. production of sulfur in all forms in 1990. All three companies use the Frasch process for sulfur mining. Penzoil produces sulfur from its Culberson mine in western Texas and is currently engaged in exploration activities in western Texas, the Gulf Coast, and elsewhere. Texasgulf currently operates one mine in Texas (Boling dome), extracting about 40,000 tpy of sulfur. Freeport currently operates two mines in the Gulf Coast.⁴ The names and locations of the smaller facilities are not available.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Sulfur is mined from both surface and underground deposits, and is recovered as a byproduct from a number of industrial processes. In sulfur mining, three techniques are applied: conventional underground methods, conventional open pit methods, and the Frasch mining method. About 90% of all sulfur mined is obtained through Frasch mining.⁵ Frasch mining and sulfur production from recovered, combined, and formed sulfur are described below in addition to the production process for sulfuric acid.

¹ Joyce Ober, "Sulfur," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 166-167.

² Gregory R. Wessel, "Sulfur Resources," from Industrial Minerals and Rocks, 6th edition, Society for Mining, Metallurgy, and Exploration, 1994, pp. 1011-1046.

³ Joyce Ober, 1995, Op. Cite., pp. 166-167.

⁴ Gregory R. Wessel, 1994, Op. Cit., pp. 1011-1046.

⁵ Ibid.

EXHIBIT 1

SUMMARY OF MAJOR PRIMARY SULFUR PROCESSING FACILITIES

Facility Name	Location
Freeport Sulphur Co.	Caminada, offshore LA
Penzoil Sulphur Co.	Culberson, W. TX
Texasgulf Inc.	Boling, TX

2. Generalized Process Flow

Frasch Mining

The Frasch mining process uses hot water to melt sulfur trapped in salt domes. The sulfur is then pumped to the surface and is either sold as a liquid or cooled and solidified into a number of forms for market. Exhibit 2 presents a process flow diagram for the Frasch process.

Recovered Elemental Sulfur (Claus Process)

Recovered elemental sulfur is a non-discretionary byproduct of petroleum refining, natural gas processing, and coking plants. Recovered sulfur is produced primarily to comply with environmental regulations applicable directly to processing facilities or indirectly by restricting the sulfur content of fuels sold or used. The principal sources of recovered sulfur are hydrogen sulfide in sour natural gas and organic sulfur compounds in crude oil. Recovery is mainly in the elemental form, although some is converted directly to sulfuric acid. Sulfur in crude oil is recovered during the refining process. Organic sulfur compounds in crude oil are removed from the refinery feed and converted to hydrogen sulfide by a hydrogenation process. The sulfur in natural gas is already in the form of hydrogen sulfide. Hydrogen sulfide from both sources is converted to elemental sulfur by the Claus process. In this process, concentrated hydrogen sulfide is fired in a combustion chamber connected to a waste heat boiler. Air is regulated to the combustion chamber so that part of the hydrogen sulfide is burned to produce sulfur dioxide, water vapor, and sulfur vapor. The high temperature gases are cooled in a waste heat boiler and sulfur is removed in a condenser. The efficiency of the process is raised by adding as many as three further stages in which the gases leaving the sulfur condenser are reheated and passed through catalytic converters and additional condensers. Finally, the total gas stream is incinerated to convert all remaining sulfur-bearing gases to sulfur dioxide before release to the atmosphere. The sulfur is collected in liquid form. Exhibit 3 presents a process flow diagram for the Claus process.

Combined Sulfur

Combined sulfur can be recovered during the smelting of nonferrous sulfides. Sulfur dioxide in the smelter gases is converted to sulfuric acid, liquid sulfur dioxide, or oleum. In the United States, byproduct sulfuric acid from nonferrous metal smelters and roasters supplied about 11% of the total domestic production of sulfur in all forms in 1990. Sulfur may also be recovered from sulfur dioxide emissions. Regenerative or throwaway flue-gas desulfurization methods may be used either to recover sulfur in a useful form or to dispose of it as solid waste. Both recovery methods may employ wet or dry systems and use a variety of compounds such as limestone, sodium carbonate, and magnesium oxide to neutralize or collect the sulfur dioxide. End products include gypsum, sulfuric acid, liquid sulfur dioxide, and elemental sulfur, all of which can be used if a local market exists. If no local markets exist, large

EXHIBIT 2
FRASCH PROCESS

Graphic Not Available.

Source: [Multi-Media Assessment of the Inorganic Chemicals Industry](#), 1980, Chapter 14.

EXHIBIT 3
CLAUS PROCESS

Graphic Not Available.

Source: Multi-Media Assessment of the Inorganic Chemicals Industry, 1980, Chapter 14.

quantities of gypsum or sulfuric acid may have to be neutralized or otherwise disposed.⁶

Formed Sulfur

Formed sulfur may be made in one of several forms, including: flakes, slates, prills, nuggets, granules, pastilles, and briquettes. To produce flakes, the sulfur is cooled and solidified on the outside of large rotating drums, from which it peels off into small flakes. To produce slates, molten sulfur is cast onto a continuous conveyor belt and is cooled with air or water so that it solidifies into a thin sheet. As the slate reaches the end of the belt, the sheet breaks into smaller pieces. Sulfur prilling can be accomplished with air or water. In air prilling, molten sulfur is sprayed from the top of a tower against an upward flow of air. As it falls, the sulfur breaks into small droplets and cools into prills. In water prilling, the sulfur is sprayed into tanks containing water, from which the prills are collected and dried. Minor modifications to prilling techniques are used to produce nuggets. Granulation involves applying successive coats of sulfur to solid particles of sulfur in a granulator until the particle size reaches the required diameter. In the Procor GX granulation process, liquid sulfur is sprayed into a rotating drum in which small seed particles of sulfur are recycled from the end of the process. Pastilles are individual droplets of molten sulfur that have been dropped on a steel belt and cooled by conduction. The Sandvik Rotoform process uses a patented Rotoformer to distribute the sulfur on the belt. At the end of the belt, the pastilles are scraped off and fall onto a collecting conveyor.⁷

Sulfuric Acid

Sulfuric acid is usually produced near consumption sites. To produce sulfuric acid, elemental sulfur or any number of sulfur-bearing materials are burned. The resulting sulfur dioxide is mixed with additional air or oxygen and passed through a packed bed of supported vanadium pentoxide catalyst. The sulfur dioxide is converted to sulfur trioxide. The gases emerging from the catalytic reactor are cooled and absorbed in 98-99% sulfuric acid to generate 98-99% acid. Plants can be either single or double absorption units. In double absorption units, tail gases from the initial absorption step are mixed with additional sulfur dioxide, reheated and passed through another catalytic reactor to form additional sulfur trioxide. This material is cooled and absorbed in a second stream of sulfuric acid to generate additional 98-99% sulfuric acid. Exhibit 4 presents a process flow diagram for the production of sulfuric acid.⁸

The process is modified somewhat if feed materials other than pure sulfur are used. Materials such as spent sulfuric acid, hydrogen sulfide, and off-gases from smelters are also used for the manufacture of sulfuric acid.⁹

If spent acid is the feed material, it is thermally decomposed to yield a gas stream containing sulfur dioxide, small amounts of sulfur trioxide, water vapor, and small amounts of organic materials. The gas stream is cooled or the sulfuric acid is scrubbed to condense out water and organics, and is then demisted to remove residual water. The purified sulfur dioxide gas stream is reheated, mixed with additional air or oxygen, and sent to catalytic converters. The process proceeds from this point as it does with pure sulfur as the feed.¹⁰

⁶ Ibid.

⁷ Ibid.

⁸ U.S. Environmental Protection Agency, Multi-Media Assessment of the Inorganic Chemicals Industry, Vol. III, 1980, Chapter 14.

⁹ Ibid.

¹⁰ Ibid.

EXHIBIT 4
SULFURIC ACID PRODUCTION

Graphic Not Available.

Source: [Multi-Media Assessment of the Inorganic Chemicals Industry](#), 1980, Chapter 14.

When smelter or pyrite roasting off-gases containing sulfur dioxide are used as the feed material, the gas stream is passed through a series of dry filtration devices to remove entrained particulate matter. The gas is cooled to remove water vapor before it can be used in the process.¹¹

Sulfur from pyrite is produced by roasting the iron sulfide to produce sulfur dioxide gas and iron oxide solid. The gas is treated to produce either elemental sulfur or sulfuric acid and the iron oxide is sold as feed for iron making. There are no wastes from this process.¹²

3. Identification/Discussion of Novel (or otherwise distinct) Process(es)

There has been sporadic production of elemental sulfur from volcanic deposits in the western United States, but the selective mining techniques used would eliminate the generation of wastes.¹³

4. Beneficiation/Processing Boundaries

Frasch Processing

Based on a review of this process, there are no mineral processing operations involved in the production of sulfur via the Frasch process.

Claus Process and Combined Sulfur

Based on EPA's review of these processes, both were determined to start with sulfur recovered from other operations such as petroleum refining and other mineral smelting operations and as such, are completely outside the scope of the Mining Waste Exclusion.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Based on existing data and best engineering judgement, none of the wastes listed below from sulfur production are expected to exhibit characteristics of hazardous waste. Therefore, the Agency did not evaluate these materials further.

Frasch Process Wastestreams

Wastewater. Wastewater from Frasch mining may contain 600 to 1,000 ppm dissolved sulfides and 14,000 to 60,000 ppm of dissolved chlorides. Bleed water retrieved from the formation is produced in amounts ranging from 38,000,000 to 1.6 billion liters per day. Well seal water is generated in amounts ranging from 5,000 to 20,000 liters per day and contains up to 60 ppm dissolved sulfides. At anhydrite plants, seal water and water recovered from the formation are treated and reused. At off-shore salt dome plants, bleed water and seal water are combined and discharged without further treatment. At on-shore facilities, bleed water, area runoff, seal water, and other wastewater are combined and sent to aeration lagoons. There, sulfides are oxidized to sulfates and thiosulfates. The sulfide content of the raw effluent is reduced from the range of 600 to 1,000 ppm to the range of 10 to 40 ppm prior to discharge.¹⁴

Air emissions. Emissions from the mine, generated during sulfur recovery, may contain hydrogen sulfide. The hydrogen sulfide fugitive emissions may range from 0 to 5 kg per kkg of product.¹⁵

¹¹ Ibid.

¹² Ibid.

¹³ U.S. Environmental Protection Agency, "Sulfur," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-55 - 2-56.

¹⁴ U.S. Environmental Protection Agency, 1980, Op. Cit, Chapter 14.

¹⁵ Ibid.

Sludge. Calcium carbonate sludge is generated by water pre treatment and ranges from 9 to 15 kg per kkg of product. The calcium carbonate water treatment sludge is recovered and reused. At anhydrite plants, it is used as drilling mud.

Filter cake. At salt dome plants, about 3.5 kg per kkg of product of waste filter cakes from sulfur filtration are generated. At salt dome facilities, filter cakes from sulfur purification are stored for future recovery of additional product.

Miscellaneous wastes such as **residues** and **spilled sulfur** are generated from the Frasch process. After processing, residues are landfilled.

2. Mineral Processing Wastes

Based on existing data and best engineering judgement, the wastes listed below from sulfur production and sulfuric acid production are not primary mineral processing wastes. Therefore, the Agency did not evaluate these materials further.

Claus Process

Tail gases. An airborne waste from product recovery is generated and contains unconverted hydrogen sulfide gas ranging from 5,000 to 12,000 ppm, 300 to 500 ppm carbon disulfide, 300 to 5,000 ppm carbon oxysulfide, and up to 200 ppm sulfur vapor. (The carbon disulfide and carbon oxysulfide are produced by side reactions of organic compounds present in the feed stream and sulfur dioxide generated in the process.) From 950 to 4,400 cubic meters of tail gases are produced per kkg of sulfur product.¹⁶ Tail gases are typically recovered and processed to recycle sulfur compounds. There are several methods used to recover sulfur compounds from these gases. The processes are described briefly below.

The SCOT process reconverts sulfur compounds in tail gases to hydrogen sulfide. This stream is scrubbed from the tail gases with amine solution, the regeneration of which releases a purified hydrogen sulfide which is recycled to the Claus process. This process recovers over 98% of the sulfur compounds in the tail gases.¹⁷

The Beavon and Stretford processes are also used to recover sulfur from tail gases. The Beavon process catalytically reduces sulfur oxides to hydrogen sulfide and the Stretford process removes the hydrogen sulfide by absorption in an amine solvent. Regeneration of the solvent releases a purified hydrogen sulfide which is converted to sulfur. About 98% removal of sulfur compounds from the tail gases is achieved.¹⁸

The Citrate process, developed by the Bureau of Mines, and the Wellman Lord process are used to recover most sulfur compounds from the tail gases as sulfur. These processes involve reduction of the sulfur dioxide present in the tail gases to sulfur.¹⁹

Spent catalysts. Spent catalysts are recycled or landfilled.²⁰

Sulfuric Acid Production

Airborne emissions from double absorption plants range from 0.5 to 3 kg per kkg of sulfur dioxide and from 0.1 to 0.15 kg per kkg of sulfuric acid mists. The high end of the range represents plants using wet feed materials. Emissions from single absorption plants are controlled in one of five ways: (1) demisters and wet scrubbers, (2) scrubbing with aqueous ammonia solutions, (3) the Wellman Lord process, (4) molecular sieves to absorb sulfur dioxide, and (5) no control.²¹

¹⁶ Ibid.

¹⁷ Ibid.

¹⁸ Ibid.

¹⁹ Ibid.

²⁰ Ibid.

²¹ Ibid.

Wastewater. This wastewater includes waste water from wet scrubbing, spilled product, and condensates. This waste contains dissolved sulfur dioxide and sulfuric acid values. This wastewater is usually neutralized and lagooned to settle suspended solids prior to discharge.²²

Spent catalyst. Spent catalyst, generally vanadium pentoxide, are usually landfilled and sometimes reprocessed.²³

D. Ancillary Hazardous Wastes

Ancillary hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents (e.g., petroleum naphtha), acidic tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, waste oil (which may or may not be hazardous) and other lubricants.

²² Ibid.

²³ Ibid.

Bibliography

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