

**U.S. DEPARTMENT OF THE INTERIOR**

**U.S. GEOLOGICAL SURVEY**

**MATERIALS FLOW OF SULFUR**

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# MATERIALS FLOW OF SULFUR

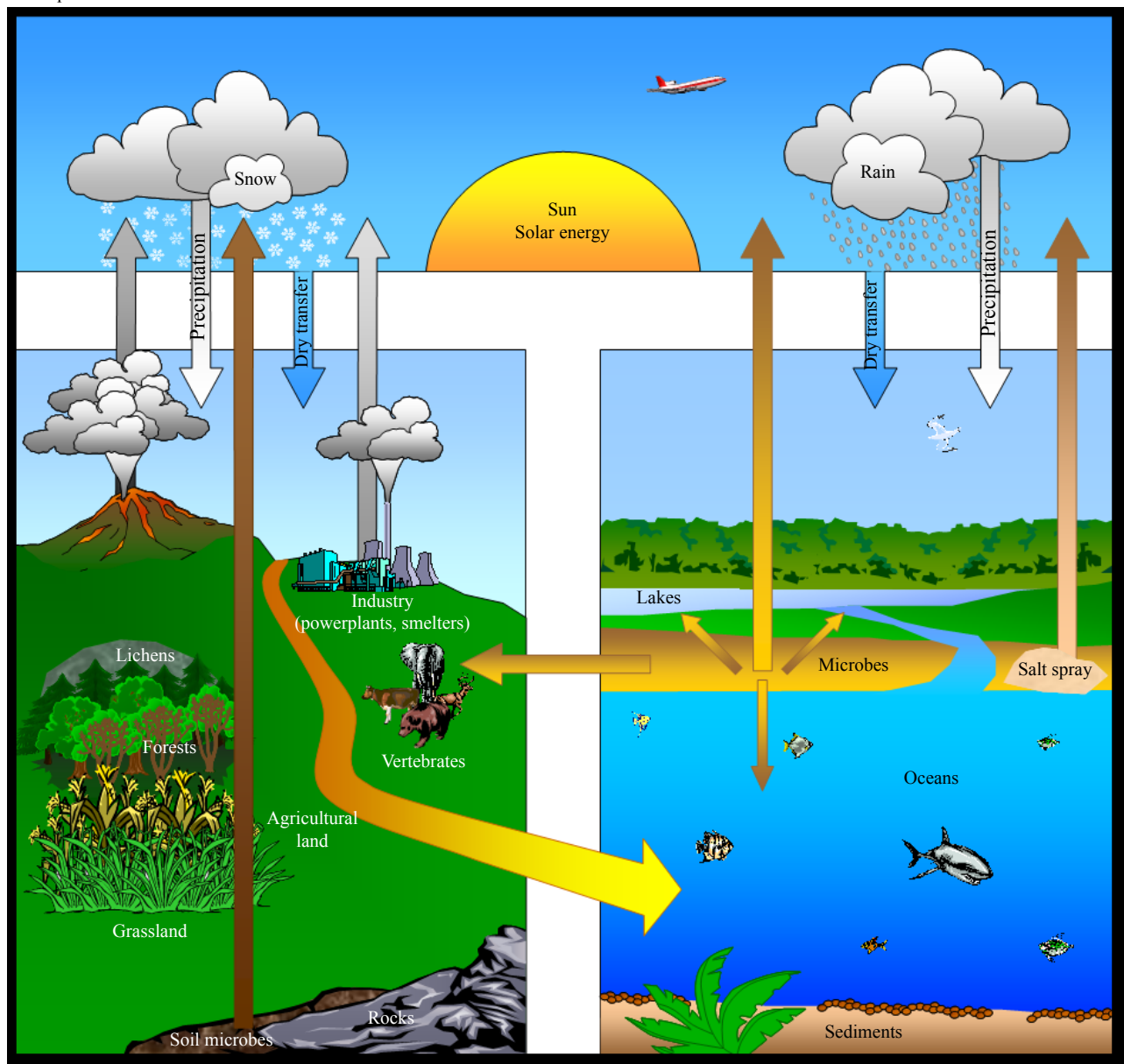
By Joyce A. Ober

## INTRODUCTION

Sulfur has long been an important component of worldwide industry. The Egyptians used sulfur compounds to bleach fabric as early as 2000 B.C., and sulfur was crucial to create specifically colored pigments used a few hundred years later. The ancient Greeks used sulfur as a disinfectant, and the Romans used it in pharmaceutical applications. When the Chinese developed gunpowder in the 13th century, sulfur was an essential component. The Industrial Revolution expanded demand for sulfur used in the production of sulfuric acid, an essential component of myriad industrial processes (Bodenlos and Nelson, 1979, p. 459). The consumption of sulfuric acid has been considered an indicator of the condition of a nation's industrial activity (Sander and others, 1984, p. 261). The more sulfuric acid consumed, the greater the industrial activity and, thus, the more robust the economy.

When considering the materials flow of any mineral, the global cycle must be considered. The scope of the global sulfur cycle dwarfs those of most other materials and is illustrated in figure 1. More than 50 million metric tons per year (Mt/yr) of sulfur in all forms is produced worldwide for industrial consumption. The natural sulfur cycle is much harder to quantify but may be comparable in size. In addition, burning fossil fuels, especially coal, liberates tremendous quantities of sulfur dioxide ( $\text{SO}_2$ ), only some of which is recovered as byproduct sulfur compounds or waste material through gas-cleaning processes; the rest is released into the atmosphere.

Atmospheric



Terrestrial

Aquatic

Figure 1. Graphic that illustrates the variety of ways that sulfur enters the environment and is transported throughout it.

The sulfur industry is different from many other important modern mineral industries in that the disposal of excess supplies of sulfur is becoming a more important issue than that of how to maintain sustainable production. Unlike other industries, which are searching for economical methods to produce a usable product from decreasing reserves and poorer grades of ore, sulfur producers must strive to find innovative uses for the continually growing sulfur supplies. As environmental concerns increase, the trend is to minimize the effects of mining by recycling mineral materials or substituting with more environmentally-friendly products. For the sulfur industry, however, increased environmental awareness results in further increases in the sulfur supply and smaller increases in the demand for sulfur in many industrial processes.

The unusual sulfur situation is a result of the changes of sulfur supply sources over the past 70 years. Whereas many mineral commodities are produced as a primary product from the mining of discrete ore bodies or as desirable byproducts from mineral processing, all the sulfur produced in North America is the result of environmental measures implemented to reduce emissions of  $\text{SO}_2$  into the atmosphere at petroleum refineries and nonferrous metal smelters and to remove poisonous hydrogen sulfide ( $\text{H}_2\text{S}$ ) gas from natural gas. Voluntary sulfur production, whether in the form of mined elemental sulfur or pyrites that are produced and burned to recover their sulfur content as sulfuric acid, has become continually less important in the global sulfur supply equation.

## THE GLOBAL SULFUR CYCLE

Although most chemical elements have a global cycle, the global sulfur cycle is unusually active and pervasive with inputs from natural and man-made sources. Much of the cycle is difficult to quantify. The amount of sulfur that is produced through mining or as environmental byproducts at oil refineries, natural gas processing plants, and nonferrous metal smelters is reasonably well defined; but the quantity of  $\text{SO}_2$  released from electric powerplants and industrial facilities in developing countries is harder to measure. Estimates of sulfur emissions from natural sources are even more difficult to determine because of the variety of sources, the variability of emissions over time, the wide range of compounds involved, and the difficulties in measuring in remote locations. Even so, the varied aspects of the sulfur cycle must be discussed, however briefly, and taken into consideration when investigating the material flow of sulfur. Another interpretation of the global sulfur cycle is shown in figure 2.

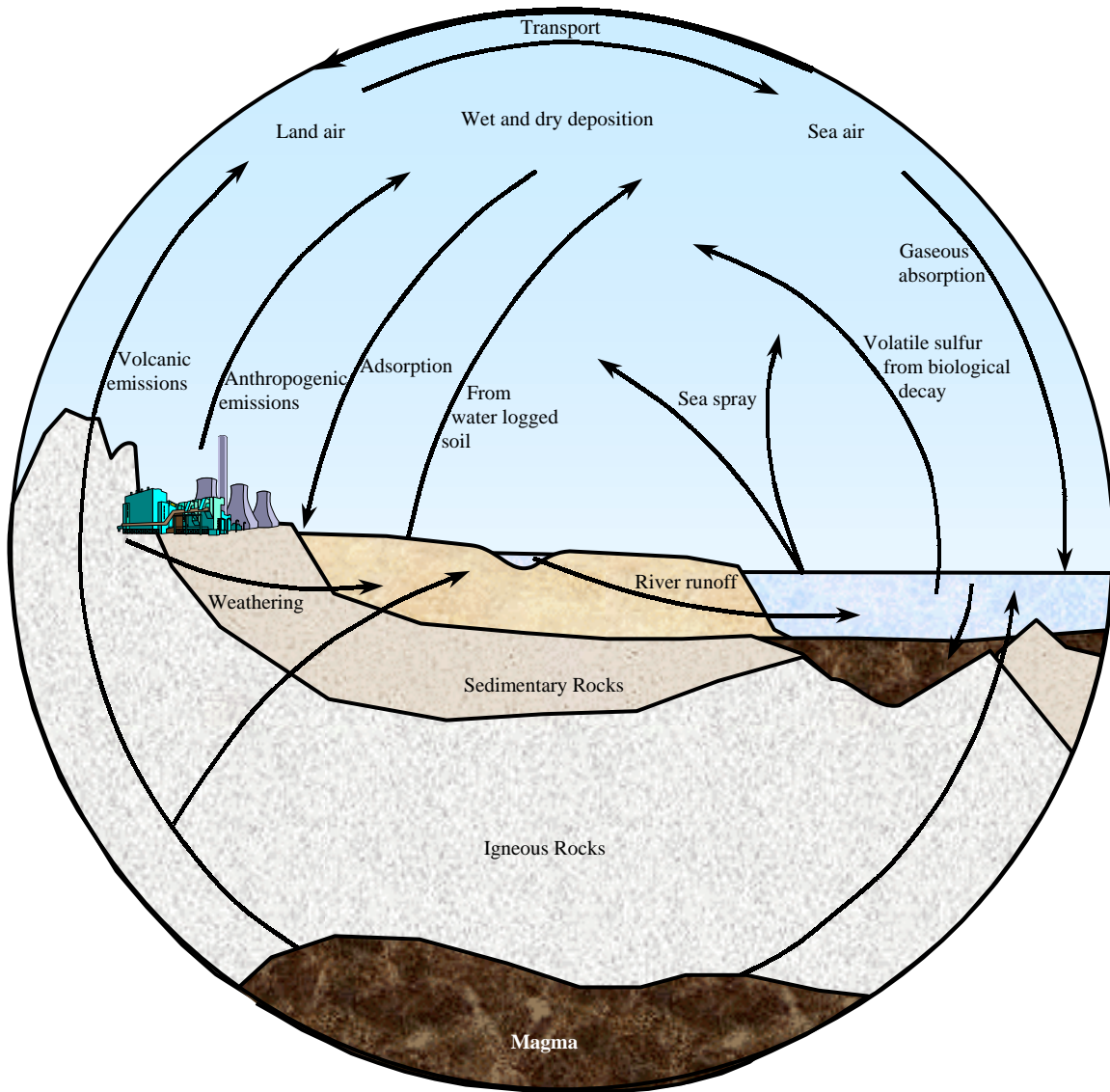


Figure 2. Chart that shows the many sulfur sources in the global cycle. Anthropogenic emissions (those caused by humans) have been studied with the intent of limiting and eliminating them. Natural emissions have occurred throughout history and will continue to maintain a dynamic sulfur cycle.

### The Natural Sulfur Cycle

The natural sulfur cycle is extremely complex and difficult to measure. Much work has been done to establish values for natural sulfur fluxes, but comparisons of these studies show tremendous variability in the estimates. Part of the problem is the pervasiveness of sulfur in nature. Sulfur is a component of many forms of rock and is estimated to average 260 grams per metric ton in the Earth's

crust, making it the 16th most abundant element (Hedrick, 1995). Another estimate suggests that it makes up 0.048 percent of the lithosphere and is the 15th most common terrestrial element, and one more source places sulfur as the 13th most abundant element making up approximately 0.06 percent of the Earth's crust (Fischer, 1984, p. 7, Bush and Semrad, 1996, p. 269). These discrepancies demonstrate the difficulty inherent in quantifying sulfur in the environment.

Sulfur occurs in the Earth's crust in a wide range of minerals and is one of the few elements that can be found in nature in its elemental state. It is found also in coal, crude oil, and natural gas in the form of many different compounds and in varying quantities. Sulfur is essential in all living things, both plants and animals (Moss, 1978). A comprehensive discussion of the pathways by which sulfur cycles throughout nature is not necessary in this context, although a brief description of some of the input sources may be useful. Table 1 lists various estimates of natural inputs to the global sulfur cycle. Estimates vary considerably, further illustrating the difficulty in determining the scope of the natural cycle.

Table 1. Natural Inputs to the Global Sulfur Cycle  
(Million metric tons per year)

	Erickson, 1960	Kellogg and others, 1972	Friend, 1973	Granat and others, 1976	Ivanov, 1983	Butcher, 1992
Biological decay:						
On land .....	110	90 (total)	58	5	18	18
In oceans .....	170	--	48	27	23	39
Volcanic activity .....	--	1.5	2	3	28	28
Sea spray:						
To ocean .....	40	44	40	40	--	--
To land.....	5	3	4	4	--	--
Total.....	45	47	44	44	140	140
Aeolian (wind-driven).....	--	--	--	0.2	20	20

Sulfide minerals in the lithosphere are weathered to sulfates, some of which eventually reach the oceans through river runoff and erosion. The sulfates that reach the oceans become components of marine sediment. Other weathered sulfates react with bacteria to form compounds that are incorporated into the soil and plant systems. Animals may then ingest the plants and the sulfur compounds are ultimately returned to the environment as sulfates (Moss, 1978, p. 27-29).

Perhaps the best known and certainly the most dramatic natural sources of sulfur are volcanoes. Most volcanic emissions of sulfur compounds occur during noneruptive periods of volcanic activity, but sulfur also is emitted during eruptions (Whelpdale, 1992, p. 6). Volcanic emissions are primarily SO<sub>2</sub> and H<sub>2</sub>S, but small quantities of sulfur trioxide (SO<sub>3</sub>), various sulfates, and elemental sulfur also may be emitted (Kellogg and others, 1972 p. 590). Most volcanic emissions enter the atmosphere, but some deposits, especially elemental sulfur, are found surrounding the volcano. Because of the nature of volcanoes, atmospheric sulfur concentrations can vary significantly with time and distance from the volcano. There are also significant variations in emissions from different volcanoes (Kellogg and others, 1972, p. 590).

Seawater contains about 2.65 milligrams of sulfate per gram of water. As bubbles of seawater break, particles of sea salt are formed and emitted into the atmosphere. This sea spray is one of the largest sources of sulfur in the atmosphere, especially over open oceans. About 90 percent of this material is believed to cycle back into the oceans with the remainder passing over the continents (Kellogg and others, 1972, p. 590). The sulfate in the seawater may come from the weathered minerals discussed previously or through the decay of oceanic organisms.

One of the more recent estimates of natural sulfur sources in the atmosphere places the input from open-ocean biogenic production—derived from the physiological activities of organisms—at 46 percent of total natural sulfur in the atmosphere; volcanic production, 18 percent; aeolian production from dust, 16 percent; terrestrial plant and soil production, 13 percent; biomass burning production, 4 percent; and coastal zone and wetland biogenic production, 3 percent (Whelpdale, 1992, p. 6).

### The Anthropogenic Sulfur Cycle

The amount of sulfur entering the atmosphere through human activity—the anthropogenic sulfur cycle—is easier to define than the natural sulfur cycle, but significant uncertainties remain to its size in less developed areas of the world. The majority of anthropogenic sulfur emissions are in the form of SO<sub>2</sub> resulting from the burning of fossil fuels—coal, petroleum, and natural gas—the smelting of nonferrous metal ores, and other industrial processes and burning (Whelpdale, 1992, p. 6). Nearly all of this sulfur is emitted into the atmosphere in the Northern Hemisphere.

Globally, man-made sulfur inputs to the atmosphere began to increase significantly early in the 20th century, and the trend continued until about the mid-1970s when environmental regulations in North America and Western Europe began to limit allowable sulfur emissions. Federal environmental regulations in the United States were first enacted in 1955 and have expanded ever since. A timeline listing important U.S. environmental legislation is shown in figure 3. The initial legislation provided funds to study the growing problem; the first direct legislation for pollution abatements was enacted in 1963. The U.S. Environmental Protection Agency (EPA) was established in 1970 and was given the responsibility of setting national pollution standards (U.S. Energy Information Agency, 1997, p. 59-61).

Environmental regulations have reduced the quantity of SO<sub>2</sub> emitted into the atmosphere, but they have not eliminated the problem. Significantly decreased emissions have been realized at many industrial facilities, but statistics on actual emissions are not readily available. Emissions at electric powerplants, especially those that are coal-fired, continue to contribute significantly to the global sulfur cycle. Of the 3.8 trillion kilowatthours of electricity generated domestically in 2000, 52 percent was produced at coal burners. About 92 percent of all coal consumed was used to produce electricity (U.S. Energy Information Administration, 2001, p. 197).

Phase I of the Clean Air Act Amendments of 1990 dealing with acid rain reduction required substantial reductions of SO<sub>2</sub> emissions from 435 electric utilities and industrial boilers; phase II, which is more stringent than phase I, began in 2000 (U.S. Energy Information Administration, 1997, p. vii). The primary goal of the entire Acid Rain Program was to reduce annual SO<sub>2</sub> emissions from electric utilities to 10 million metric tons (Mt) less than was emitted in 1980 (U.S. Energy Information Administration, 1997, p. 45). Changes in SO<sub>2</sub> emissions since 1980 are illustrated in three maps using EPA data in figure 4.

The operators of the facilities chose from several options for meeting emission reduction requirements. The most popular and the least expensive method chosen for reducing emissions was switching fuel to lower sulfur coal or blending coals with different sulfur levels to obtain a lower average sulfur content. Much of the SO<sub>2</sub> emission problems originate at powerplants in the eastern region of the United States. Coal supplies are plentiful there but relatively high in sulfur. Many eastern power facilities began to purchase low-sulfur western coal or specified lower sulfur content in eastern coal that was purchased (U.S. Energy Information Administration, 1997, p. 5-6). Other utilities did not actually reduce their emissions but purchased additional allowances so that they were able to make no changes. Emission allowances were an important part of the legislation, permitting allocated allowances to be used by individual operations to meet emission requirements. When companies met or surpassed their required emissions reductions, they were able to sell their allowances to the highest bidders, who could be other utilities. Some of these allowances were purchased by nonindustrial groups that, in effect, retired the emission allowances, permanently removing that pollution from the equation (U.S. Energy Information Administration, 1997, p. 5-6).

The most expensive strategy for reducing emissions was the installation of flue gas desulfurization (FGD) equipment that cleaned the SO<sub>2</sub> from the system off-gases. These systems also are the most efficient emission reducing strategy, with the capability to remove 95 percent or more of the SO<sub>2</sub> from stack gases. There are many different FGD systems, but all rely on a chemical reaction with a sorbent to remove SO<sub>2</sub>. The systems use either wet or dry processes and produce waste or byproducts of high volume. The most common scrubbing systems result in a synthetic gypsum FGD material (U.S. Energy Information Administration, 1997, p. 9-10). In 2000, 23.3 Mt of FGD materials was produced as coal combustion products; 4.38 Mt, or 18.8 percent, found commercial application. About 70 percent of that was FGD gypsum used in wallboard, a manufactured building material used to make walls and ceilings in building construction (Kalyoncu, 2001). Although still a minor contributor to domestic wallboard production, FGD gypsum use in this application is growing, and most new wallboard plants are being built with the intention of using FGD gypsum instead of mined gypsum (Olson, 2001).

Several outdated and small-capacity powerplants were closed rather than alter their units to reduce emissions. Another strategy that was used on a limited basis to reduce emissions from electric utilities was repowering. Some operations were repowered to use fuels other than coal, such as fuel oil or natural gas, fuels that burn cleaner than coal (U.S. Energy Information Administration, 1997, p. 11).

Emissions were considerably lower in 1999, the last year for which complete data are available, than they were before the legislation was enacted in 1989, as shown in table 2. Even these reduced emissions, however, continue to represent the largest man-made source of sulfur emissions. It is too early to measure the effects of phase II that effects more than 2,000 facilities and requires emission allowances that are one-half those in phase I.

The regulations focused on coal-burning powerplants have reduced atmospheric SO<sub>2</sub> emissions, but have not significantly contributed to the availability of commercial sulfur products. One powerplant repowered to a coal gasification process that produces elemental sulfur; another recovers sulfuric acid. Neither of these operations are of adequate size to contribute to the U.S. sulfur industry significantly.



	Legislation and Date	Role of Federal Government
1950s	Act to Provide Research and Technical Assistance Relating to Air Pollution Control (1955)	Provided research, technical, and financial aid to States.
1960s	Clean Air Act of 1963	This was the first direct regulation concerning pollution abatement. Federal funds were made available to States and local pollution control agencies; mediation was made available for disagreements between States.
	Air Quality Act of 1967	Created air quality regions and established criteria for setting air quality levels. States were required to set comparable standards.
1970s	Clean Air Act Amendments of 1970	Expanded Federal role in air pollution control. Gave the U.S. Environmental Protection Agency (EPA) responsibility of setting national ambient air quality standards (NAAQS); introduced national standards for new sources of air pollution. Nation was divided into 274 air quality control regions.
	1971	
	1973 1974	Established waivers and extensions of motor vehicle emissions standards.
	1976 } Clean Air Act amendments and extensions	
	Clean Air Act Amendments of 1977	Classified air quality control regions as attainment or nonattainment; established program to prevent significant deterioration; made special allowances for coal from Eastern States; strengthened standards; tightened motor vehicle emissions standards.
1980s		
1990s	Clean Air Act Amendments of 1990	Special attention to reducing SO <sub>2</sub> and NO <sub>x</sub> mitigating the adverse effects of acid rain with the goal of reducing SO <sub>2</sub> emissions in 2010 by 10 million metric tons below the 1980 baseline using pollution allowances; established list of 189 regulated hazardous air pollutants; required all major sources of air pollution to obtain operating permits; strengthened enforcement provisions for the EPA.

Figure 3. Chart that lists important environmental legislation that has been enacted in the United States since 1956, the year of the first such law. These dates are important because sulfur dioxide (SO<sub>2</sub>) emissions were the focus of many early environmental concerns. Regulations limiting SO<sub>2</sub> emissions have driven the growth of recovered sulfur and byproduct sulfuric acid production.

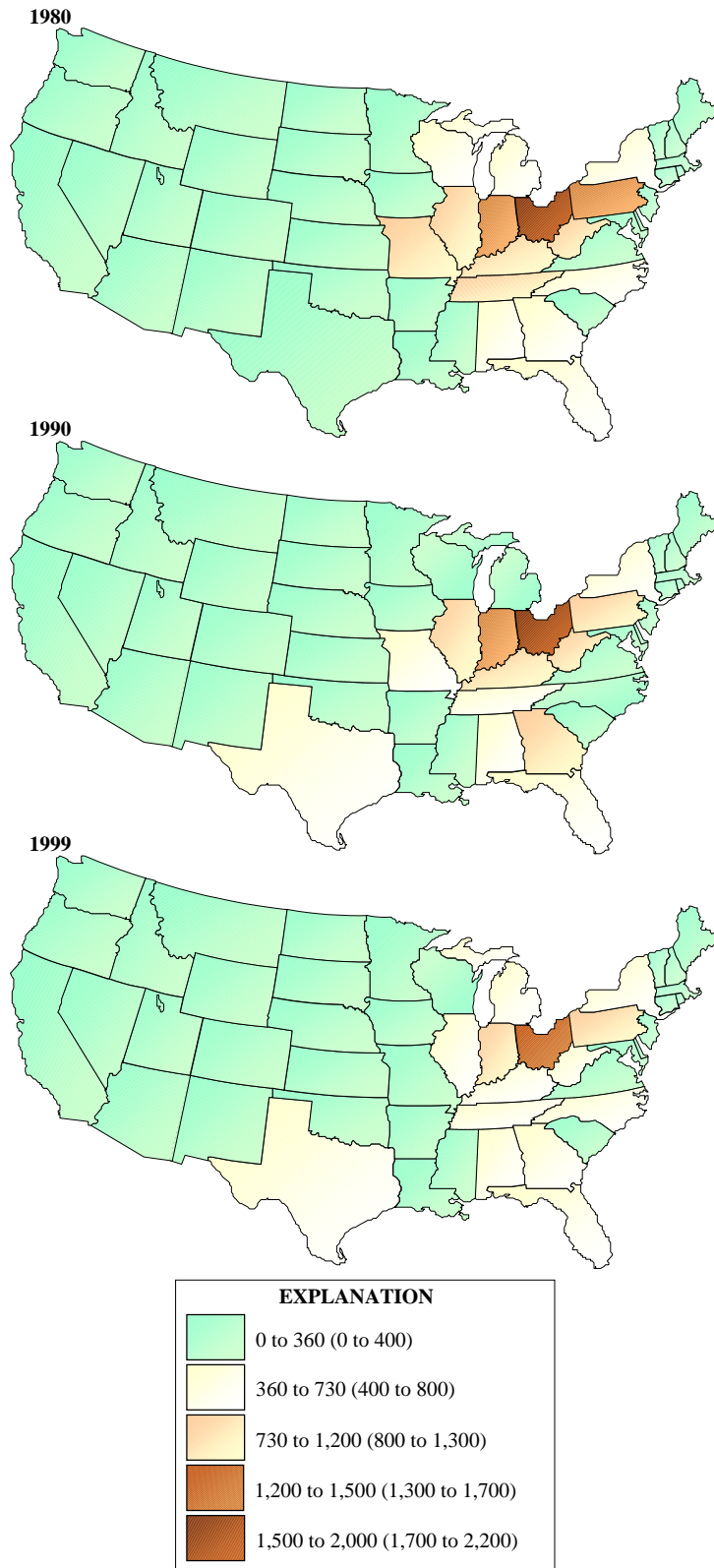


Figure 4. Maps that show how sulfur dioxide (SO<sub>2</sub>) emissions have changed since 1980, the base year for the Clean Air Act Amendments of 1990. SO<sub>2</sub> emissions are concentrated in the Midwest. This has not changed for the past 20 years, but the air quality has improved in nearly all States. Emissions are reported in thousand metric tons, and the values in the parentheses are in thousand short tons.

Table 2. Sulfur Dioxide Emissions from Electricity Generators, by Fuel Type  
(Thousand metric tons of sulfur dioxide)

	Coal		Petroleum		Natural gas		Other <sup>1</sup>		Total
	Percentage		Percentage		Percentage		Percentage		Quantity
	Quantity	of total	Quantity	of total	Quantity	of total	Quantity	of total	
Electric utilities:									
1989.....	13,786	94.9	743	5.11	1	0.01	4	0.02	14,533
1990.....	13,582	95.8	588	4.15	1	0.01	5	0.03	14,176
1991.....	13,461	95.7	601	4.27	1	0.01	4	0.03	14,066
1992.....	13,284	96.3	503	3.64	1	0.01	4	0.03	13,791
1993.....	13,044	95.8	567	4.16	1	0.01	3	0.02	13,614
1994.....	12,552	96.2	487	3.73	1	0.01	6	0.05	13,047
1995.....	10,209	97.0	303	2.88	1	0.01	9	0.09	10,522
1996.....	10,724	96.8	348	3.15	1	0.01	2	0.02	11,074
1997.....	10,678	95.6	494	4.42	1	0.01	1	0.01	11,174
1998.....	10,571	93.9	689	6.11	1	0.01	1	0.01	11,261
1999 <sup>p</sup> .....	10,246	94.4	609	5.61	2	0.02	1	0.01	10,857
Nonutility power producers:									
1989.....	497	82.4	82	13.53	1	0.15	24	4.06	603
1990.....	671	63.6	175	16.58	1	0.09	209	19.76	1,056
1991.....	600	60.0	145	14.52	1	0.09	255	25.50	1,000
1992.....	606	55.2	230	20.97	1	0.08	261	23.78	1,099
1993.....	643	55.7	241	20.91	1	0.08	269	23.27	1,154
1994.....	723	55.9	297	22.95	1	0.07	273	21.12	1,293
1995.....	625	53.9	277	23.87	1	0.08	257	22.14	1,159
1996.....	715	51.9	372	27.01	1	0.07	289	21.01	1,377
1997.....	<sup>2</sup> 335	55.5	<sup>2</sup> 173	28.64	<sup>2</sup> --	--	<sup>2</sup> 96	3.69	<sup>2</sup> 604
1998.....	319	54.5	185	31.58	--	--	82	13.93	586
1999 <sup>p</sup> .....	784	69.8	246	21.89	--	--	93	8.32	1,123
All power producers:									
1989.....	14,283	94.4	825	5.45	2	0.01	28	0.19	15,137
1990.....	14,253	93.6	764	5.01	2	0.01	213	1.40	15,232
1991.....	14,060	93.3	746	4.95	2	0.01	259	1.72	15,066
1992.....	13,890	93.3	733	4.92	2	0.01	265	1.78	14,890
1993.....	13,687	92.7	808	5.47	2	0.01	271	1.84	14,768
1994.....	13,275	92.6	784	5.47	2	0.01	279	1.95	14,340
1995.....	10,835	92.7	580	4.96	2	0.02	266	2.28	11,682
1996.....	11,439	91.9	719	5.78	2	0.01	292	2.35	12,452
1997.....	<sup>2</sup> 11,013	93.5	<sup>2</sup> 667	5.66	<sup>2</sup> 1	0.01	<sup>2</sup> 97	0.05	<sup>2</sup> 11,778
1998.....	10,890	91.9	874	7.37	1	0.01	83	0.70	11,847
1999 <sup>p</sup> .....	11,030	92.1	855	7.13	2	0.02	94	0.79	11,980

p Preliminary data.

<sup>1</sup>Plants fired by light oil, methane, coal-oil mixture, propane gas, wood, and refuse.

<sup>2</sup>There is a discontinuity in this time series between 1996 and 1997. Prior to 1997, data are nonutility emissions for the production of electricity and thermal output. Beginning in 1997, data are for the production of electricity only.

Source: U.S. Energy Information Administration, Annual Energy Review

## SULFUR SUPPLY

As the 21st century begins, sulfur recovered for environmental reasons is the predominant source of sulfur worldwide. In fact, in the United States, environmental sulfur meets all domestic demand. The United States became the world's largest elemental sulfur producer in about 1905, when a unique process for mining sulfur achieved profitability. The dominance of the U.S. industry continued in 2000, but the primary production sources have changed dramatically.

At the turn of the 20th century, the only significant production of elemental sulfur was in Sicily, an island in the Mediterranean Sea, off the coast and part of Italy. Sulfur ores were mined there using conventional mining methods, but the processes for recovering the sulfur from the ore were unusual. Early in the development of the Sicilian industry, sulfur ore was stacked in piles with ventilation holes and drainage ports at the bottom of the pile. The sulfur in the ore was then ignited at several locations throughout the piles. The heat from the combustion of the sulfur caused other sulfur in the pile to melt, drain through the pile of ore, and run out of the holes at the bottom (Day, 1885, p. 872-873).

Variations on this very primitive process were developed, but recovery was always very poor, ranging from 30 to 50 percent. The remainder of the sulfur that was not retained in the ore upon completion of the process was released into the atmosphere as SO<sub>2</sub>. As early as 1885, the environmental damage caused by emissions of sulfur was recognized. The Italian Government restricted the processing of the ore to certain times throughout the year, opposite the primary growing season.

During the time that Italian sulfur dominated the global sulfur industry, many companies were searching for other ways to meet the growing industrial demand for sulfur. Pyrites were being burned to recover their sulfur content as sulfuric acid and other methods were being investigated to melt or dissolve the sulfur out of ores. Sulfur was known to be contained in petroleum and natural gas, but none was recovered; the sulfur either remained in the final products or was emitted into the atmosphere.

### Frasch and Other Native Sulfur

Sulfur deposits were identified in the region around the Gulf of Mexico in the United States and Mexico in the 19th century. These deposits, however, had proven impossible to mine using conventional mining methods owing to the depth of the deposits and the geologic conditions of the area in which they were found. Dr. Herman Frasch began testing a novel process for Union Sulphur Co. in Calcasieu Parish, La., for melting the sulfur underground and pumping it to the surface. He made his initial attempts at sulfur production with the process that became known as the Frasch process in late 1894. In 1903, the process achieved its first commercial success at Sulphur Mine, La. (Haynes, 1959, p. 28-62).

The second Frasch mine began production at Bryan Mound in Brazoria County, Tex., in 1912, after Union Sulphur's initial patents for the Frasch process had expired. The city of Freeport, Tex., was established at the mouth of the Brazos River to service the mine. The company incorporated to produce the first sulfur in Texas took its name from the town it built (Freeport Sulphur Co., undated).

After Union Sulphur began Frasch mining in 1894, 8 companies established 36 mines during the 20th century. The length of service of these mines varied from less than 2 years for several mines to one mine on Boling Dome in Texas that operated for 65 years, which produced more than 82 Mt by the time it closed in 1993 (Bush and Semrad, 1996, p. 273). Freeport-McMoRan Sulphur Co., which was one of the variations of name under which Freeport Sulphur operated, was the only remaining sulfur mining company in the United States in 2000 at its Main Pass 299 Mine in the Gulf of Mexico, 51 kilometers (km) off the Louisiana coast. On August 31, 2000, the final domestic Frasch sulfur mine, shown in figure 5, closed because of low sulfur prices, high fuel costs, and technical problems.

The description of the Frasch process is as follows: Hot water is injected directly into the sulfur-containing mineral strata, melting the crystalline sulfur, which is then lifted to the surface with air. The successful execution of the process, however, is much more complex, with each Frasch operation requiring unique variations to meet the specific demands of the deposit.

Because sulfur has a relatively low melting point at 119.3° C, it is possible to melt it with superheated water which is water that has attained a temperature above its boiling point because it is under pressure. When superheated water at about 165° C is pumped, under sufficient pressure to keep the water from boiling, into wells drilled into the sulfur formation, the elemental sulfur melts and pools around the bottom of the wells. The molten sulfur is lifted to the surface with compressed air (Fischer, 1984, p. 23-24). Early in the century, at the point in the process when the sulfur reached the surface, it was pumped into wooden forms or molds where it cooled and solidified. Modern facilities use insulated pipes to move the sulfur to heated storage tanks where it is held until transfer to a terminal from which it is shipped to customers. Currently, when large quantities of excess sulfur are stockpiled, the process is similar to that of the early days of the industry. Molten sulfur is poured into molds, where it cools and solidifies, creating huge blocks of solid sulfur from which the term "poured to block" is derived.

The Frasch sulfur process only works under very specific geologic conditions. Deposits amenable to the process have proven to be either salt domes or bedded evaporite deposits in which permeable native sulfur deposits are enclosed in impermeable formations (Morse, 1985, p. 786). The elemental sulfur results from the bacterial alteration of anhydrite or gypsum, in the presence of hydrocarbons, into limestone and H<sub>2</sub>S. The H<sub>2</sub>S then oxidizes to sulfur through contact with oxygenated water that percolates through the formation or through the action of anaerobic, sulfur-reducing bacteria (Bodelenos and Nelson, 1979, p. 459).

Figure 6 shows the structure of a sulfur-containing salt dome and the system used to extract the sulfur. Other conditions are required for the economic implementation of the Frasch process. The requirements include (1) a large, porous, sulfur-rich deposit; (2) an impervious cap rock above the deposit; (3) an adequate and dependable supply of water; and (4) a source of inexpensive fuel for



Figure 5. Photograph that shows the last sulfur mine in the United States, Freeport-McMoRan Sulphur Inc.'s Main Pass Mine, that closed in August 2000. Located about 51 kilometers (32 miles) offshore, it was the largest structure in the Gulf of Mexico with its platform extending more than 1.6 kilometers (more than 1 mile). *Photo courtesy of Freeport McMoRan Sulphur Inc.*

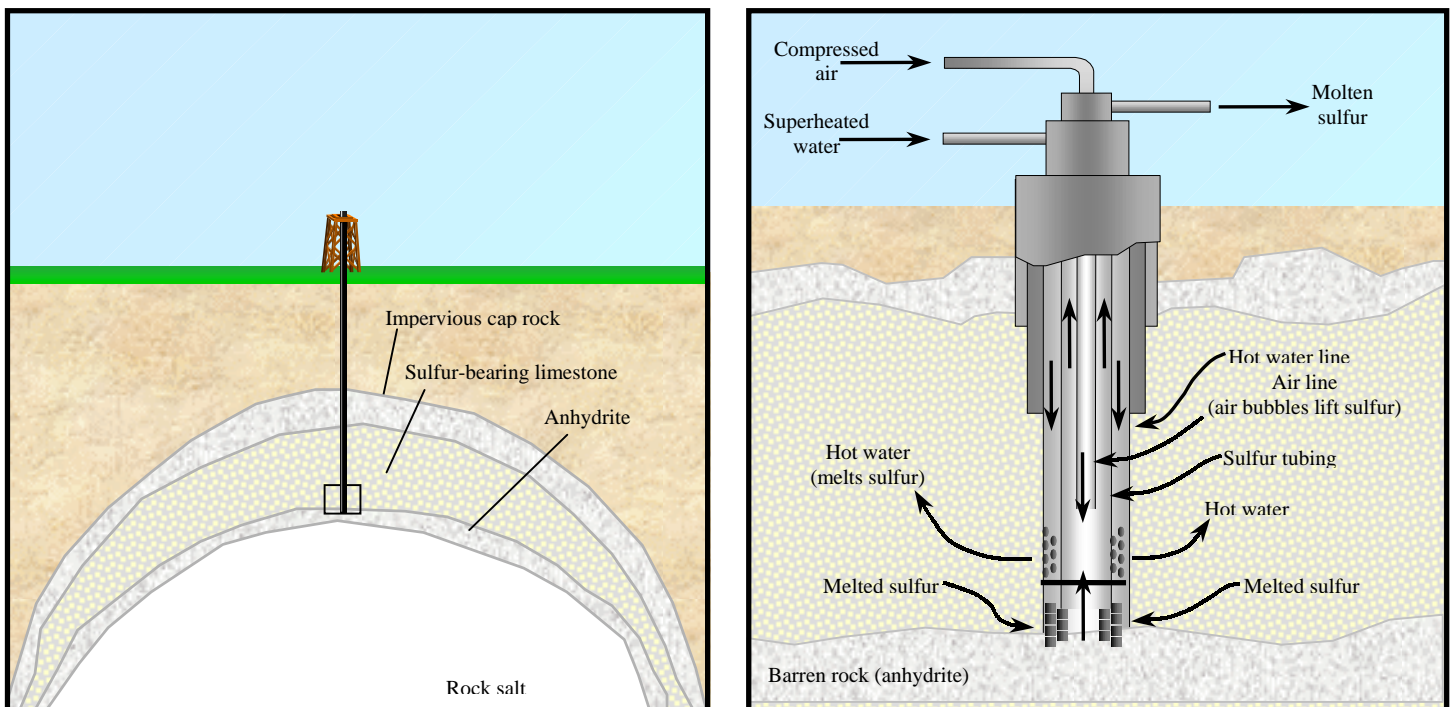


Figure 6. Illustration that shows the structure of a sulfur-containing salt dome and the details of the Frasch pump used to extract the sulfur from underground formations. Superheated water is pumped into the formation to melt the sulfur. The molten sulfur is lifted to the surface with compressed air.

heating the vast quantities of water required to melt the sulfur and to provide power for other energy-consuming components of the process (Toon, 1986, p. 18).

The Frasch process was the vehicle that propelled the United States into the forefront of world sulfur production; Frasch mines operated on salt domes in Louisiana and Texas and on bedded evaporite deposits in western Texas. U.S. Frasch production peaked at more than 8 Mt in 1974 when 12 mines were operating (Merwin and Keyes, 1976, p. 1237). In 1982, production of recovered sulfur surpassed that of Frasch for the first time (Morse, 1983). U.S. Frasch production ceased in 2000, after nearly one century of operation. Figure 7 shows U.S. Frasch and other native sulfur production in the 20th century. Although native sulfur resources remain in place at Main Pass and other locations in the United States, reopening of previously closed operations or development of new Frasch mines is highly unlikely.

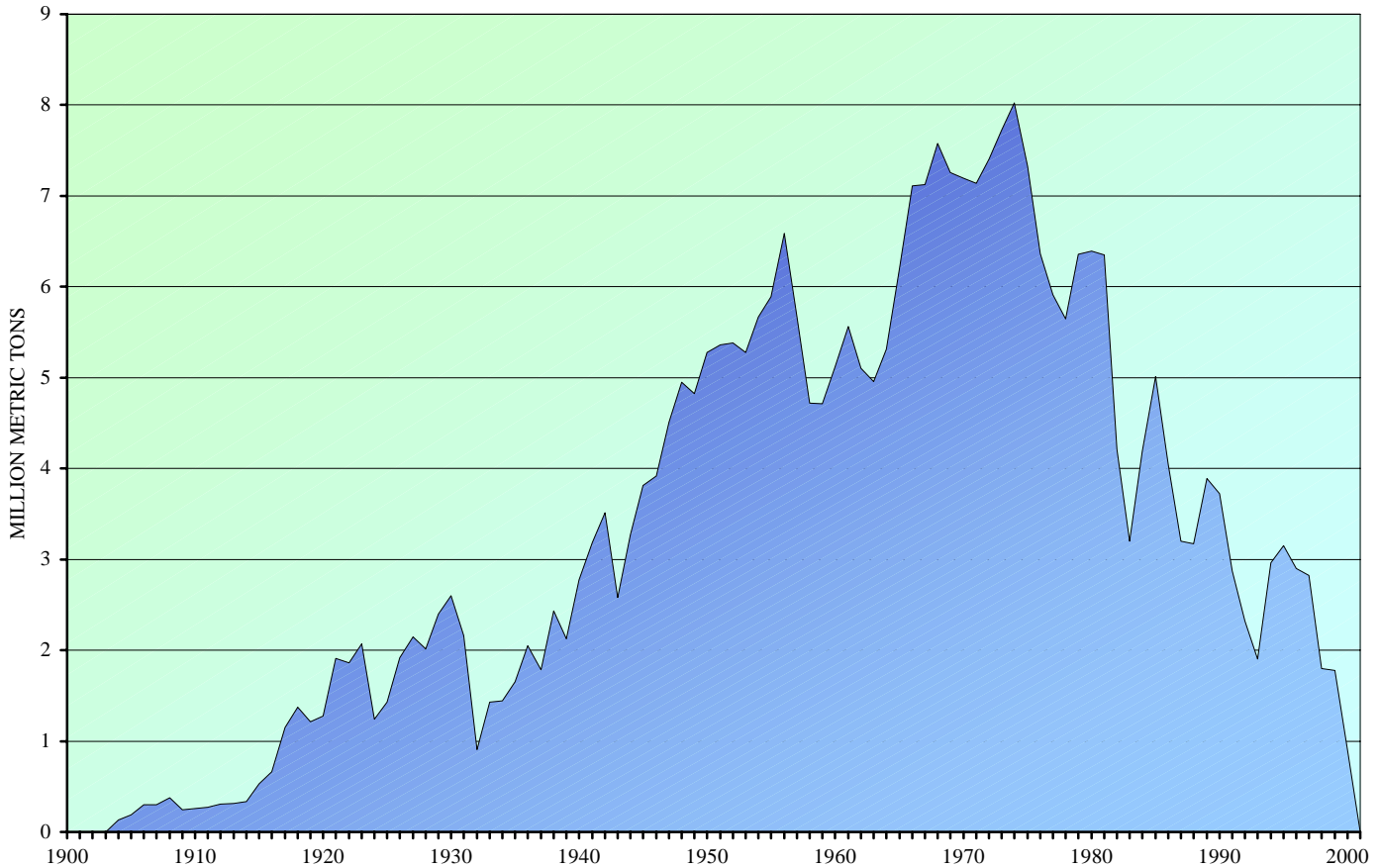


Figure 7. Chart that shows the birth and demise of the Frasch sulfur industry in the United States. Early production data included some native sulfur produced via conventional mining methods, but it was quickly dwarfed by Frasch production. Production peaked in 1974 at about 8 million metric tons. Domestic sulfur mining ceased completely in August 2000.

Frasch mines at bedded evaporite deposits were developed in a few other countries and on Mexican salt domes. Iraq began producing Frasch sulfur in 1972 at its Mishraq Mine with an initial capacity of 250,000 metric tons per year (t/yr) that expanded to 1 Mt/yr in 1974 (Merwin, 1974, Merwin and Keyes, 1976, p. 1249). The Mishraq deposit possibly is the largest native sulfur deposit in the world, with an estimated 100 to 250 Mt of sulfur resulting from bacterial activity (Barker and others, 1979). Little is known about events in the Iraqi sulfur industry since 1990. Iraq's invasion of Kuwait in August 1990 precipitated the gulf war in 1991 during which United Nations (UN) forces bombed many of Iraq's industrial complexes. Although the sulfur operation was not damaged, sanctions imposed after the war curtailed exports of sulfur (Sulphur, 1991). The level of operation at Mishraq since then is not known, but an agreement that began in 2000 for Iraq to supply Jordan Phosphates Mines Co. with sulfur was believed to include sulfur produced at Mishraq. Jordan invoked an article of the UN charter that allows a UN member to not implement a sanction if it is against that country's domestic interests. The price of the Iraqi sulfur was discounted by about 30 percent from material available elsewhere in the region (Sulphur, 2000b).

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Sulfur production at salt domes in Mexico similar to those developed in the U.S. Gulf Coast region began in 1954 (Larson and Marks, 1955). The decline in demand for mined sulfur resulted in the closure of the last Mexican Frasch mine in 1993 (Ober, 1994, p. 1172). From 1954 to 1993, seven mines operated in Mexico and produced a total of more than 55 Mt of sulfur (Bush and Semrad, 1996, p. 273; Ober, 1994, p. 1185).

Elemental sulfur deposits were discovered in Poland in 1954. Initial production was at a surface mine using conventional methods. Eventually, two surface mines and three modified Frasch process mines were developed. The Polish industry also suffered from the increased production of sulfur from recovered sources (Karolak, 1997). Two Frasch mines remained in operation during 2000. One of these mines, however, closed in September 2001 (Sulphur, 2001).

Production of Frasch and other native sulfur has decreased significantly in the former Soviet Union since 1988, when native sulfur production reached its peak. Production in Russia, Turkmenistan, and Ukraine was believed to have ceased completely by 2000.

Until the Frasch process was commercialized, 95 percent of world sulfur was from Sicily. Output in the United States surpassed that of Italy for the first time in 1913 (Delahanty, 1931). The Italian sulfur industry began to falter with the growing success of the Frasch industry and increased production of recovered sulfur throughout the world. Native sulfur production in Italy only surpassed 100,000 metric tons (t) twice after 1960 and ceased completely in 1985 (Morse, 1987, p. 912).

Small quantities of native sulfur have been produced throughout the world from volcanic deposits. This type of deposit is usually too small, too difficult to process, and too remote to develop on a commercial scale. Production is limited to meet very localized demand (Bush and Semrad, 1996, p. 282-283).

## Recovered Sulfur

In the context of this report, recovered sulfur is defined as the elemental sulfur recovered for environmental reasons during the processing of natural gas and petroleum refining. The U.S. Bureau of Mines first reported recovered sulfur production data for the United States in 1938; prior to that time, unspecified quantities of sulfur were produced, especially during treatment of natural gas, but disposed of as waste. Sulfur recovery has grown in importance over the years to become the leading source of sulfur in the United States starting in 1982 and the only source of elemental sulfur with the closure of the last domestic sulfur mine in August 2000.

Since 1938, domestic sulfur recovery has risen steadily, with increases in recent years coming almost exclusively from petroleum refining as shown in figure 8. Production from natural gas has averaged between 2 and 2.5 Mt/yr for the past 20 years. Sulfur from petroleum refining continues to grow as more high-sulfur crude oils are processed and increasingly stringent environmental regulations require lower atmospheric sulfur emissions and lower sulfur content in finished fuels.

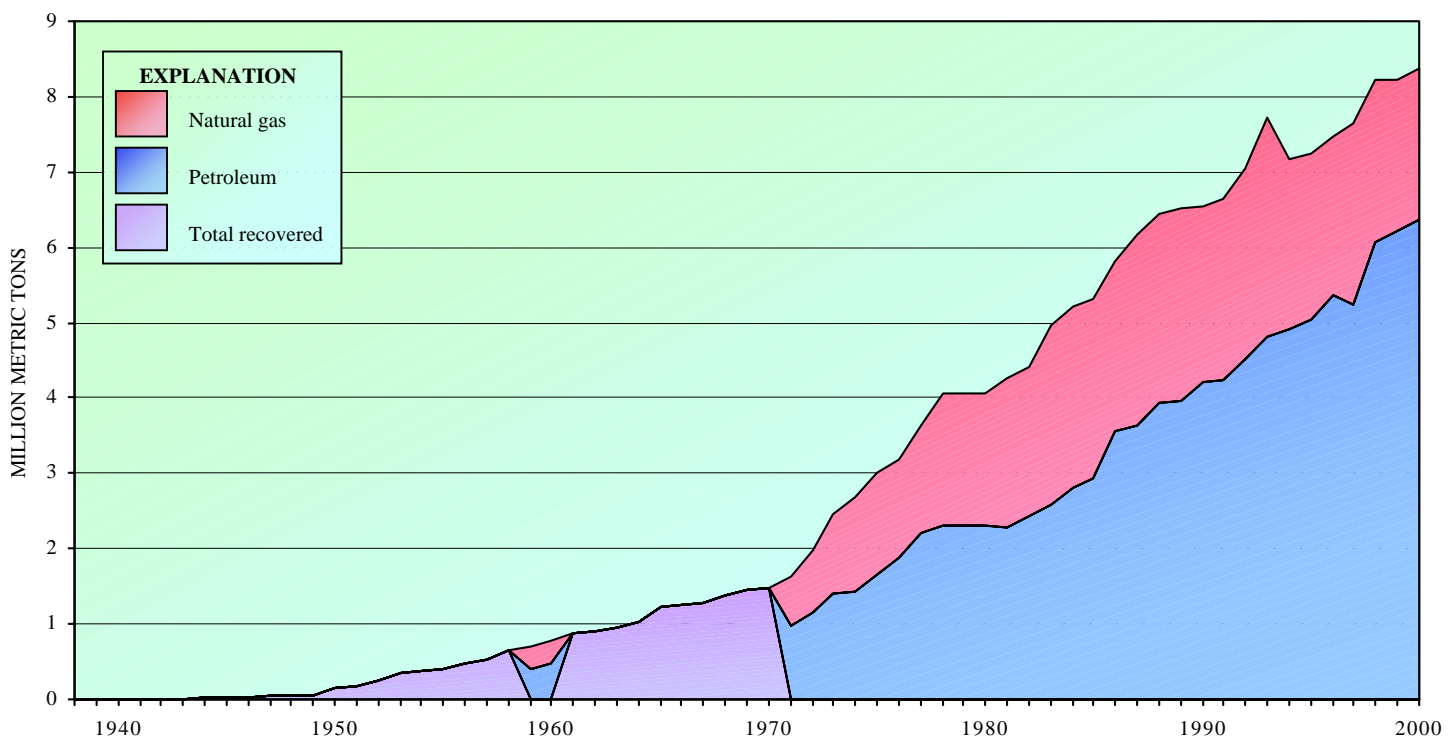


Figure 8. Chart that shows the steady growth in recovered sulfur from petroleum refineries and natural gas since 1938. The sources of recovered sulfur were identified in 1959 and 1960 and from 1971 to the present.

Most fossil fuels contain sulfur compounds in various forms. Natural gas wells almost always contain H<sub>2</sub>S. Concentration of H<sub>2</sub>S varies considerably by location, but the gas must be processed because H<sub>2</sub>S is extremely toxic, even at relatively low concentrations. In addition to some H<sub>2</sub>S, crude oil can contain many different sulfur compounds that can be classified in such general categories as mercaptans and thiophenes, which are hydrocarbon compounds where sulfur has replaced another atom in the organic molecule. Increasing quantities of sulfur are recovered at oil refineries as a result of environmental regulations that limit allowable atmospheric emissions of SO<sub>2</sub> at the refineries and the maximum concentration of sulfur in finished fuels in order to eliminate SO<sub>2</sub> emissions when the fuels are burned. Coal also contains appreciable quantities of organic sulfur compounds that are released as SO<sub>2</sub> upon burning. Technologies to remove sulfur from coal before combustion have been developed, and processes to remove SO<sub>2</sub> from flue gases are used at many electric powerplants and industrial facilities. In most cases, SO<sub>2</sub> from coal burning is recovered as a byproduct or waste material. Only a few small operations have been built that recover sulfur from coal combustion as a usable sulfur product, and actual production from this type of operation is extremely small in comparison with the total quantity of sulfur produced at oil and gas operations annually. Figure 9 shows how sulfur production sources changed during the 20th century.

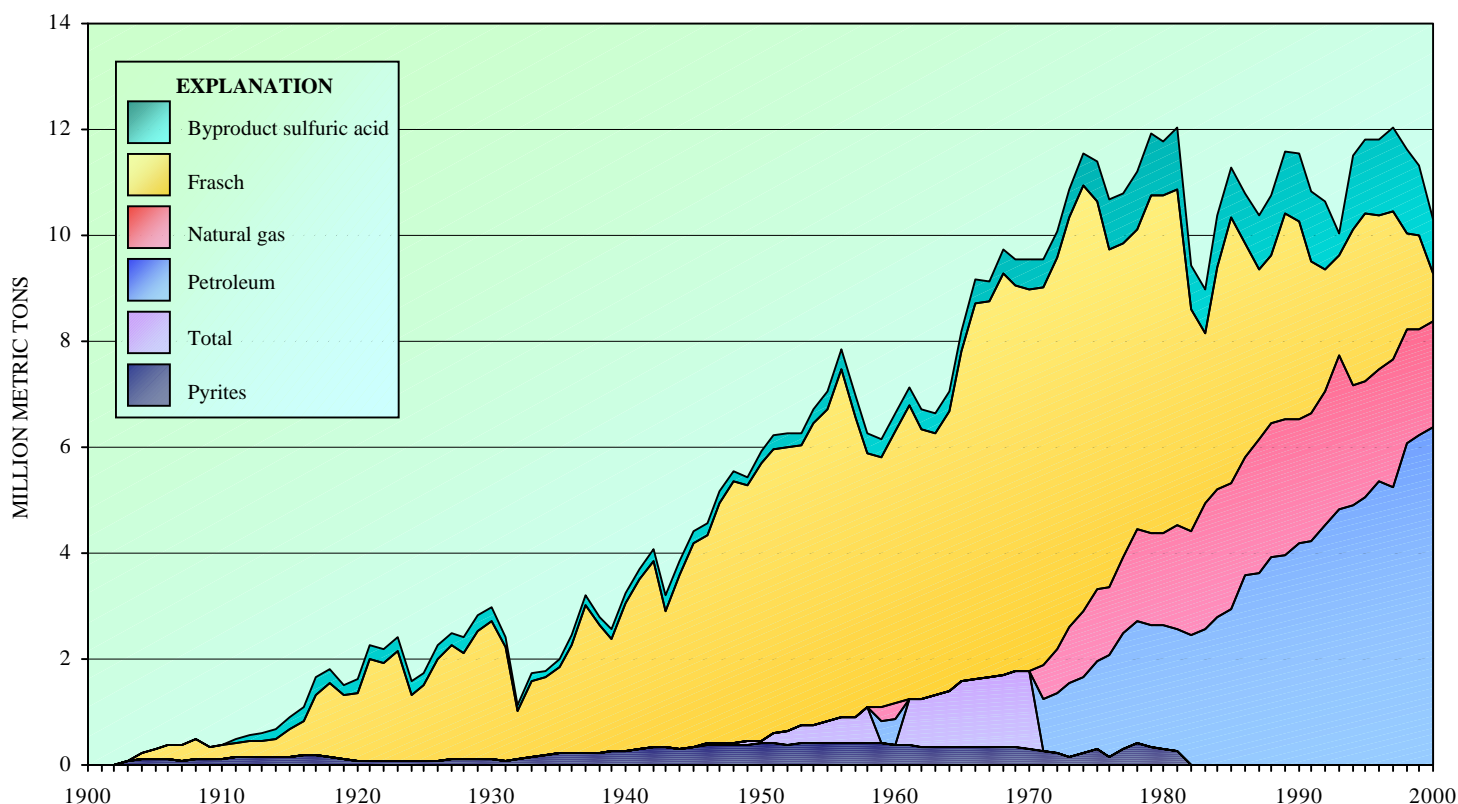
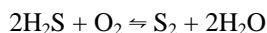


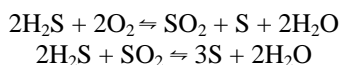
Figure 9. Chart that shows how production of sulfur in all forms has changed over time.

**Natural gas.**—H<sub>2</sub>S must be removed from natural gas because of its extreme toxicity. It also causes corrosion problems; but these are minor when compared to the hazards of breathing even very low concentrations of H<sub>2</sub>S. At natural gas processing facilities, the first step in recovery of sulfur is the separation of H<sub>2</sub>S from the rest of the natural gas stream. The natural gas containing H<sub>2</sub>S—known as sour gas—is passed through a solvent in which the H<sub>2</sub>S dissolves and the desirable portions of the natural gas are insoluble. The solvent is then heated, and the H<sub>2</sub>S is expelled from the solution (Fischer, 1984, p. 33-35). The most common solvents used are amines, which are organic derivatives of ammonia (Schmerling, 1981, p. 71).

After the different components of the gas have been separated, H<sub>2</sub>S is converted to elemental sulfur by means of the Claus process—named after its inventor, British chemical engineer C.F. Claus (Zwicker, 1990, p. 12). The process was developed in 1883 based on the reaction shown below in which H<sub>2</sub>S is burned to yield elemental sulfur and water:



Only under ideal conditions does this reaction occur exactly as described. The process has been modified over time, and modern Claus reactors incorporate a two-step process that takes advantage of the following reactions:





In the first step of the process, insufficient oxygen is present to convert all the  $H_2S$  to  $SO_2$ , thus also causing elemental sulfur and water to be formed. In the second stage, the reaction product  $SO_2$  from the first reactor is mixed with additional  $H_2S$ , completing the formation of elemental sulfur and water usually with the aid of a catalyst—a compound that promotes the reaction without undergoing any change itself. The sulfur is condensed and removed in molten form from the reaction vessel and stored until shipping or used on-site (Leffler, 2000, p. 179-180).

An example of a typical sulfur management system is shown in figure 10. A more detailed illustration of the Claus process in illustrated in figure 11.

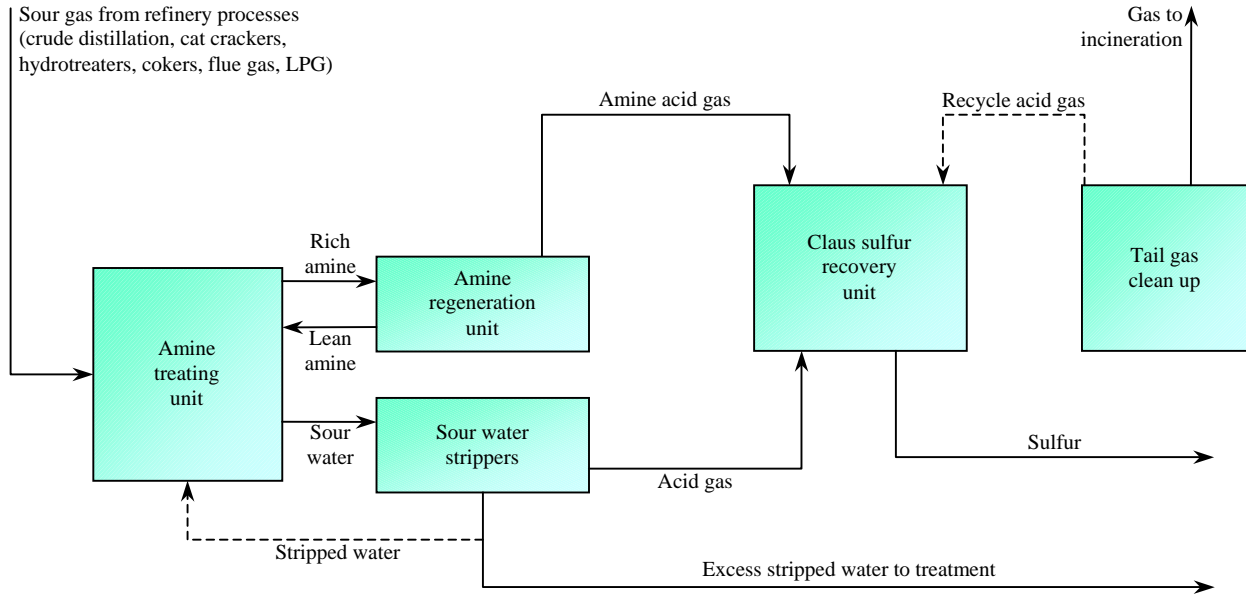


Figure 10. Flow diagram that shows the basic steps used in most sulfur recovery operations. Sour gas, which is gas that contains hydrogen sulfide ( $H_2S$ ), is handled similarly at natural gas processing facilities and petroleum refineries.

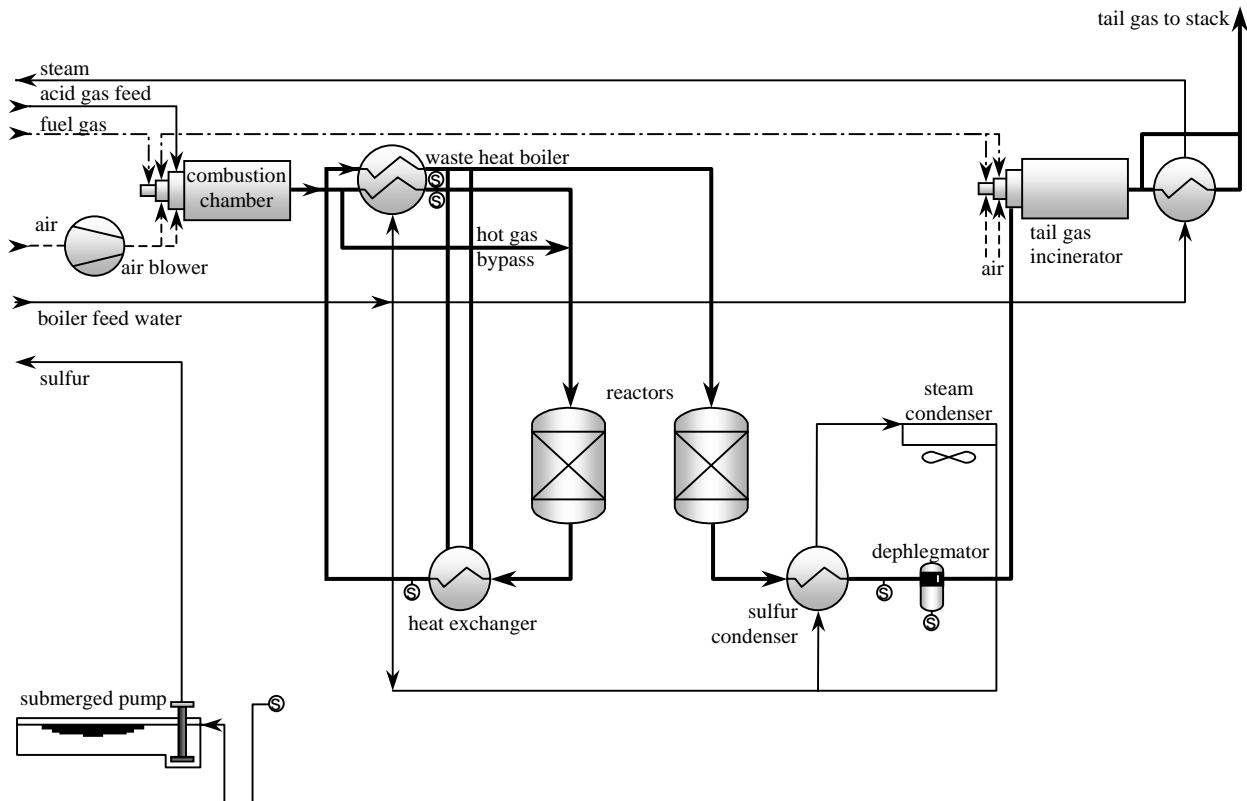


Figure 11. Diagram that illustrates the Claus sulfur recovery process used at natural gas processing facilities and petroleum refineries.

**Petroleum.**—During the early days of the petroleum industry, very simple distillation was the only process used to refine crude oil. When oil was discovered in the United States in 1859 near Titusville, Pa., Colonel Edwin Drake and his investors were looking for a product to compete with whale oil for use in oil lamps. The low density, low boiling point portions of the crude petroleum, later to be known as gasoline, were considered waste and burned for disposal. The only desired product was kerosene for lamps. The heavier portions of the oil where most of the sulfur concentrated was soon recognized as good fuel for industrial boilers and steam engines. It was not until the invention of the internal combustion engine that the value of gasoline as a fuel was recognized (Leffler, 2000, p. 4).

Crude oil is a complex mix of hydrocarbon compounds, ranging from simple compounds with small molecules and low densities to very dense compounds with extremely large molecules. Any of these compounds can contain sulfur. An average crude oil contains about 84 percent carbon, 14 percent hydrogen, 1 to 3 percent sulfur, and less than 1 percent each nitrogen, oxygen, metals, and salts (Occupational Safety & Health Administration, 1999). As demand increased for lighter fuels, such as gasoline and jet fuel, more complicated processes were developed to break larger particles apart to produce increasing quantities of the more desirable, lower density compounds. These processes often involved reactions that could also break the sulfur apart from the organic compound as H<sub>2</sub>S, the same sulfur compound often found in natural gas, with all the same undesirable properties. Until about 1970, any H<sub>2</sub>S produced in the refining process was used as refinery fuel and burned along with the other gaseous hydrocarbons released during the process. Burning the H<sub>2</sub>S produced SO<sub>2</sub> that was released into the atmosphere, which was considered a nuisance rather than a hazard.

As refining increased and the atmosphere around refineries became more noxious, SO<sub>2</sub> emissions came under fire as a significant contributor to air pollution and acid rain that was damaging the environment throughout the Northern Hemisphere, especially in and downwind from industrial areas. The first major national environmental legislation, the Clean Air Act of 1963 limited the quantity of allowable emissions, particularly SO<sub>2</sub> at stationary sources of pollution, such as manufacturing facilities and powerplants (U.S. Energy Information Administration, 1997, p. 60-61). Oil refineries were required to install equipment to reduce the amount of SO<sub>2</sub> to allowable quantities or process crude oils with very low sulfur content, resulting in very low SO<sub>2</sub> emissions. Concern was not limited to SO<sub>2</sub> emissions at the refinery; automobile exhaust was recognized as a large source of SO<sub>2</sub> in the atmosphere. As environmental concerns increased, State and Federal regulations have further limited emissions.

These factors resulted in tremendous growth in sulfur recovery capacity and production. Figure 12 shows how recovered sulfur production at oil refineries in the United States increased faster than refinery input as a result of increased sulfur recovery requirements and a higher average sulfur content in the petroleum being refined. From 1971 to 2000, petroleum refinery input increased an average of 1.08 percent per year. During the same period, sulfur recovered at refineries increased an average of 6.89 percent per year, more than six times as quickly.

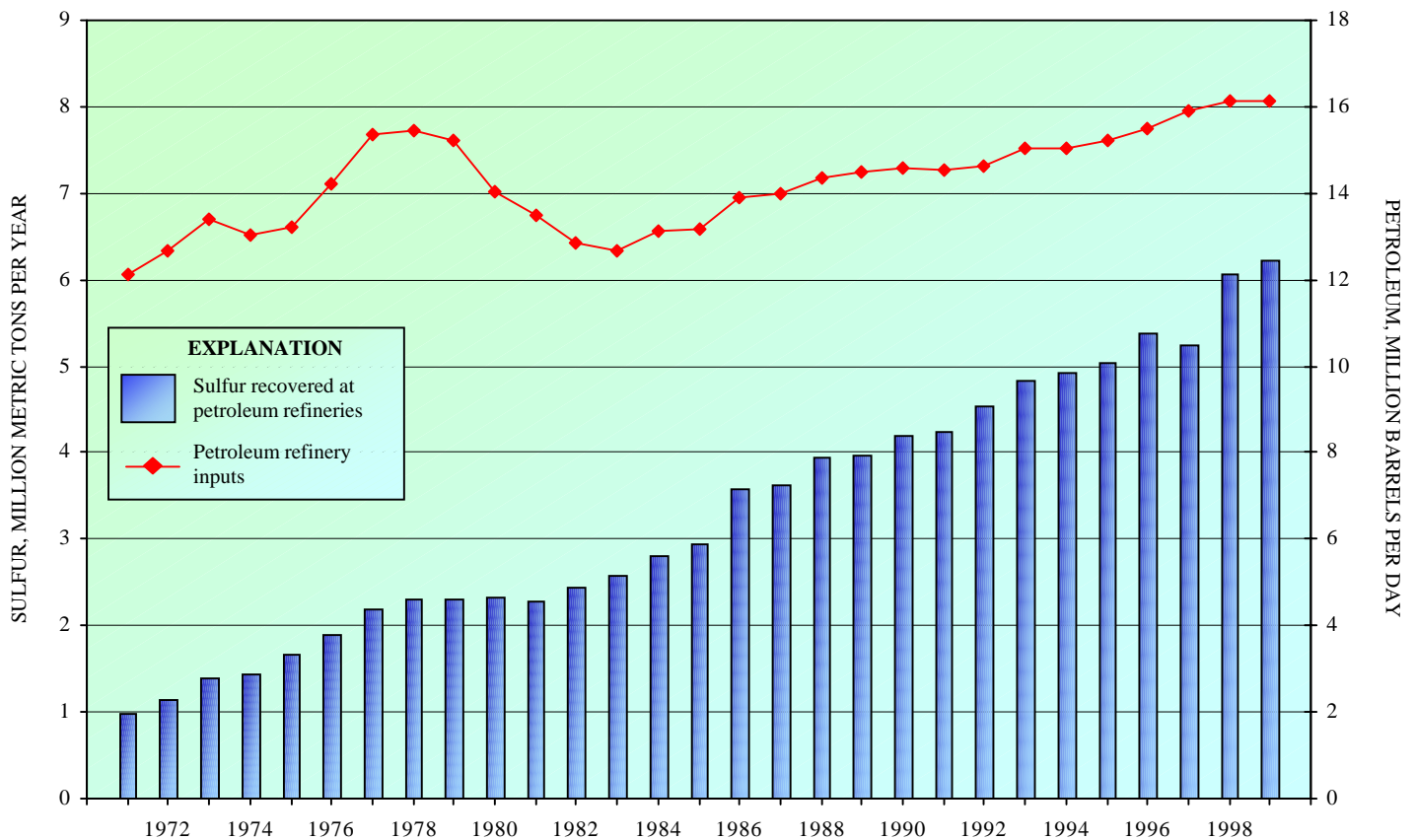


Figure 12. Chart that shows that sulfur production at petroleum refineries has increased at a faster rate than the refineries have increased input.

Petroleum routinely undergoes a hydrogenation process in order to remove the majority of sulfur from the crude oil. In this process, pressurized, high-temperature hydrogen reacts with the sulfur in the organic compounds to form H<sub>2</sub>S. The H<sub>2</sub>S then is removed from the gas stream and converted to elemental sulfur in the same type of process used at natural gas processing facilities—solvent extraction followed by the Claus process.

The efficiency of the Claus process for sulfur recovery from gas streams containing H<sub>2</sub>S is dependent on the concentration of the H<sub>2</sub>S being treated. Modifications in the Claus process have been necessary to improve the recovery of sulfur. Table 3 lists the general requirements for different H<sub>2</sub>S concentrations.

Table 3. Sulfur Recovery Process Variations Required for Different Hydrogen Sulfide Concentrations of Sour Gas

H <sub>2</sub> S concentration	Process and modifications
50% or more.....	Straight Claus.
20% - 50% .....	Claus with split flow configuration.
12% - 30% .....	Claus with oxygen enrichment.
5% - 15% .....	Claus with gas and air preheat.
Less than 5% .....	Claus with supplemental sulfur burning.

Even with all the modifications to the Claus process, not all the sulfur is recovered. Typical sulfur recovery efficiency at Claus plants is 90 to 96 percent for a two-stage reactor and 95 to 98 percent for a three-stage reactor. If the depleted process gas is within acceptable limits, then it is incinerated in the final stage of the Claus process to oxidize all the remaining sulfur compounds, and the remainder is emitted into the atmosphere. Usually, however, the so-called tail gas must undergo further processing to remove as much of the sulfur as technically possible to meet environmental requirements. In the United States, 99.9 percent recovery efficiency is required at sulfur recovery plants with capacity of at least 20 metric tons per day (t/d). Amine-based tail gas treatment is the most common process in the United States, where sulfur compounds in the tail gas are converted to H<sub>2</sub>S, separated, and recycled to the Claus plant. Other developed countries have similar requirements. Canada requires sulfur recovery of 98.5 percent at 50-t/d plants and 99 percent for 2,000-t/d operations. The European Union (EU) mandates 98.5 percent sulfur recovery. Germany, a member of the EU, has set higher standards of 99.8 percent for 20- to 50-t/d plants and 99.5 percent for those larger than 50 t/d. Japanese operations must recover 99.8 percent of sulfur; and Taiwan has the highest standard at 99.95 percent recovery (Connock, 1998, p. 34).

Several companies are developing biological processes for desulfurizing crude oil, natural gas, and Claus plant tail gases. If any are commercialized, then biodesulfurization processes could require significantly less energy and fewer reagents than more traditional desulfurization techniques; but no biological facilities have been installed at major refineries or natural gas facilities. The technology has not yet been proven on a large scale.

**Oil Sands.**—Although not currently produced in the United States, oil sands represent a large source of recovered sulfur, especially in Canada. Alberta has huge deposits of oil sands with estimated reserves of 300 billion barrels of recoverable crude oil that also contain 4 to 5 percent sulfur (Stevens, 1998). The Athabasca oil sands are a mixture of sand, water, clay, and bitumen, a naturally occurring viscous mixture of heavy hydrocarbons. Because of its complexity, bitumen is difficult or impossible to refine at most oil refineries. It must be upgraded to a light-oil equivalent before further refining, or it must be processed at facilities specifically designed for processing bitumen. Oil sands with more than 10 percent bitumen are considered rich; those with less than 7 percent bitumen are not economically attractive (Oil & Gas Journal, 1999). During the upgrading and refining of the oil sands, significant quantities of sulfur must be recovered using processes described for conventional oil refining.

### Sulfur in Other Forms

Production from sulfur resources and environmentally mandated sulfur recovery does not always result in elemental sulfur. Pyrites historically competed with elemental sulfur for predominance as the raw material for sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) production. Off-gas SO<sub>2</sub> can be recovered as other sulfur products, most often byproduct H<sub>2</sub>SO<sub>4</sub> and sometimes liquid SO<sub>2</sub>, H<sub>2</sub>S, or ammonium sulfate. Because of increased environmental concerns, however, the importance of byproduct H<sub>2</sub>SO<sub>4</sub> is nearly double that of pyrites as a source of H<sub>2</sub>SO<sub>4</sub> worldwide. The other compounds are not nearly as significant.

**Byproduct Sulfuric Acid.**—The recovery of SO<sub>2</sub> released during the smelting of nonferrous metals is a major source of sulfur for industrial use. In this case, sulfur values are recovered as H<sub>2</sub>SO<sub>4</sub> rather than elemental sulfur as is the case in Frasch and recovered sulfur production. Historically, sulfides have been the most important ore minerals for the production of the nonferrous metals, copper, lead, molybdenum, and zinc in the United States. Tremendous quantities of SO<sub>2</sub> are liberated during the processing of these sulfide minerals into their metals. Environmental regulations limit these emissions, necessitating SO<sub>2</sub> recovery at smelters. Byproduct H<sub>2</sub>SO<sub>4</sub> production is the most appropriate method for reducing such emissions.

The most commercially important sulfide minerals used for copper production are chalcopyrite (CuFeS<sub>2</sub>), covellite (CuS), chalcocite (Cu<sub>2</sub>S), bornite (Cu<sub>5</sub>FeS<sub>4</sub>), enargite (Cu<sub>3</sub>AsS<sub>4</sub>), and tetrahedrite (3Cu<sub>2</sub>S•Sb<sub>2</sub>S<sub>3</sub>) (Jolly, J.L.W., 1985, p. 8). Sulfide ore concentrates fed to copper smelters are about one-third sulfur by weight (BHP Copper Inc., [undated], p. 5). This sulfur is driven off

as SO<sub>2</sub> during the multistage smelting process, and the sulfur-containing off-gases are captured and routed to a H<sub>2</sub>SO<sub>4</sub> plant. At the acid plant, the gas mixture containing SO<sub>2</sub> is passed with oxygen over a catalyst, usually vanadium pentoxide, to convert the SO<sub>2</sub> to sulfur trioxide (SO<sub>3</sub>), which is then absorbed in H<sub>2</sub>SO<sub>4</sub> where it reacts with excess water to produce additional H<sub>2</sub>SO<sub>4</sub> (Sander and others, 1984, p. 280). H<sub>2</sub>SO<sub>4</sub> production will be described in more detail in the “Sulfur Demand” section of this report. Modern smelting techniques, such as flash and oxygen-enriched, increase the SO<sub>2</sub> content of the gas streams, allowing for more economic sulfur recovery.

In 2000, 81 percent of the byproduct sulfuric acid produced in the United States was from copper smelters as shown in figure 13, even though copper smelting was contracting following closure of three of seven primary copper smelters in 1999. The remaining domestic byproduct acid was produced at lead, molybdenum, and zinc smelters (Ober, 2002, p. 76.3). In Canada, significant quantities of smelter acid are produced at nickel smelters. At lead, molybdenum, nickel, and zinc operations, H<sub>2</sub>SO<sub>4</sub> is recovered through similar processes.

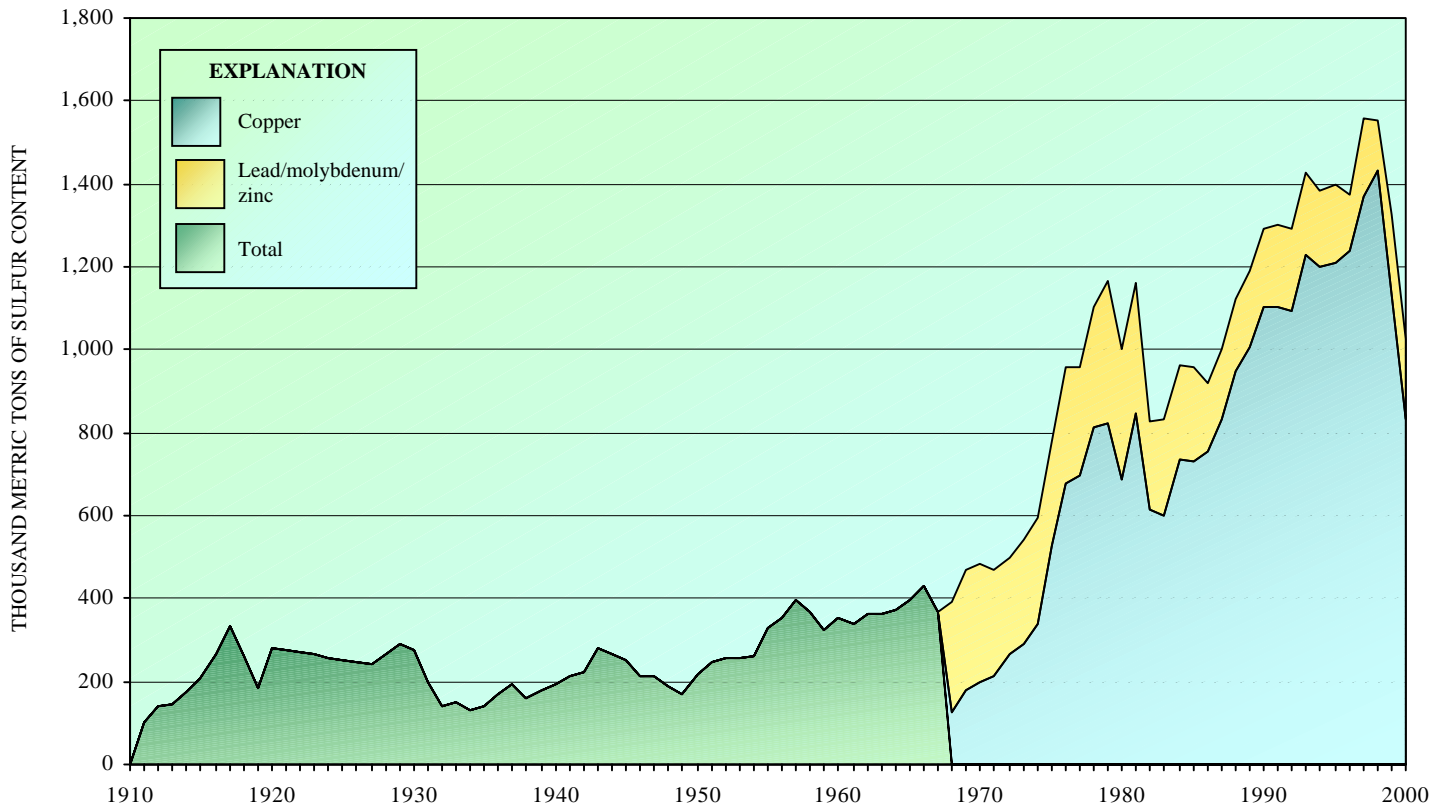


Figure 13. Chart that shows historic production of byproduct sulfuric acid. Prior to 1968, data were reported as total production with no differentiation regarding the type of operation. After that, the dominance of the copper industry becomes evident.

The most important ore mineral of lead is galena (PbS) (Woodbury, 1985, p. 437). Molybdenum, often a byproduct of copper production, is produced from molybdenite (MoS<sub>2</sub>) (Blossom, 1985, p. 521). Nickel is most often recovered from pentlandite [(Ni,Fe)<sub>9</sub>S<sub>8</sub>] (Kuck, [undated]); and sphalerite (ZnS) is the most common zinc ore mineral, and it is often associated with PbS (Jolly, J.H., 1985, p. 296).

Early days of these industries saw much of the SO<sub>2</sub> released into the atmosphere, although byproduct acid production was reported beginning in 1911. U.S. environmental regulations initiated in 1970 restricted SO<sub>2</sub> emissions and necessitated adoption of new smelting technologies and the installation of additional facilities to remove SO<sub>2</sub> and other pollutants from off-gas streams. Technological developments have made it possible to recover as much as 99.9 percent of the SO<sub>2</sub> emitted during the smelting process. Kennecott Utah Copper Corp. built a new flash smelter that opened in 1995 and had the ability to recover 99.9 percent of SO<sub>2</sub> emissions (Kennecott Utah Copper Corp., 2000).

With regulated SO<sub>2</sub> capture, production of byproduct H<sub>2</sub>SO<sub>4</sub> is not dependent on sulfur demand, but rather it is related to the performance of the metals industry, especially copper. The production of copper concentrates for smelting in the United States has declined sharply since 1997 because some domestic mines have curtailed higher cost nonleach production or, where mineralogy allows, converted to leach production. As a result, the closure of three copper smelters in the United States in 1999 that remained inactive through 2001 limited the capacity for byproduct H<sub>2</sub>SO<sub>4</sub> production.

**Pyrites.**—Pyrites have been an important source of sulfur for the production of  $H_2SO_4$  for as long as  $H_2SO_4$  has been an important industrial acid. Pyrites were widely traded early in the 20th century. Although their importance has dwindled, especially since about 1980, 15 countries still mined pyrites for local consumption in 2000.

Pyrites are various ferrous sulfide minerals that are mined for their sulfur content. Their production is dependent on demand for  $H_2SO_4$ . Before the Frasch process was developed, domestic and imported pyrites were the most important sources of sulfur in the United States. With the tremendous increases in production from Frasch operations starting in 1904, pyrites became less important as a sulfur source, but their use fluctuated with changes in sulfur demand. When elemental sulfur supplies were tight, pyrites production could increase to satisfy demand. Although overshadowed first by Frasch sulfur, then recovered sulfur, and finally byproduct  $H_2SO_4$ , small but significant pyrites production continued in the United States until 1988. Pyrites production trends are shown in figure 14.

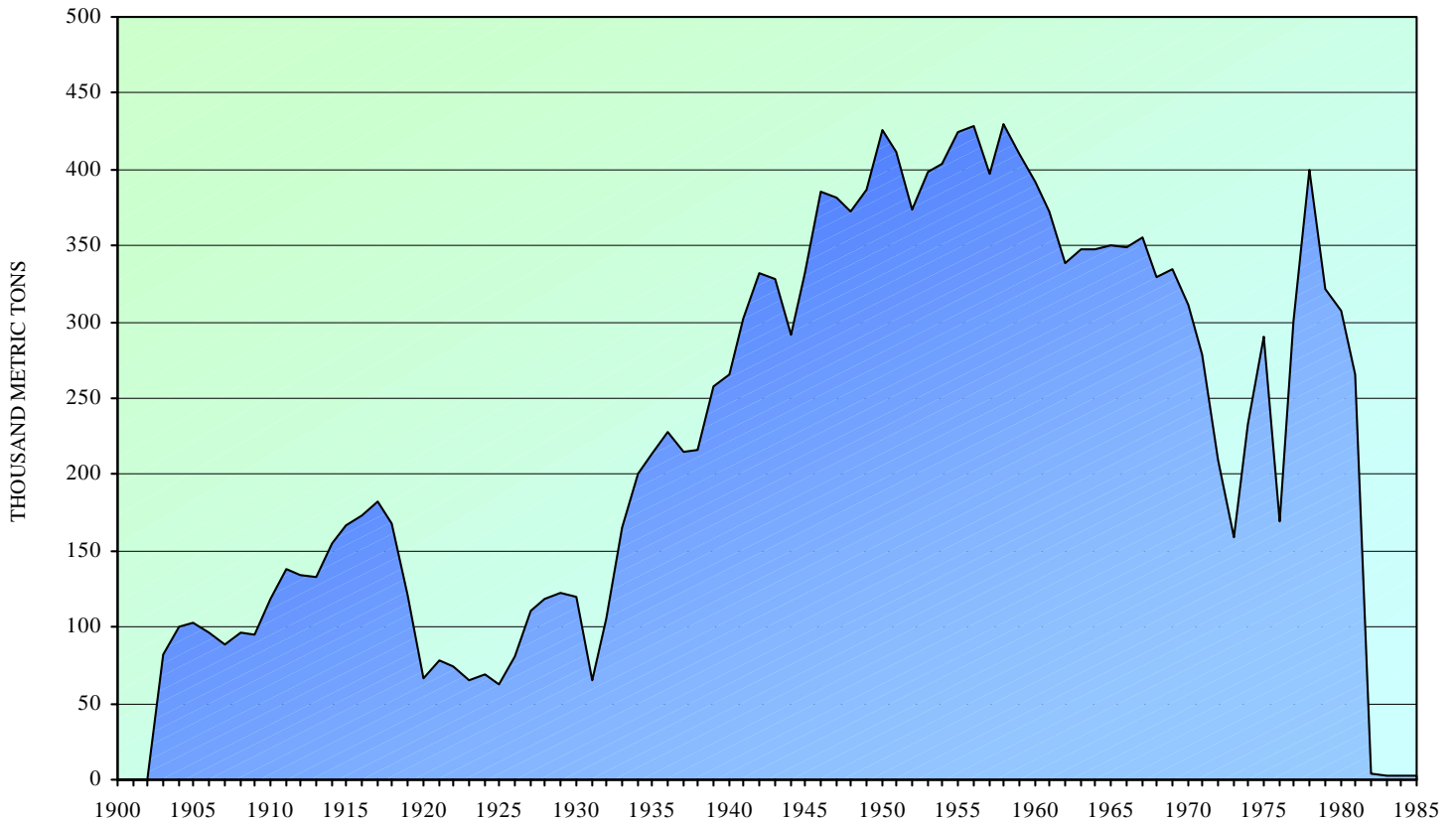


Figure 14. Chart that shows the production of pyrites in the United States. Pyrites production varied greatly from year to year from the first reports of its production until 1982 when its production became insignificant.

Pyrites are used only when the industrial application requires  $H_2SO_4$ . The actual process for producing  $H_2SO_4$  from pyrites is similar to its production at nonferrous smelters. In the U.S. pyrites-based  $H_2SO_4$  plants, pyritic ores containing 40 to 50 percent sulfur were roasted, producing  $SO_2$  for  $H_2SO_4$  production. Pyrites roasting produced a cinder byproduct that was sometimes leached to recover nonferrous metals and sometimes sold as iron ore (Morse, 1985, p. 786).

Pyrites are less desirable as raw material for  $H_2SO_4$  for several reasons. In the era of increasing concern for environmental protection, the most important factor limiting pyrites use is disposal of the cinder waste, which is rarely used in other applications. Another environmental concern limiting use of pyrites is that emission controls for pyrites burners are more complicated than those for sulfur burning  $H_2SO_4$  plants owing to the range of impurities contained in pyrites.

Other factors that make pyrites-based  $H_2SO_4$  plants less attractive than sulfur-based acid plants are economic. The capital cost of building a pyrites plant is two to two-and-one-half times higher than that for a sulfur-based plant partly because the processing of pyrites is more complicated than that of sulfur. More complicated emissions controls also are more expensive. Because the cinder residues are no longer useful byproducts, there is a cost involved in disposing of the material in environmentally and economically acceptable ways. Another important factor in choosing sulfur burning over pyrite roasting for  $H_2SO_4$  production is the comparative cost of raw materials. Low elemental sulfur prices, obviously, enhance its attractiveness as a substitute for pyrites (Kyhle, 1983).

Worldwide, pyrites production and use have declined with limited production in most countries. Figure 15 shows that as worldwide production in all forms has increased, the importance of pyrites as a source of sulfur has declined. In 2000, the only countries whose major source of sulfur was pyrites were China, Finland, India, North Korea, and Zimbabwe, of which only China and Finland were the

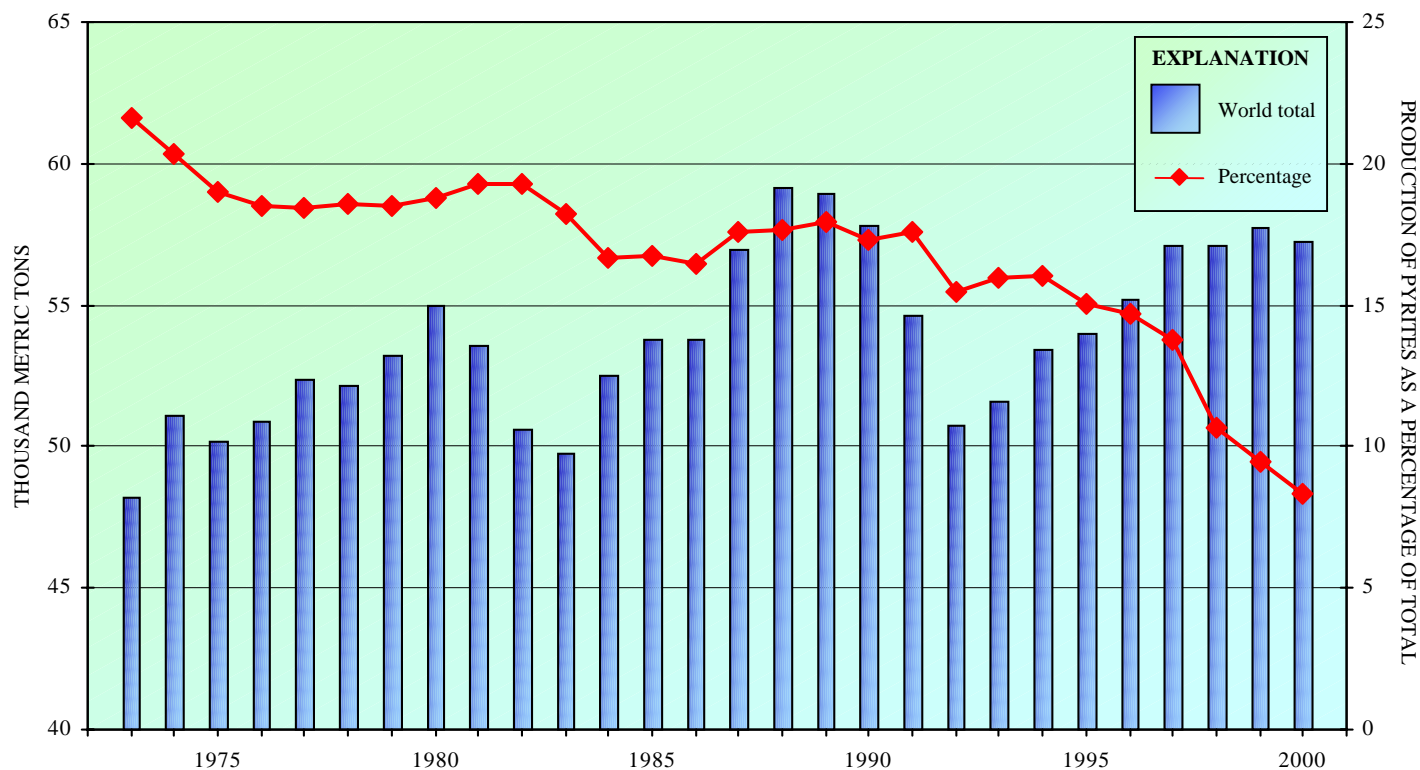


Figure 15. Chart that shows the relative importance of pyrites as a source of world sulfur production. Over time, the importance of pyrites as a sulfur source has decreased worldwide. In 1973, pyrites accounted for about 22% of world sulfur production; that figure dropped to less than 10% in 2000.

major producers of sulfur in any form. Pyrites production in these countries is trending downward. In 2000, China produced 71 percent of pyrites worldwide, which accounted for 65 percent of that country's sulfur production. Even in China, however, significant decreases are occurring in pyrites production, with production decreasing by 44 percent from 1997 to 2000 (Ober, 2002, p. 76.20). Driven by economic and environmental reasons, many of China's pyrites roasters were converted to use elemental sulfur (Fertilizer Markets, 1999). This is done by including sulfur pastilles or pellets with sand or cinders as the pyrites roaster feedstock. Most of the imported sulfur used for this purpose originates in Canada (Cunningham, 1999).

In 2000, just 8.3 percent of world sulfur demand was met with 4,770 Mt of sulfur from pyrites, a considerable decrease from 1973 when pyrites provided 21.6 percent of the total world sulfur demand of 48.2 Mt. Declines in world production and consumption of pyrites should continue.

**Other Sources.**—In some operations, sulfur is recovered as one of the intermediate compounds produced in the recovery process. Operators may choose to recover H<sub>2</sub>S or SO<sub>2</sub>, depending on local needs and markets; the volume of such products, however, is insignificant in the scope of the commercial sulfur industry. The end product at a unique FGD operation designed to reduce emissions of SO<sub>2</sub> at a coal gasification plant in North Dakota is ammonium sulfate [(NH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub>], a fertilizer compound.

## SULFUR DEMAND

Sulfur is used in such a wide variety of industries that listing them all is nearly impossible, although the end uses explained in detail represent the vast majority of sulfur consumption. Figure 16 shows sulfur sources and the categories of industries in which it is consumed, either as elemental sulfur or  $H_2SO_4$ . Most sulfur is converted to  $H_2SO_4$  before it is used. More  $H_2SO_4$  is produced in the United States every year than any other industrial chemical; production in 2000 was 39.9 Mt containing approximately 13.1 Mt of sulfur (U.S. Census Bureau, 2001). Sulfur is unusual in that for many of its end uses, especially those that require sulfur as  $H_2SO_4$ , the sulfur is not part of the final product. Although needed for the synthesis of many compounds and the successful accomplishment of numerous industrial processes, sulfur often circulates continuously through the process or is incorporated in its waste stream.

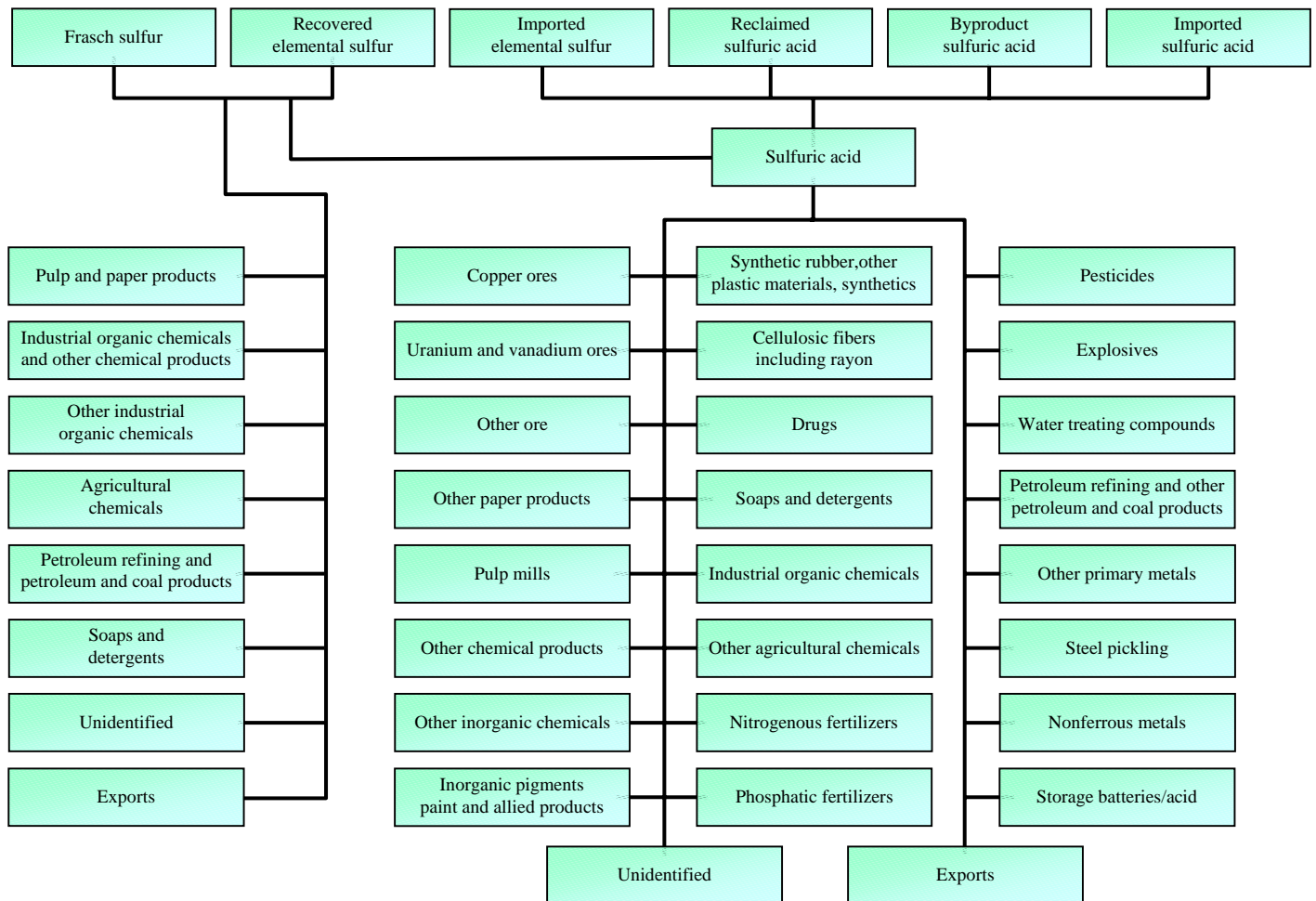


Figure 16. Flow diagram that shows the possible sources of sulfur and some of the possible end-use categories. Some end uses require elemental sulfur, but most require that the sulfur be converted to sulfuric acid before use.

Although U.S. consumption is increasing at a slower rate than domestic production, the United States still consumes more sulfur than is available from domestic sources. Sulfur production is compared to sulfur consumption in figure 17. The years where the consumption was higher than production, the United States was a net importer. Given stable demand, closure of the last Frasch sulfur mine could result in additional import dependence. Canada and Mexico have been the traditional sources for imported sulfur, although recent years have seen increased imports from Venezuela. Germany, Poland, and Saudi Arabia have been minor sources of imports during periods of reduced Frasch output, especially in 1999 and 2000.

The imbalance between domestic supply and demand could have been expected to cause increased prices for elemental sulfur. This did not occur because sulfur is an oversupply situation in much of the world, including Canada and Mexico. The worldwide sulfur transportation infrastructure is well developed, and world sulfur trade has become widespread. The sulfur handling capacity and the development of broad transportation networks have made prices less dependent on local supplies because competitive prices can be offered from many different regions.

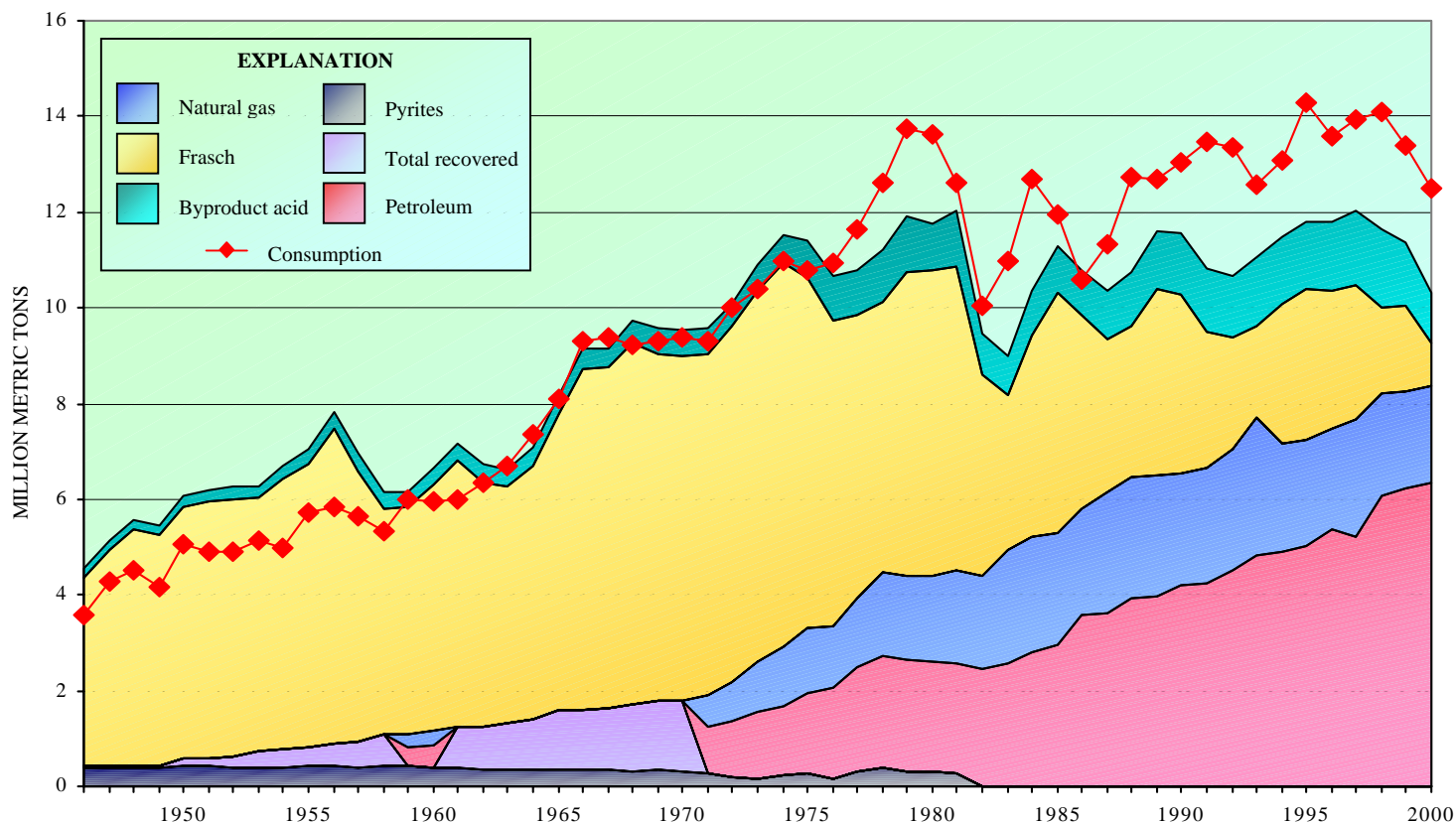


Figure 17. Chart that compares domestic sulfur production to consumption. Since 1976, consumption has exceeded production, necessitating imports to make up the difference.

### Domestic Consumption

In the United States and in the rest of the world, between 80 and 90 percent of sulfur is consumed as  $H_2SO_4$ , and nearly all countries make the majority of their  $H_2SO_4$  by burning elemental sulfur. Other U.S. domestic sources of  $H_2SO_4$  are byproduct  $H_2SO_4$  from metal smelters and imported  $H_2SO_4$ , which is probably smelter byproduct also.

The U.S. Geological Survey collects data from producers of sulfur and sulfuric acid concerning the industries in which their products are used according to the standard industrial classification of industrial activity. These classifications group industries together by generalized types. They do not list very specific end uses, but some assumptions can be made to estimate quantities consumed in specific end uses. Figure 18 shows the flow of sulfur in the United States in 2000, from its sources to the consuming industries. Elemental sulfur is used in the chemical industry to produce  $H_2SO_4$ , but it also is used directly in plant nutrient sulfur, petroleum refining, pulp and paper processing, and synthetic rubber production. Some of the major uses for  $H_2SO_4$  are copper ore leaching, phosphate fertilizer and other agricultural chemical production, petroleum refining, and other chemical manufacturing. Figure 19 shows how phosphate fertilizer production dominates sulfur consumption.

### Sulfuric Acid

About 90 percent of all sulfur consumption in the United States is in the form of  $H_2SO_4$ . Because so much sulfur is consumed as  $H_2SO_4$  and the acid is so important to industry, a detailed description of its properties and production process are included here.  $H_2SO_4$  is a strong acid that, when in dilute form, will dissolve all base metals. A chemical property that makes  $H_2SO_4$  important in industrial uses is its ability to decompose salts of most other acids. The most important application of this property is in the reaction with phosphate rock to produce phosphoric acid and calcium sulfate (Sander and others, 1984, p. 270-273).



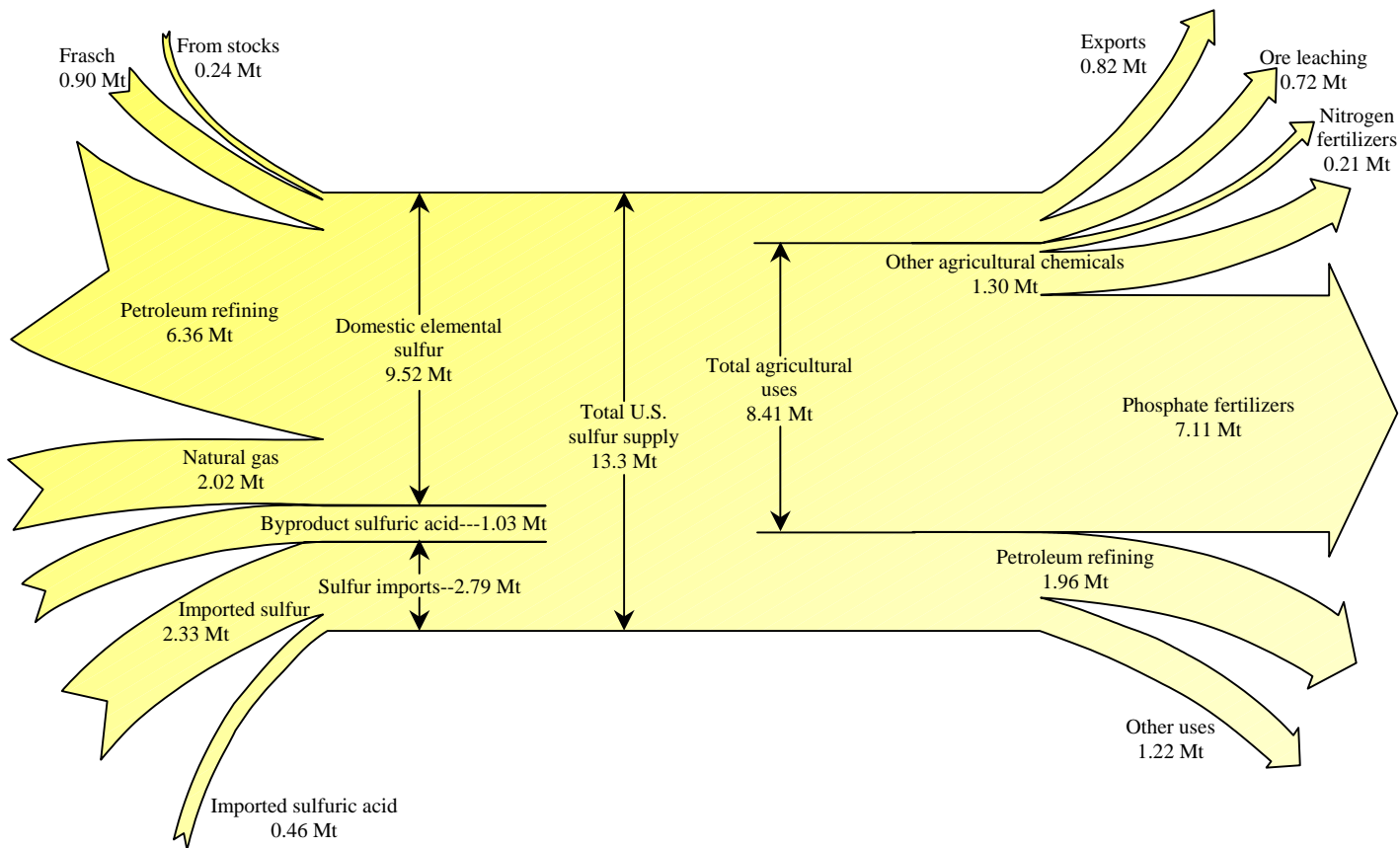


Figure 18. Figure that shows the flow of sulfur in the United States in 2000. The sources and the industries that consume the sulfur are at opposite ends of the arrow. Data listed are in million metric tons (Mt).

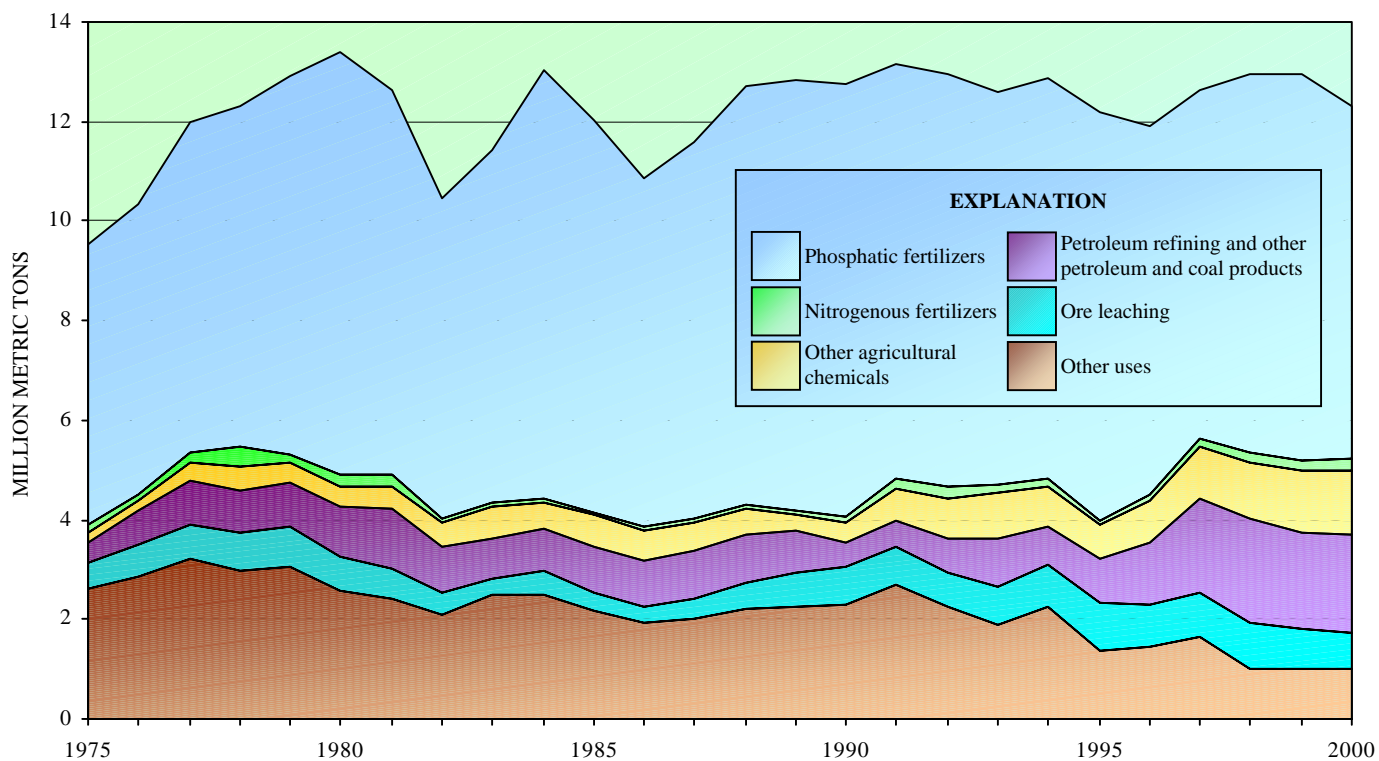
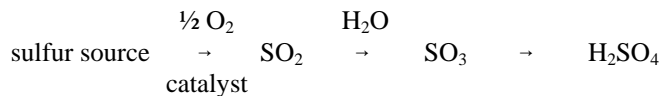


Figure 19. Chart that shows the end uses of sulfur and sulfuric acid. In addition to the uses listed, sulfur and sulfuric acid are consumed in a wide variety of other industries.

The basic equations for H<sub>2</sub>SO<sub>4</sub> production are the same regardless of the process used or the source of the sulfur. The reaction sequence goes as follows:



Actual production is much more complicated than this, and processes vary significantly as do requirements for different sulfur sources.

The earliest commercial process for H<sub>2</sub>SO<sub>4</sub> production, the chamber process, was first used in 1746 (Sander and others, 1984, p. 274). In this process, oxides of nitrogen acted as catalysts to oxidation of SO<sub>2</sub> to SO<sub>3</sub> in a lead chamber reaction vessel. Because the maximum concentration of the H<sub>2</sub>SO<sub>4</sub> product from the chamber process is about 77 to 78 percent, much lower than that used in most industrial applications, the process is considered obsolete, with very limited production from plants of this type (Donovan and Salamone, 1983, p. 190).

The contact process replaced the chamber process early in the 20th century because it could produce the much more concentrated acid (about 98 percent) needed for the production of synthetic dyes, organic chemicals, and the explosives required during World War I (Donovan and Salamone, 1983, p. 190). The first contact process, using a platinum catalyst to oxidize SO<sub>2</sub> to SO<sub>3</sub>, was developed in 1831. It continues to be used with improvements, especially in the type of catalysts used. Vanadium pentoxide eventually replaced platinum as the dominant catalyst owing to its insensitivity to catalyst poisons and its lower cost; a cesium-promoted vanadium catalyst was a later catalyst innovation. A second absorption stage was added in the contact process, optimizing the efficiency of the conversion of SO<sub>2</sub> to SO<sub>3</sub>, reducing SO<sub>2</sub> emissions significantly, and improving the environmental performance of modern sulfuric acid plants. Nearly all H<sub>2</sub>SO<sub>4</sub> plants in developed countries use double absorption systems in order to comply with environmental regulations limiting SO<sub>2</sub> emissions at chemical operations (Sander and others, 1984, p. 274-276). Typical double absorption plants, as shown in figure 20, are able to recover 99.5 to 99.8 percent of the SO<sub>2</sub> produced at the sulfur burner, and some are even more efficient (Donovan and Salamone, 1983, p. 204). Single absorption contact plants can treat their tail gas, sometimes by producing ammonium sulfate, to meet environmental standards.

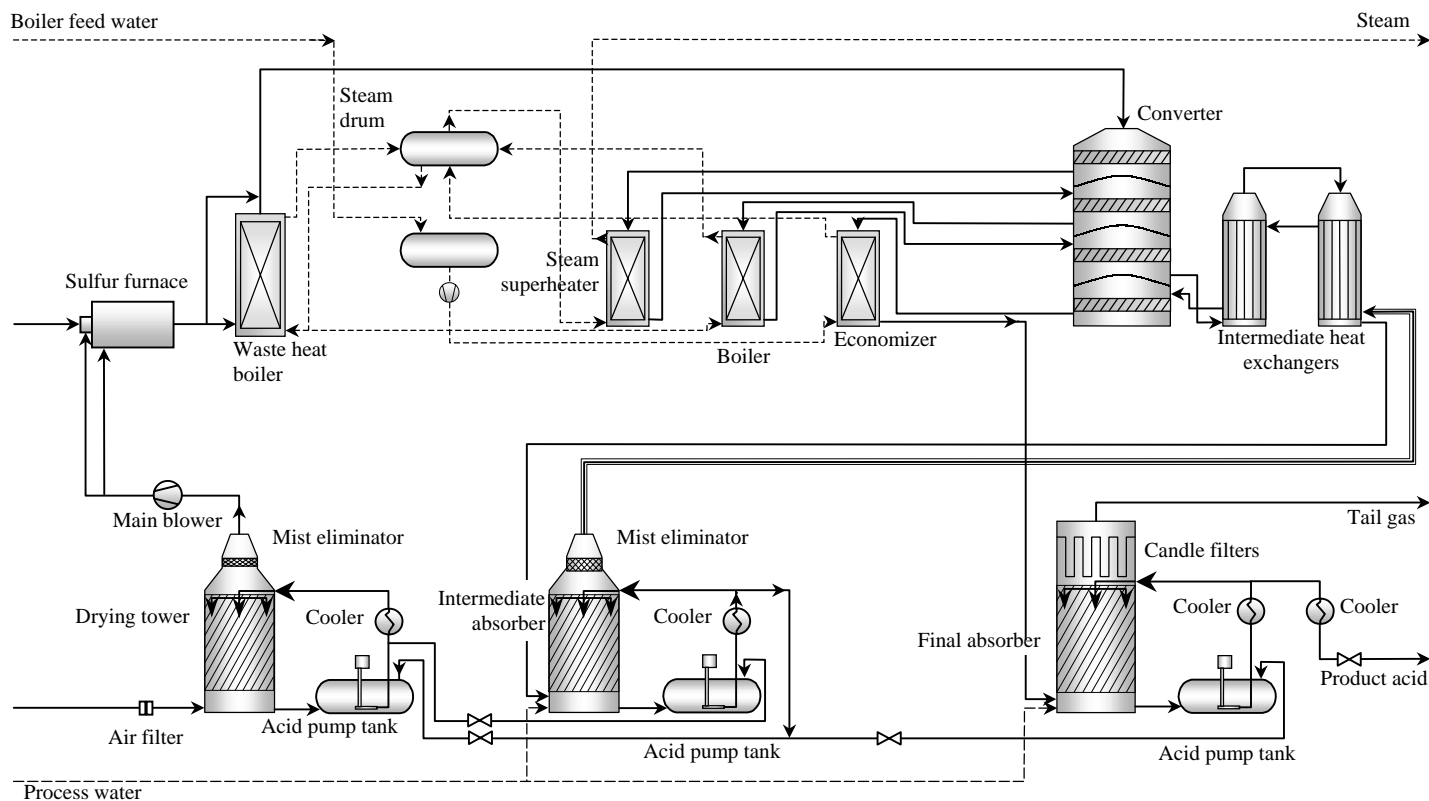


Figure 20. Flow diagram that illustrates the processes of a sulfur-burning, double-absorption sulfuric acid plant.

Many of the steps of the contact process and double absorption process are the same, with addition of some extra steps for double absorption. Different raw materials require some variations, but the basic steps and apparatus are required with extra steps inserted to deal with site specific issues. These steps and equipment are described in the box on the next page.

Elemental sulfur burners create very little waste. Processes have been developed to treat the tail gases to allow almost complete recovery of SO<sub>2</sub>, reducing emissions to extremely low levels. The most common waste produced at sulfur-based H<sub>2</sub>SO<sub>4</sub> plants is

## DOUBLE ABSORPTION SULFURIC ACID PROCESS

**1. Sulfur melting and, if necessary, purification.**—This step varies depending on the type of sulfur used. Melting and purification are required if the sulfur is in solid form. Most modern  $\text{H}_2\text{SO}_4$  producers receive elemental sulfur in molten form so the melting process is unnecessary. When formed sulfur is purchased, it must be melted so it can be pumped to the sulfur burner. Solid sulfur must be purified after melting because frequently it is contaminated with moisture, acidity, dust, and debris during transport. Melting the sulfur eliminates the moisture. Acidity requires the addition of an alkaline material and filtration. Solids are removed through settling or filtration. Molten sulfur then is pumped to the sulfur burner.

**2. Sulfur burner.**—Sulfur burner designs vary, but the purpose is the same at all installations. Sulfur is pumped through nozzles and burned in air to produce  $\text{SO}_2$ . Most sulfur burners are steel shells lined with insulating and fire brick. The  $\text{SO}_2$  concentration in the burner can vary, but usually ranges from 9 to 11 percent. Significant quantities of heat are produced during burning.

**3. Blower.**—The blower draws in air to propel the gases throughout the plant.

**4. Drying tower.**—The air supplied by the blower must be dried before proceeding through the rest of the process. Heated  $\text{H}_2\text{SO}_4$  is used to dry the air. Acid concentrations vary according to the design and size of the plant. Many plants use 98 percent  $\text{H}_2\text{SO}_4$ , and others, especially very large plants, use 93 percent acid. The drying tower is constructed of steel, lined with acid-resistant brick, and packed with partition rings and a cast iron distributor.

**5. Waste heat boiler.**—After leaving the burner, the  $\text{SO}_2$ -containing gas is cooled in a fire-tube or water-tube boiler with cast iron finned protecting sleeves on steel tubes. The heat recovered is used to make steam for use in other parts of the plant or can be converted to electricity.

**6. Hot gas filter.**—The hot gases may be filtered, especially if melted sulfur is purified through the settling process. The filter is a steel shell with external insulation, packed with sized, crushed fire brick. Because most  $\text{H}_2\text{SO}_4$  plants filter molten sulfur prior to the burner, few facilities need to filter the hot gas.

**7. Converter system.**— $\text{SO}_2$  gases are converted to  $\text{SO}_3$  in a steel shell containing trays of catalyst. The gases usually pass over vanadium catalyst trays up to four times to maximize conversion of  $\text{SO}_2$ . The conversion reaction is exothermic, requiring cooling apparatus following the first three passes. This heat may be recovered in steam superheaters or boilers. In the double absorption adaptation of the contact process, gases are drawn from the converter, usually between passes three and four, and directed to an intermediate absorber. Unreacted gases are then returned for the fourth pass through the converter.

**8.  $\text{SO}_3$  cooling.**—The  $\text{SO}_3$  gas leaving the converter is cooled in an economizer to around  $232^\circ\text{C}$  where the excess heat is used to produce more steam for other uses. Other equipment may be used to cool the gas to a lower temperature.

**9. Oleum system.**—Special apparatus is required to produce oleum (fuming  $\text{H}_2\text{SO}_4$  containing free  $\text{SO}_3$  dissolved in  $\text{H}_2\text{SO}_4$ ). This system requires one or two unlined towers prior to the final absorbing tower. Two towers in series are required if 40 percent oleum (109 percent  $\text{H}_2\text{SO}_4$  equivalent) is produced.

**10. 98 percent absorption system.**—The absorber is very similar to the drying tower. Concentrated acid (98- to 99-percent) circulates through the absorber where the  $\text{SO}_3$  is absorbed into the acid. In the double absorption version of the contact process, absorption is accomplished in intermediate and final absorbers. Coolers are needed to eliminate the excess heat formed during the absorption.

**11. Product acid.**—If 98 to 99 percent acid is the desired product, the acid is allowed to flow through the cooler to storage tanks. If lower concentration  $\text{H}_2\text{SO}_4$  is the desired product, a mixing device to dilute the concentrated acid and additional cooling is required (Monsanto Chemical Co., [undated], p. 20-28).

waste heat. Different methods to recover the waste heat produce steam that is used in other parts of the plant or can be used to produce electricity. Power generation at  $\text{H}_2\text{SO}_4$  plants is called cogeneration. In the United States, the Public Regulatory Policies Act of 1978 required power companies to purchase excess power from cogenerators at a price comparable to what it would cost the utility to produce an equivalent incremental quantity of electricity at their own facility. This provision has made it possible for the heat recovery systems to be profitable to the  $\text{H}_2\text{SO}_4$  producers, improving the economics of the plant (Connock, 1999b).

Smelter-based  $\text{H}_2\text{SO}_4$  plants use the double absorption process to strip their off-gases of  $\text{SO}_2$ . The biggest difference between sulfur-burning and byproduct  $\text{H}_2\text{SO}_4$  plants is the lack of sulfur burner at smelters. Smelter gases have lower  $\text{SO}_2$  content and more impurities requiring slightly different steps and higher gas-flow capabilities to produce comparable quantities of  $\text{H}_2\text{SO}_4$ . Figure 21 shows a diagram of a byproduct  $\text{H}_2\text{SO}_4$  plant.

## Agricultural Chemicals

**Phosphoric Acid and Phosphate Fertilizers.**— $\text{H}_2\text{SO}_4$  is an essential component of these manufacturing processes; more  $\text{H}_2\text{SO}_4$  is consumed in the conversion of phosphate rock into phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and other phosphate fertilizers than is consumed in all other industries. Because of this, the fortune of the sulfur industry is very closely tied to the fortune of the phosphate industry. Phosphorus is one of the three essential nutrients (along with nitrogen and potassium) for plant growth. Naturally occurring phosphate

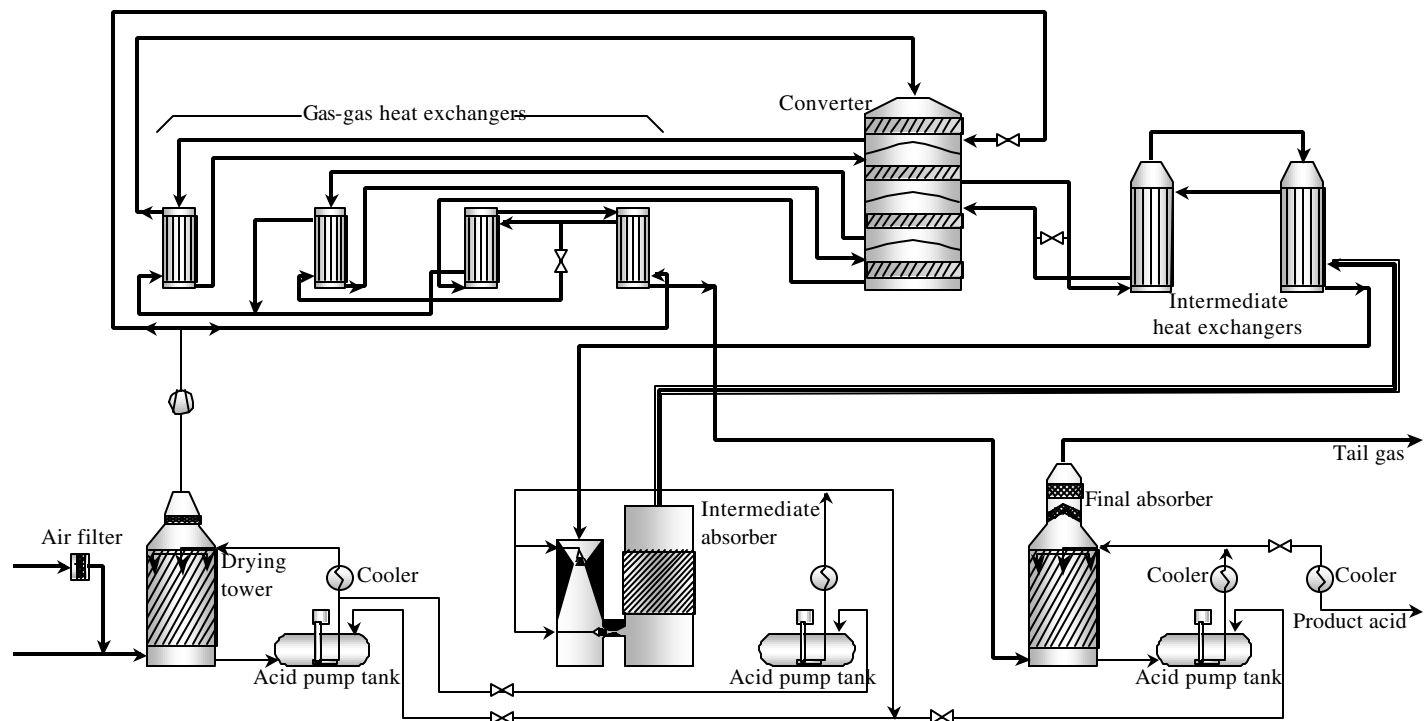
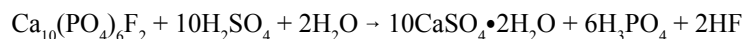


Figure 21. Flow diagram that illustrates the processes of a sulfuric acid plant for metallurgical feed gas.

minerals are insoluble, and for plants to efficiently use this nutrient, the phosphate minerals must be processed into soluble compounds. Most phosphate fertilizer producers use  $H_2SO_4$  produced at plants at or near their phosphate processing facilities to convert the phosphate ores. Although other processes for producing  $H_3PO_4$  and phosphate fertilizers have been developed,  $H_2SO_4$  remains the preferred acidulating agent because of its easy availability, low cost, and well established technology. A flow diagram for a typical U.S. phosphate operation is shown in figure 22.

The most common phosphate mineral is fluorapatite, a fluorine-containing calcium phosphate mineral represented by the chemical formula  $3Ca_3(PO_4)_2 \cdot CaF_2$  or  $Ca_{10}(PO_4)_6F_2$ . Phosphate materials, whether ores or fertilizers, are classified by quality or strength according to their equivalent phosphorus pentoxide ( $P_2O_5$ ) content. Phosphate ores used for phosphate fertilizer production in Florida and North Carolina are 4 to 16 percent  $P_2O_5$  and are beneficiated to 30 to 32 percent  $P_2O_5$ . In the Western United States, fertilizer-grade phosphate rock contains at least 31 percent  $P_2O_5$ ; beneficiation grade ores with 18 to 28 percent  $P_2O_5$  are beneficiated to achieve acid grade, which is then used to produce  $H_3PO_4$ . Elemental phosphorus, which is used to produce other phosphorus chemicals and high-purity  $H_3PO_4$  for use primarily in the industrial cleanser and food industries, is produced from 24 to 31 percent phosphate rock in electric furnaces (Stowasser, 1985, p. 580, 583). The high cost of electricity and improvements in the purification process available for use with fertilizer-grade phosphoric acid have led to the substitution of purified fertilizer-grade phosphoric acid in most chemical and high-purity applications.

The most common process for producing  $H_3PO_4$  from phosphate rock is called wet process phosphoric acid (WPPA) where finely ground phosphate rock is digested with 93 percent  $H_2SO_4$  for about 8 hours. The reaction is as follows:



Although the complete reaction occurs very quickly, the long digestion time allows for the proper formation of gypsum crystals (Bixby and others, 1966, p. 9). Most  $H_3PO_4$  is then used to produce other types of phosphate fertilizers such as triple superphosphate containing 46 percent  $P_2O_5$ ; monoammonium phosphate, 52 percent  $P_2O_5$ ; and diammonium phosphate, 46 percent  $P_2O_5$ . Purified  $H_3PO_4$  is consumed in industrial and food uses. The majority of domestic phosphate producers base their various fertilizer types on phosphoric acid. A lower quality phosphate fertilizer, single superphosphate (SSP), is produced by mixing pulverized phosphate rock with  $H_2SO_4$  and curing. This fertilizer is less popular than the others listed because it contains a relatively low  $P_2O_5$  content (18-20 percent) with no nitrogen value (Stowasser, 1985, p. 583). Nevertheless, its sulfur content makes SSP a desirable fertilizer in Brazil and India. Table 4 lists estimates of the quantity of sulfur and sulfuric acid used to make various phosphate products.

Florida produces approximately 75 percent of the domestic  $H_3PO_4$  output (Klein, 1996). Because so much phosphate rock is processed in Florida, mostly in the center of the State, this part of the country is one of the largest sulfur markets in the world. The sulfur used in the  $H_3PO_4$  process, ends up as part of the gypsum (calcium sulfate) waste generated as part of WPPA production.

**Nitrogen Fertilizers.**—Nitrogen fertilizers require a fraction of the sulfur that is consumed in the production of phosphate fertilizers. Ammonium sulfate, the only significant sulfur-containing nitrogen fertilizer, is a very small portion of the entire nitrogen fertilizer market. In 2000, it represented about 2 percent of the market (Kramer, 2002, p. 55.5). Most ammonium sulfate is produced as a

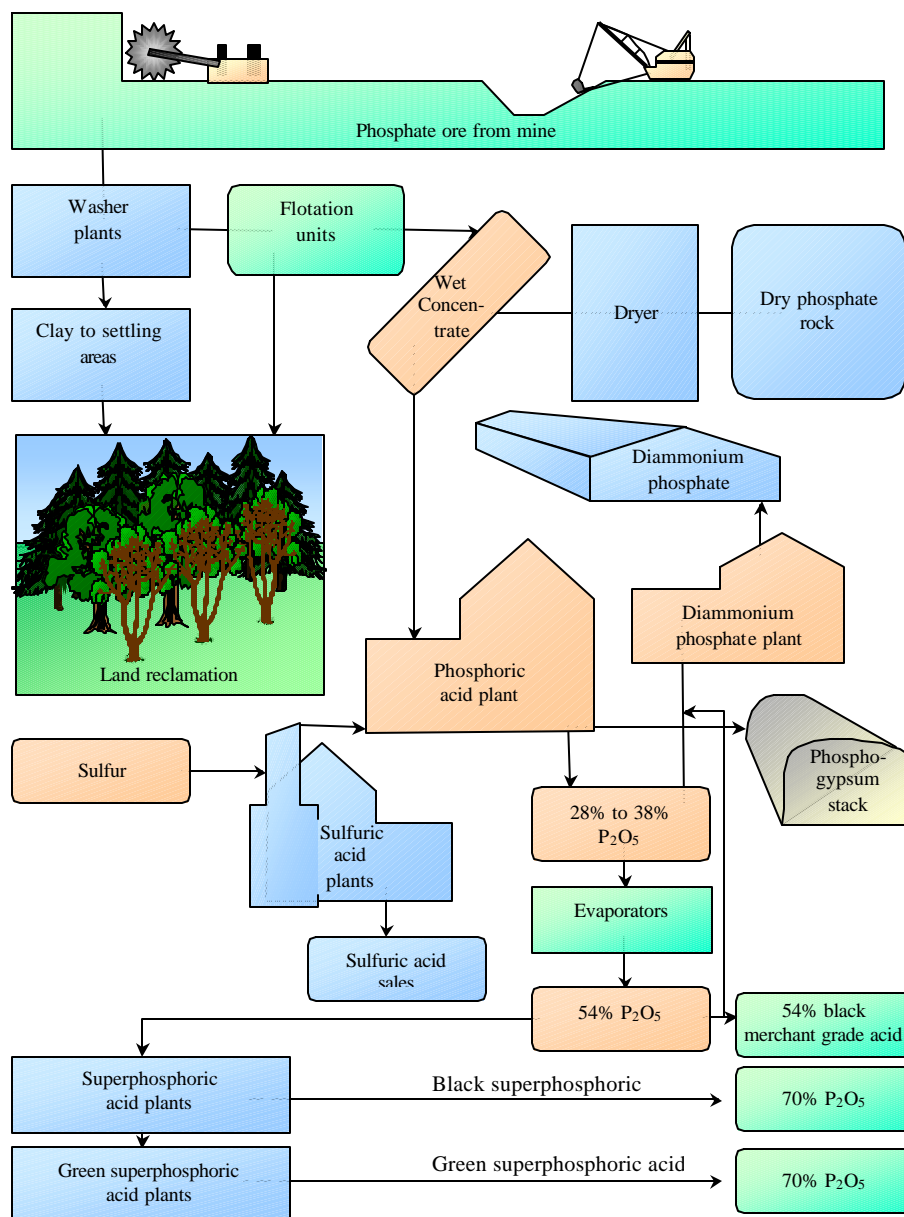


Figure 22. Flow diagram that shows the typical process followed at U.S. phosphate fertilizer production operations. P<sub>2</sub>O<sub>5</sub> is phosphorous pentoxide and MGA is merchant grade acid.

Table 4. Estimates of Sulfur Consumption for Fertilizer Products

Phosphate product (per metric ton P <sub>2</sub> O <sub>5</sub> content)	Sulfur requirement (metric tons)	Sulfuric acid requirement (metric tons)
Wet process phosphoric acid (WPPA).....	0.915	2.80
Single superphosphate (SSP) .....	0.121	0.37
Triple superphosphate (TSP) .....	0.314	0.96
Monoammonium phosphate (MAP).....	0.493	1.51
Diammonium phosphate (DAP).....	0.431	1.32
Ammonium sulfate (AS) .....	0.242	0.74

byproduct of other industrial processes. Production of caprolactam, for example, which is an intermediate in the production of the nylon-6 fiber, results in an ammonium sulfate byproduct. This process is discussed in more detail in the “Caprolactam” section of this report.

Ammonium sulfate also is produced as an environmental byproduct at a coal gasification facility in North Dakota. At this plant, Wyoming coal is converted to synthetic natural gas and releases SO<sub>2</sub> in the process. An ammonia scrubbing system is used to remove the SO<sub>2</sub> flue gases, producing ammonium sulfate as a byproduct that is marketed for agricultural uses.

**Plant Nutrient Sulfur.**—Nitrogen, phosphate, and potassium are recognized as the most important plant nutrients. Increasingly, however, agronomists have emphasized the importance of sulfur in the nutrition of plants. Ammonium sulfate’s fertilizer value is related to its nitrogen content (21 percent) as well as its sulfur content (24 percent) as sulfate. The sulfate sulfur in ammonium sulfate is a form that is readily available for crop uptake. Other benefits to maintaining the proper nitrogen sulfur ratio to plant growth are improved protein and amino acid content and chlorophyll seed formation.

Over the past 20 years, soils have become increasingly deficient in sulfur for several reasons. Larger crop yields have removed larger quantities of sulfur. Environmental regulations limiting SO<sub>2</sub> have significantly reduced atmospheric deposition of sulfur. Reduced sulfur content of transportation fuels has limited SO<sub>2</sub> emissions from vehicles, reducing deposition from those sources. Finally, increased conservation tillage where crop residues are not plowed back into the soil and left to decompose on the surface has reduced the mobility of the sulfate ion in the subsoil, making it less available to crops (H.J. Baker & Bro., Inc., 2001).

In addition to ammonium sulfate and phosphate-sulfate fertilizers, elemental sulfur products have been developed to provide elemental sulfur for crop nutrition. Because large particles of elemental sulfur oxidize to the sulfate form very slowly, limiting the crop nutrient value of the sulfur, plant nutrient sulfur (PNS) products have been formulated to deliver small sulfur particles that decompose more readily into the sulfate form. The particles can be agglomerated into granules with a binding material that makes the sulfur easier to handle, limiting the sulfur dust, and improving the safety of handling finely divided sulfur. Other products incorporate elemental sulfur with 10 percent bentonite clay. After application, the clay swells as it absorbs soil moisture, breaking off the sulfur in a variety of particle sizes.

Other factors affect the conversion of sulfur to sulfate besides particle size. Rising soil temperature increases bacterial activity and conversion. Moist soils also promote transformation. Specific types of bacteria (*thiobacillus oxidans*) in the soil are necessary for the conversion to occur, and colonies expand with regular application of elemental sulfur. The sulfur must be in close contact with the soil organisms for sulfate formation to occur (Tiger Industries Ltd., 1999).

**Other Agricultural Uses.**—Other agricultural uses require elemental sulfur. Sulfur is used as a supplement in animal feeds and in salt blocks. Animal feed sulfur is of high purity and small particle size. Finely divided sulfur is also used in agriculture as fungicides, insecticides, and miticides. Wettable sulfur powders can be mixed with water and sprayed on plants to act as a fungicide or a miticide, reducing fungus formation in crops and killing mites. Dusting and flowable sulfur are used on vine crops, such as grapes, tomatoes, and peanuts, as fungicide. Sulfur sprays are used to rid the interior of poultry houses from depluming mites, tiny organisms that can cause poultry to lose their feathers. Many of these products can also be used as soil amendments to correct high alkalinity in the soil (Georgia Gulf Sulfur Corp., 2000).

## Petroleum Alkylation

In addition to being the largest source of recovered sulfur in the United States, petroleum refining is a large consumer of sulfur in the form of sulfuric acid. Crude oil is a complex mix of hydrocarbons that must be separated and recombined to optimize the products manufactured from each barrel of crude; the ultimate goal is to obtain the most gasoline possible from each barrel of oil (Leffler, 2000, p. 85).

In petroleum refining, several different processes, including distillation, vacuum flashing, and catalytic cracking, are used to separate the various hydrocarbon compounds contained in crude oil. In general, the lighter the product (lower density) and the fewer carbon atoms per molecule, the lower the boiling point and the more volatile the compound. As the number of carbon atoms molecules contain increases, the compounds become heavier, and the boiling point goes up. This makes it possible to separate the various hydrocarbon compounds into products within specific ranges of boiling points and densities as shown in figure 23.

The densest, largest molecules are the least desirable products, and processes have been developed to “crack” the molecules into smaller, more manageable, and more desirable products. Many refineries have thermal or catalytic crackers, the apparatus that refiners use to break some of the larger petroleum molecules into smaller, more desirable molecules. Refiners use the products of crackers and simpler distillers in alkylation facilities to combine some of the smaller compounds that result from cracking and distillation into compounds that meet gasoline fuel requirements (Schmerling, 1981, p. 48-51). The product from this process is known as alkylate, a high quality gasoline blending component with such desirable properties as high octane number, low vapor pressure, and high heat of combustion. Alkylate also blends easily with other gasoline components and additives and optimizes the quantity of gasoline that can be produced from a barrel of oil. Because it contains saturated hydrocarbons and very low impurities, it burns cleanly, promoting long engine life and limiting atmospheric emissions of harmful compounds (Liolios, 1989). In the United States, about 11 percent of the gasoline blending stock is alkylate (Albright, 1990a).

Alkylation reactions typically combine isobutane (a saturated, branched hydrocarbon with 4 carbon atoms and 10 hydrogen atoms) with any of several light olefins (unsaturated hydrocarbons containing one carbon-carbon double bond and an equal number of carbon and hydrogen atoms). The olefins used in alkylation are usually propylene, butylene, or any combination of the two. For the reactions between the isobutane and either propylene or butylene to occur, a catalyst is required. Most alkylation plants use H<sub>2</sub>SO<sub>4</sub> or hydrofluoric acid (HF) as the catalyst (Schmerling, 1981, p. 53). In the context of this report, the H<sub>2</sub>SO<sub>4</sub>-based operations are of more

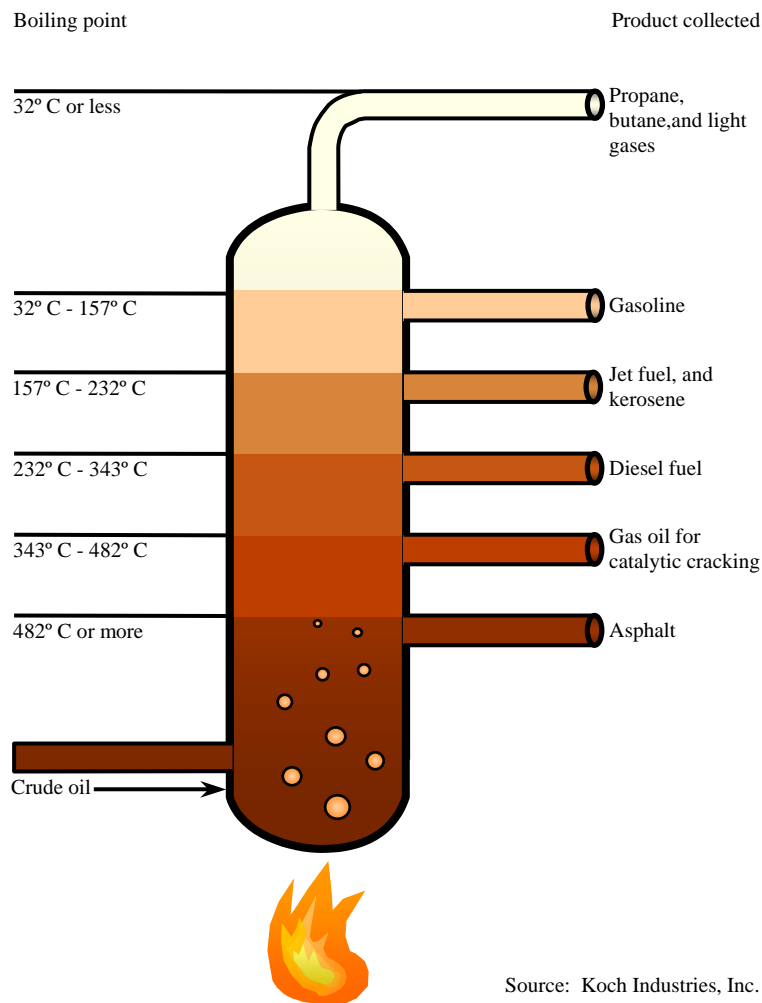
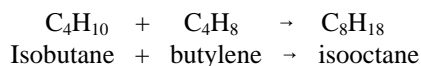
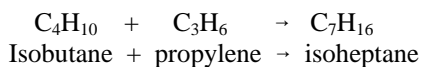


Figure 23. Diagram that shows the products derived at the various boiling points of crude oil. Crude petroleum can be separated into various products through distillation. The various products are differentiated according to appropriately determined ranges of boiling points.

interest. HF-based operations, however, are of interest because  $H_2SO_4$  is required for the production of HF. HF-based operations will be discussed later.

The most important reactions in the alkylation process are as follows:



A graphic representation of these reactions is shown in figure 24. The  $H_2SO_4$  catalyst acts to enhance the reaction without actually changing during the process. Figure 25 shows a simplified diagram of an alkylation plant, which includes the seven main components: the chiller, the reactors, the acid separator, the caustic wash, and three distilling columns.

Because  $H_2SO_4$  alkylation performs best at around 4° C (40° F) and is highly exothermic (heat is produced during the reaction), the olefin and isobutane are pumped through a chiller and mixed with  $H_2SO_4$  as they are pumped into the reactors, which are also refrigerated. While the reactants are passing through the reactors, they are mixed continually to ensure good contact among the hydrocarbons and the acid catalyst to optimize the reaction. After exiting the reactor, the acid is separated from the hydrocarbons and recycled to the reactor. The hydrocarbons are treated in a caustic wash to remove any traces of  $H_2SO_4$  that remain following acid separation. The final step is to separate the alkylate product from any other unreacted isobutane or other reaction products (Hachmuth, 1994; Leffler, 2000, p. 86-88).

The acid is continually cycled through the process; but as it cycles, it becomes diluted and contaminated from impurities in the hydrocarbon feeds.  $H_2SO_4$  that enters the alkylation reactor starts out at about 99 percent concentration; as it cycles through the

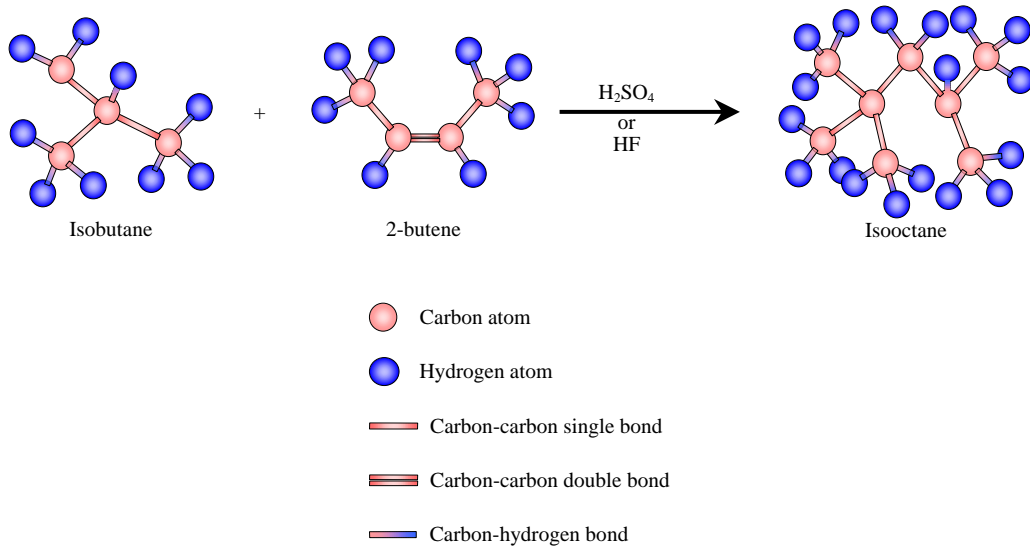


Figure 24. Illustration that shows the alkylation reaction used to produce gasoline. During alkylation, two light low-carbon molecules react to form a larger molecule that is a higher quality motor fuel.  $\text{H}_2\text{SO}_4$  is sulfuric acid, and HF is hydrofluoric acid.

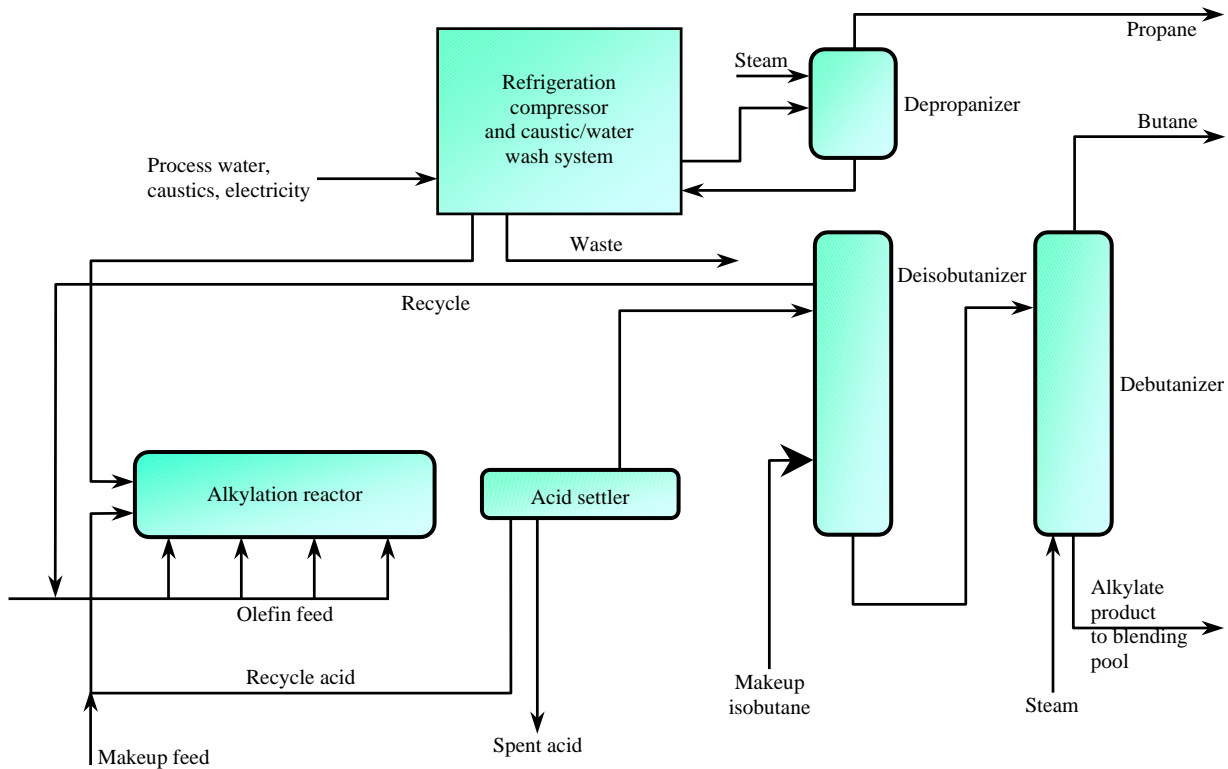


Figure 25. Flow diagram that shows the sulfuric-acid-based alkylation process.

process, it picks up water that enters the process with the olefins and reduces the concentration of the acid. Some tar, a thick brownish mix of hydrocarbons, forms in the process and separates with the acid, causing contamination (Leffler, 2000, p. 88). Other impurities from the hydrocarbon feed may be soluble in the acid, causing further contamination. Because the concentration of the  $\text{H}_2\text{SO}_4$  catalyst is important to the efficiency of the alkylation reaction, when the concentration of  $\text{H}_2\text{SO}_4$  decreases to about 88 percent, a portion of the contaminated  $\text{H}_2\text{SO}_4$  is withdrawn and replaced with fresh acid. The contaminated, dilute  $\text{H}_2\text{SO}_4$  is then regenerated to its original purity and concentration. The regeneration plant may be at the refinery, or the acid may be shipped to another location for regeneration (Energetics Inc., 1998, p. 77).  $\text{H}_2\text{SO}_4$  regeneration will be discussed in the “Recycling” section of this report.



In the United States, H<sub>2</sub>SO<sub>4</sub> alkylation requires about 10 kilograms per barrel (kg/bbl) of alkylate produced. Domestic H<sub>2</sub>SO<sub>4</sub> alkylation capacity is about 500,000 barrels per day (bbl/d), requiring about 5,000 t/d of sulfuric acid, about 1.8 Mt/yr of H<sub>2</sub>SO<sub>4</sub>, containing almost 600,000 t of sulfur. The HF alkylation capacity is also about 500,000 bbl/d. This process uses 93 percent less acid than H<sub>2</sub>SO<sub>4</sub>, about 0.069 kg/bbl. Because each kilogram (kg) of HF produced requires about 2 kg of H<sub>2</sub>SO<sub>4</sub>, domestic HF alkylation requires about 25,000 t/yr, containing about 8,000 t of sulfur, but this is included in the HF requirements rather than with alkylation, to avoid double counting. HF is the preferred alkylation catalyst in Europe; the estimated worldwide consumption of H<sub>2</sub>SO<sub>4</sub> in alkylation is about 1.9 Mt (Hachmuth, 1994). Other alkylation technologies using solid catalysts and/or improved liquid catalysts are under development. These processes would not require H<sub>2</sub>SO<sub>4</sub> (Albright, 1990b).

Regulations requiring clean-burning gasoline increased the demand for alkylate for blending reformulated gasoline. Other important blending components are ethanol and methyl tertiary butyl ether (MTBE), which are used to increase the oxygen content of the fuel. Environmental concerns regarding MTBE contamination of ground water have prompted proposals to ban the use of that compound in gasoline. If this occurs, then demand will increase for alkylate and ethanol, thus potentially increasing demand for H<sub>2</sub>SO<sub>4</sub> for alkylation (Sulfuric Acid Today, 2000). Because U.S. refineries and alkylation plants have been operating nearly at capacity for most of the past decade, significant increases in alkylation production will depend on the construction of new alkylation facilities. The degree to which H<sub>2</sub>SO<sub>4</sub> alkylation demand grows will depend on the alkylation technology chosen for new operations.

## Ore Processing

Smelting of nonferrous metals has been a major source of sulfur in the form of byproduct acid since early in the 20th century, but more recent developments in the metals industry make them major consumers of H<sub>2</sub>SO<sub>4</sub> also. Processes have been developed that dissolve the various metals from the host rock with solvents, frequently H<sub>2</sub>SO<sub>4</sub>, and then recover the desired metals from the solutions. Copper has been produced through variations of this method since about 1967. Nickel can be produced using a pressure acid leach (PAL) process. Technically, it could be possible to produce other metals through variations of H<sub>2</sub>SO<sub>4</sub> leaching processes, but no commercial processes for other metals have been developed.

**Copper.**—Traditional copper processing involves the smelting of sulfide ore concentrates to produce blister copper for refining, an energy intensive and relatively high-cost method for copper production. While leaching of ores and concentrates (including vat leaching with electrowinning and ore waste leaching with precipitation) had been practiced on a relatively small scale, development of improved extractants, the availability of inexpensive smelter acid, and the pressure to reduce production costs led to wider scale adoption of solvent extraction-electrowinning (SX-EW) technology for the recovery of copper from oxide copper resources. SX-EW production avoids much of the cost associated with the beneficiation and smelting and, at least initially, allowed for very-low-cost production from waste piles where copper mining costs had been defrayed by traditional sulfide ore production. These techniques were subsequently applied to mine-for-leach oxide ores and acid-soluble sulfide ores.

Copper minerals that are readily leachable are the oxides and the secondary sulfides that are described in the table 5. The oxide minerals are readily leached with dilute sulfuric acid. The secondary sulfides require the addition of an oxidizing agent, usually ferric iron, which oxidizes the copper to make it more soluble (Ramey, 1995, p. 5)

Table 5. Copper Minerals Amenable to Sulfuric Acid Leaching

Mineral	Formula
Oxide mineral types:	
Copper carbonates:	
Malachite .....	Cu <sub>2</sub> CO <sub>3</sub> (OH) <sub>2</sub>
Azurite .....	Cu <sub>3</sub> (CO) <sub>2</sub> (OH) <sub>2</sub>
Copper silicate, chrysocolla.....	CuSiO <sub>3</sub> ·nH <sub>2</sub> O
Copper chloride, atacamite .....	Cu <sub>2</sub> (OH) <sub>3</sub> Cl
Copper sulfate, brochanite .....	Cu <sub>4</sub> SO <sub>4</sub> (OH) <sub>6</sub>
Copper oxides:	
Tenorite.....	CuO
Cuprite .....	Cu <sub>2</sub> O
Secondary sulfide minerals:	
Chalcocite.....	Cu <sub>2</sub> S
Digenite.....	Cu <sub>9</sub> S <sub>5</sub>
Covellite .....	CuS

For solvent extraction to be successful, the extractant used requires several properties, including the ability to extract the copper from the acid in a manner compatible with leaching and metal recovery process; stability under process circuit conditions; solubility in an inexpensive solvent, such as kerosene; minimal formation of stable emulsions or crud; safety; and low cost (Kordosky, 1992).

During the 1960s, General Mills, Inc. identified an organic reagent that would efficiently and selectively strip the copper from the dilute H<sub>2</sub>SO<sub>4</sub> solution and that met other requirements. In 1967, Ranchers Development Co. implemented the new SX-EW technology at its Bluebird Mine in Miami, Ariz. Products from the first operations were not of consistent quality, but subsequent plants showed that consistently high-quality copper could be produced (Ramey, 1995). The advent of environmental legislation in the 1960s and

1970s that required the capture of SO<sub>2</sub> at smelters resulted in significant production of H<sub>2</sub>SO<sub>4</sub> from those sources and increased the availability of low-cost H<sub>2</sub>SO<sub>4</sub> for copper leaching facilities (Gillen, 1996). By 1990, 25 percent of U.S. refined copper produced from primary materials (mined, not recycled) used SX-EW and in 2000, 36 percent (Edelstein, 1996, p. 252, Edelstein, 2002, p. 22.3).

The SX-EW process has been improved and adapted for use at specific locations. The SX-EW process has four basic steps, which are as follows:

1. During the leaching step, dilute H<sub>2</sub>SO<sub>4</sub> called raffinate is applied to piles of ore. As the weak acid passes through the ore, it dissolves the copper from the minerals. The copper-laden pregnant leach solution flows out of the bottom of the ore piles and is collected in ponds from which it is pumped to a solvent extraction plant. A small percentage of domestic production comes from in situ leaching of oxide ores using an injection and recovery well system.

2. At the extraction plant, the pregnant leach solution is intimately mixed with the organic reagent dissolved in an organic solvent. The reagent selectively removes the copper from the acid solution into the organic phase. When the extraction is complete, the two solutions are allowed to settle, with the lighter organic solution floating on top of the depleted leach solution from which most of the copper has been removed. This usually requires multiple passes to ensure optimum copper recovery. The depleted leach solution (raffinate) is recycled to the ore piles to begin the leaching process again. The copper-rich organic solution is pumped to the stripping section of the plant for further processing.

3. The organic solution is mixed with a concentrated sulfuric acid electrolyte that strips the copper from the organic solution. The solutions are allowed to settle once again and then separated. The organics are recycled to the extraction tanks to repeat the process. The copper-containing electrolyte is pumped to the electrowinning tankhouse. The net effect is to concentrate the copper in the leach solution from around 1 to 6 grams per liter (g/L) to about 35 g/L in the electrolyte.

4. In the electrowinning cells, lead plate anodes alternate with thin sheets of copper, stainless steel, or titanium that act as the cathodes. The electrolyte solutions fill the electrolytic cells and a direct current passes from the anodes through the electrolyte, causing copper ions from the electrolyte solution to plate onto the cathodes. After 7 to 10 days, 99.99-percent-copper-containing cathodes weighing from about 90 to 115 kg are removed from the cells, rinsed and prepared for sale or further processing in to other copper products.

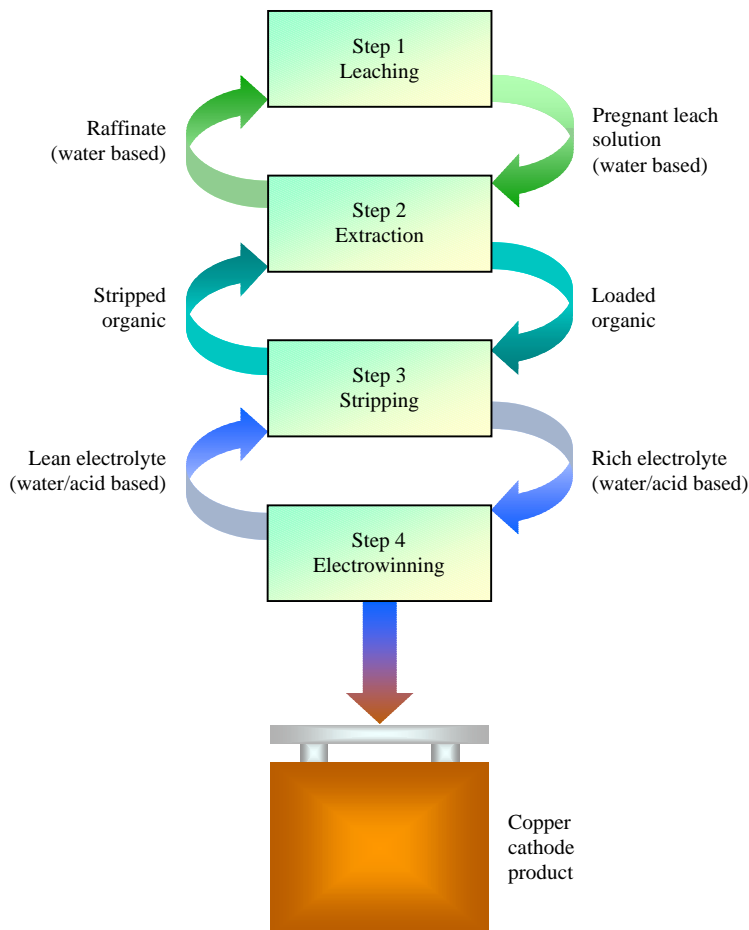
The SX-EW process, as illustrated in figure 26, incorporates three closed loop circuits for the raffinate, organic reagent and solvent, and electrolyte stages, with solutions being constantly recycled and not discarded (Phelps Dodge Mining Co., [undated], p. 8-9). Although H<sub>2</sub>SO<sub>4</sub> is recycled in the leaching process, it is constantly being consumed by the system and must be replenished. In 1995, an estimate placed the quantity of H<sub>2</sub>SO<sub>4</sub> consumed in U.S. SX-EW operations at about 2.1 Mt containing about 680,000 t of sulfur (Gillen, 1996). The actual quantity of H<sub>2</sub>SO<sub>4</sub> consumed in copper leaching varies by location, but generally ranges from 3 to 5 kg per kilogram of copper produced (Ramey, 1995, p.11). Using an average of 4 kg of acid per kilogram of copper, consumption of H<sub>2</sub>SO<sub>4</sub> used to produce SX-EW copper in 1999 was nearly 2.4 Mt of H<sub>2</sub>SO<sub>4</sub>, containing about 870,000 t of sulfur.

Most future developments of copper operations in the United States are expected to be SX-EW projects. The domestic copper industry has experienced a slump starting in the late 1990s with mine production falling by 17 percent from 1997 to 1999. SX-EW production declined in 1999 and 2000 with several closures or reduced production owing to cessation of mining, but production rose to a record high level in 2001. Phelps Dodge Mining Co. converted its Morenci, Ariz., site to all leach SX-EW in 2001 (Edelstein, 2002, p. 55). A new solvent extraction copper operation was planned for development in Utah that would use byproduct sulfuric acid produced at Kennecott's smelter (Sulphur, 2000a). Upon completion, the increased SX-EW capacity would require a comparable increase in sulfuric acid consumption for the process.

Decreased byproduct acid production resulting from the closed smelters coupled with the expansion of solvent extraction operations in the same geographic area presented the potential of tight acid supplies for the new SX-EW capacity. Phelps Dodge is considering the option of installing a sulfur burner for the sulfuric acid plant at its shuttered Hidalgo, N.M., smelter. The company then would be able to supply its leach operations with virgin acid from Hidalgo (North America Sulphur Service Sulphur Newsletter, 2000a). Poorer than expected financial results for the company in the first half of 2000 initially delayed action on the sulfur burner plan, but the project was likely to be reactivated (North America Sulphur Service Sulphur Newsletter, 2000b). SX-EW operations are expanding in the rest of the world also, especially in Australia, Chile and Peru. According to data compiled by the International Copper Study Group (2002, p. III), world SX-EW capacity has grown to 2.5 Mt in 2000 from 700,000 t in 1990 and was anticipated to reach 3.2 Mt in 2005. With large reserves of leachable copper ores identified around the world, SX-EW processing holds the potential for significant growth and, with it, significant increases in sulfur and H<sub>2</sub>SO<sub>4</sub> consumption (Gillen, 1996).

**Nickel.**—Nickel ores can also be classified as oxides, silicates, or sulfides. The majority of world nickel production is obtained through the smelting of sulfide ores, the most common of which is pentlandite [(Ni, Fe)<sub>9</sub>S<sub>8</sub>]. Nickel laterites—primarily composed of nickeliferous limonite [(Fe,Ni)O(OH)] and garnierite (a hydrous nickel silicate)—are also significant sources of primary nickel (Kuck, [undated]). Most laterite deposits have elevated levels of cobalt and iron, and cobalt production can be a positive factor in determining the feasibility of developing a deposit. Laterites are processed using at least four different technologies. They can be smelted directly to a ferronickel product through an energy-intensive pyrometallurgical process during which cobalt is not recovered separately. A second process leaches the ore with an ammonia solution. Nickel and cobalt are separated in this process, but recovery of both metals is relatively low (Bolton and others, 1997). The third process—the PAL process—has grown in importance because it can recover more than 90 percent of both nickel and cobalt content. It is of particular interest in the context of this report because it consumes up to 30 t of H<sub>2</sub>SO<sub>4</sub> per metric ton of nickel produced (Sulphur, 2000c, p. 32). The fourth process uses sulfur or pyrite to produce a nickel-cobalt matte.

The first PAL operation was built in Moa Bay, Cuba, with production beginning in 1959 (Bilbrey and Long, 1960, p. 811). PAL developments languished elsewhere until the technology was adapted to process Australian material in 1997. Since that time, three



Source: Phelps Dodge Morenci, Inc.

Figure 26. Flow diagram that illustrates the solvent extraction-electrowinning process. The process consists of a series of closed-loop circuits. The sulfuric acid ( $H_2SO_4$ ) that dissolves the copper from the leachable minerals is stripped of copper in the extraction step and returned to the ore piles to leach more copper.  $H_2SO_4$  is used to strip copper from the solvent and as the electrolyte in the electrowinning step.

PAL projects have been commissioned in Australia. Another PAL operation is under construction, and several other greenfield projects are under consideration worldwide. The entire nickel/cobalt recovery process is complicated and varies significantly by location. Simplified flow diagrams of the three operations in Australia are shown in figure 27. The actual PAL portions of the facilities where the  $H_2SO_4$  consumption occurs are quite similar.

After the ore is crushed to the appropriate size and mixed with water to produce a slurry, the slurry is heated, thickened and pumped into the reaction vessel. The reaction vessel is a titanium-lined autoclave in which the ore slurry is mixed with concentrated sulfuric acid and heated to  $250^\circ C$ . The extreme conditions force approximately 98 percent of the metal content of the ore to dissolve in the acid. After about 75 minutes of agitation in the autoclave, the leach material is removed from the autoclave, depressurized, and cooled. Then the metal-bearing solution is separated from the leach tailings slurry, which is neutralized with lime and limestone and pumped to the tailings evaporation pond (Cobalt News, 1999). The leach solution is partially neutralized with limestone, and air, hydrogen, and additional limestone are then added to precipitate iron, copper, and chromium impurities, which are sent to a second the tailings pond. Processing of the remaining nickel/cobalt-bearing liquid varies considerably as do the final products of cobalt briquettes, cobalt cathode, cobalt powder, cobalt sulfide, nickel briquettes, and nickel cathode (Connock, 1999a). Although some of the  $H_2SO_4$  is recycled through the process, much of it forms a waste calcium sulfate (gypsum) product during neutralization and is discarded with other tailings.

### Other Industrial and Chemical Uses

Agricultural uses, ore processing, and petroleum refining represented 93 percent of identified sulfur consumption in 2000 (Ober, 2002, p. 76.17). Smaller quantities of sulfur are used in a myriad other industrial processes. Some of these are listed individually below and others are discussed briefly. Some end uses are not discussed because of their relative lack of importance to the entire sulfur industry, space constraints, and the difficulty in identifying all possible uses.

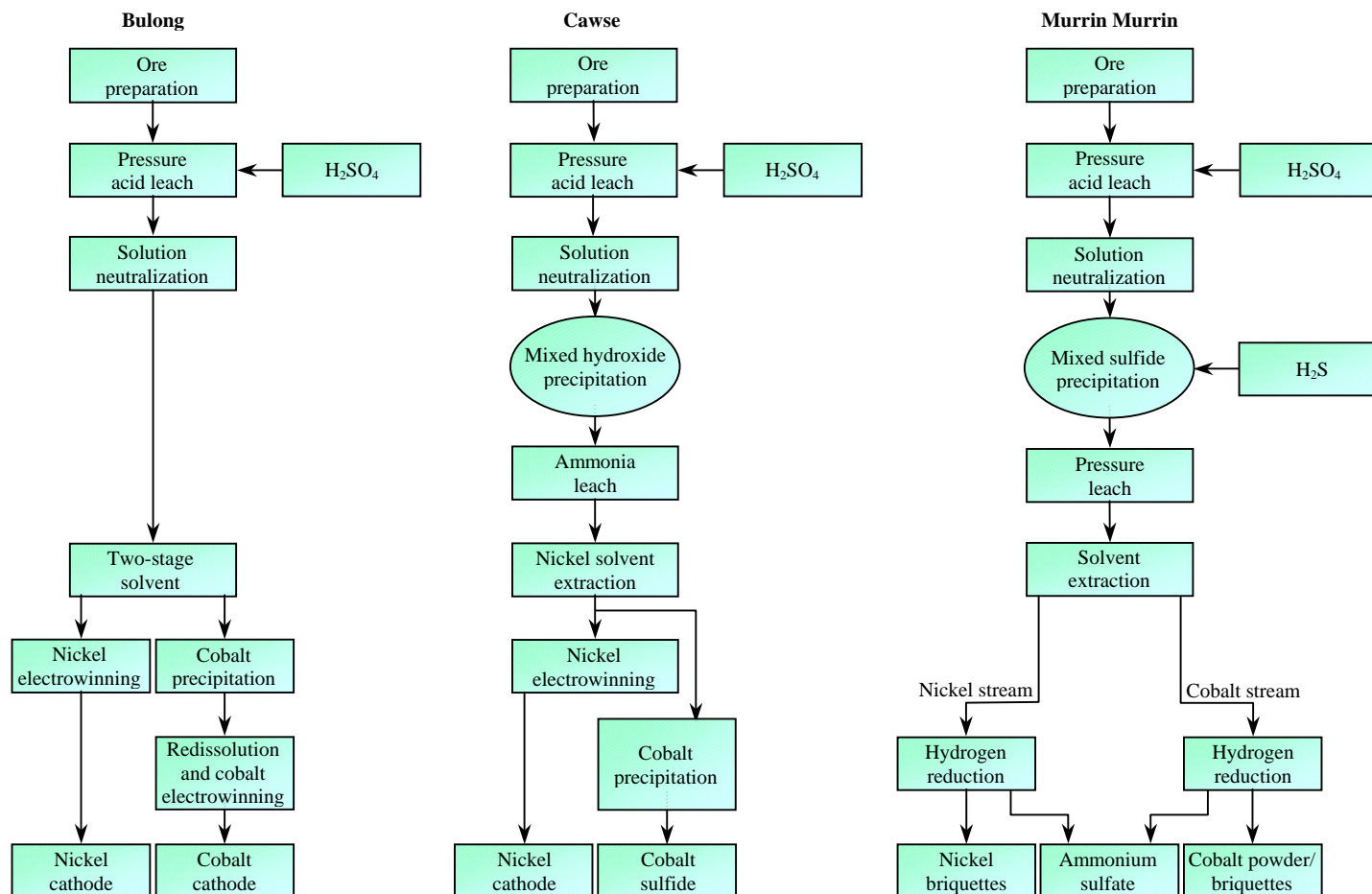


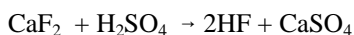
Figure 27. Diagram that shows the operations of Australia's nickel-cobalt pressure acid leach operations. The basic concept of operations is the same for all producers. The final products vary considerably by location.

**Caprolactam.**—Another industrial use of  $\text{H}_2\text{SO}_4$  is the source of one sulfur compound used in agriculture. Ammonium sulfate is a byproduct from the production of caprolactam ( $\text{C}_6\text{H}_{11}\text{NO}$ ), an organic chemical that is a precursor for the nylon-6 polymer that is used in carpets, other textile products, and plastics. The production process is very complex, requiring numerous complicated reactions among inorganic and organic chemicals. A very simplified diagram of the caprolactam process is shown in figure 28. The major raw materials are sulfur, ammonia, and benzene, which can be converted to cyclohexane. In intermediate steps, sulfur is converted to  $\text{H}_2\text{SO}_4$ , ammonia is converted to hydroxylamine, and cyclohexane becomes cyclohexanone. The three intermediates are combined to form caprolactam and ammonium sulfate. Caprolactam is the monomer that is converted to the nylon-6 polymer.

This process is unusual in that as it consumes  $\text{H}_2\text{SO}_4$ , it produces a usable sulfur byproduct, ammonium sulfate, that is used in agriculture. In effect, it is a sulfur-consuming industry and a sulfur-chemical-producing industry. Caprolactam production is one of the few industrial uses for sulfur where sulfur does not end up as a component of waste. Variations on the caprolactam production process result in different byproduct production volumes of ammonium sulfate through the actual reaction and subsequent neutralization of the reaction products. The amount of ammonium sulfate produced in the caprolactam processes varies from 1.7 to 4.4 t of ammonium sulfate per ton of caprolactam. World capacity for caprolactam production is nearly 4.0 Mt. It is not known, however, which processes are used at various operations, making estimates of byproduct ammonium sulfate production difficult (Fisher and Crescentini, 1992).

**Hydrofluoric Acid.**—Hydrofluoric acid (HF) is a strong inorganic acid that is used in several industrial processes. In the United States, about 54 percent of HF consumption is in the production of fluorocarbons, a class of chemicals used as refrigerants, propellants, and plastic foam blowing agents. Other fluorine-derived chemicals consume about 32 percent of HF. Metal treatments, such as stainless steel pickling, consume 5 percent of HF; petroleum alkylation also consumes about 5 percent; and aluminum producers use about 4 percent of HF consumption to make aluminum fluoride. The production of HF represents approximately 1.5 percent of the world's sulfuric acid consumption (Will, 2000).

Sulfuric acid is used to produce HF through its reaction in a rotating steel kiln with finely ground acid-grade fluorspar (the mineral calcium fluoride) as follows:



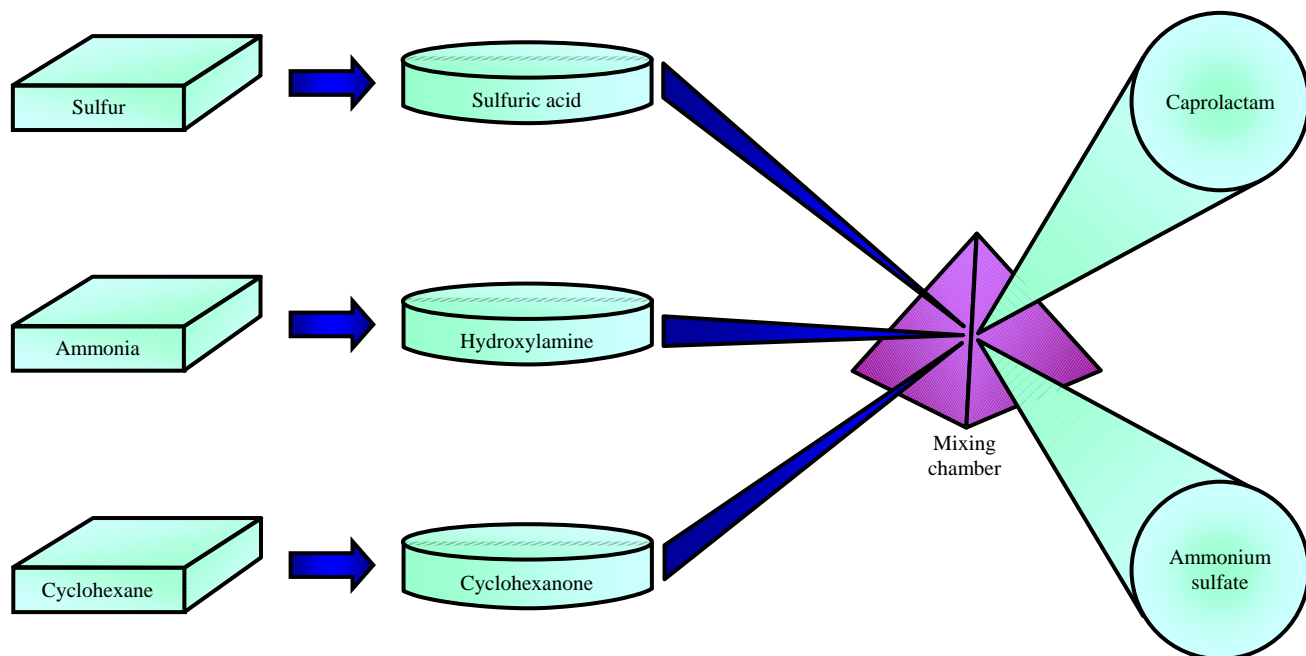


Figure 28. Flow diagram that illustrates the production process for caprolactam. Caprolactam is an intermediate material used in the production of nylon-6. Its production process is very complex, but it can be simplified to show that the raw materials undergo several reactions that eventually result in caprolactam and byproduct ammonium sulfate. The ammonium sulfate is used as a fertilizer.

About 2.4 t of fluorspar and 2.7 t of 96 to 98 percent  $\text{H}_2\text{SO}_4$  produce about 1 t of HF. The kiln is maintained at  $200^\circ\text{C}$  to  $250^\circ\text{C}$ ; the retention time is between 30 and 60 minutes. An excess of  $\text{H}_2\text{SO}_4$  is used to ensure the optimum conversion to HF (Doorebus, 1977). A flow diagram of the HF production process is shown in figure 29. About 4 t of waste gypsum is produced for every ton of HF produced.

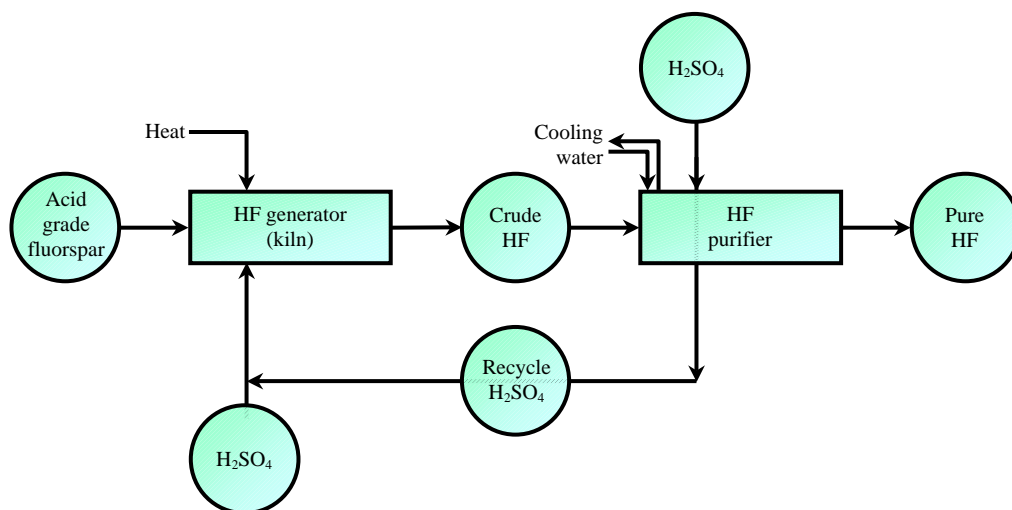


Figure 29. Flow diagram that shows the production of hydrofluoric acid (HF). Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is important for the production of HF. An excess of  $\text{H}_2\text{SO}_4$  reacts with fluorspar at high temperatures to produce HF.

**Pulp and Paper Manufacturing.**—During pulp and paper processing, wood is treated to separate the cellulose fibers from the lignin and extractive substances, such as resinous and fatty acids, that make up the wood particles. The cellulose fiber that has been treated is known as pulp, which is further processed by bleaching and drying to produce a material that is used to make paper. The quality and type of paper produced is determined by the amount of processing the pulp undergoes.

Wood is treated in mechanical or chemical pulping processes. In mechanical processes, wood particles are torn apart, with all the materials contained in the wood remaining in the pulp. Paper made from mechanical pulp is used for lower quality papers, such as newsprint and paperboard. Chemical pulping dissolves and separates the lignin and the extractive substances from the wood fibers by means of chemical reactions. Chemical pulp is used to produce higher quality paper. Chemical pulp from softwood produces strong

paper owing to the wood's long fibers. Hardwood chemical pulp is ideal for making fine papers because of its short fibers. Waste paper has become an increasingly important source of pulp for paper making, but chemical pulping of virgin fibers is the more important in relation to the sulfur industry.

Two chemical processes are used to produce pulp, the sulfate and the sulfite processes, both of which use sulfur chemicals. Several different sulfur chemicals are used in pulp and paper processing, including sulfuric acid, sulfur, sulfur dioxide, magnesium sulfate, aluminum sulfate, and sodium-based sulfur-containing chemicals. In the sulfate process, which is also known as the kraft process and is the more widely used of the two processes, the pulp is cooked with an alkaline cooking liquor; in the sulfite process, the cooking liquor is acidic (ForestSweden, [undated]).

The kraft process is used for 73 percent of global wood pulp production. Mechanical pulping is the source of 21 percent of available pulp. The sulfite process represents 6 percent of pulp production. Because the kraft process is of much greater concern to the sulfur industry, it will be described in greater detail here. The kraft process is used to make strong, long fibers by cooking the wood in a sodium- and sulfur-based liquor at about 148° C (300° F) and 1,030 kilopascal (150 pounds per square inch, psi). The ratio of sodium to sulfur is important for the process to achieve the best possible separation of fiber from lignin. The fiber and cooking liquor are separated with the fiber being sent for paper production or further processing if it is to be used to produce high quality paper. Bleaching removes more lignin from the pulp as well as improving the whiteness and brightness of the fiber.

Lignin is separated from the spent cooking liquor, which also contains sodium and sulfur compounds. The lignin is used as a fuel to produce energy and steam for the plant, and cooking chemicals are recovered from the remainder of the spent liquor. In order to improve the economics of the system and minimize environmental emissions, the cooking liquor circuit and the bleaching operations have been improved to allow only small losses of the cooking and bleaching chemicals, necessitating only small requirements of make-up chemicals and, thus, less sulfur than had previously been the case.

The primary sulfur chemicals used in the kraft process are aluminum sulfate, magnesium sulfate, sodium sulfate, sodium hydrosulfide, sulfur, and H<sub>2</sub>SO<sub>4</sub>. H<sub>2</sub>SO<sub>4</sub> is the most important of the sulfur chemicals in pulp manufacturing and is used in many steps in the process as shown in figure 30. It is used to produce chlorine dioxide that is used in the bleaching process, for pH adjustments in the bleach plant, for acidulation in the evaporation stripping step, and in boiler water treatment ion exchange regeneration. As more pulp mills are moving away from elemental-chlorine-based systems, an increasing amount of H<sub>2</sub>SO<sub>4</sub> will be used in the chlorine-dioxide-based bleaching systems in an effort to reduce dangerous chlorinated organic emissions. Aluminum sulfate is used to treat incoming water or for paper sizing. Magnesium sulfate is an additive for protecting pulp strength in oxygen-based delignification and bleaching systems. Sodium sulfate and sodium hydrosulfide are used to replace sodium and sulfur lost during processing. Elemental sulfur is burned to produce SO<sub>2</sub> that, in turn, is used to make chlorine dioxide for bleaching. The use of all these chemicals, except magnesium sulfate and H<sub>2</sub>SO<sub>4</sub>, is decreasing. Magnesium sulfate consumption is growing but is insignificant in comparison to the consumption of H<sub>2</sub>SO<sub>4</sub>. Typically, chloride dioxide generation uses 80 percent of the H<sub>2</sub>SO<sub>4</sub> required in a plant using oxygen delignification to produce elemental-chlorine-free paper. Table 6 shows where sulfur chemicals can be found in a typical kraft process pulp mill (Bernar, 2000).

Table 6. Typical Sources of Sulfur in Bleached Kraft Pulp Mills

Source	Amount of sulfur (kilogram of sulfur per metric ton <sup>1</sup> )
Wood, water, and chemicals .....	0.3-0.5
Fuel oil to lime kiln and recovery boiler .....	1.0-2.0
Tall oil production .....	<sup>2</sup> 2.0-3.0
Chloride dioxide generation.....	<sup>3</sup> 0-15
Magnesium sulfate for oxygen stage .....	0-0.8
Total .....	3.5-25.5

<sup>1</sup>Air-dried metric tons.

<sup>2</sup>Spent acid from chlorine dioxide production can be used often.

<sup>3</sup>Depending on the type of process and valid for a mill using up to 40 per air-dried metric ton of chlorine dioxide expressed as active chlorine.

Source: Bernar, 2000.

**Sulfur Construction Materials.**—Although not widely used currently, sulfur construction materials can offer improvements over more traditional materials, especially in specific applications. Sulfur construction materials include sulfur concrete and sulfur-extended asphalt pavements as well as precast concrete components, extrusions, and cast-in-place forms.

About 3.2 million kilometers (2.0 million miles) of paved highways, roads, and streets comprise the majority of the ground transportation network in the United States, 93 percent of which is paved with asphalt-type materials (Weber and McBee, 2000, p. 2). Asphalt is a heavy organic byproduct of petroleum refining. It was typically high-volume and low-cost, making it a attractive to the road-construction industry. As demand for such high-quality petroleum products as gasoline grew, pressure mounted for the petroleum industry to improve refining technology to produce more high-quality products and less asphalt and other low-value

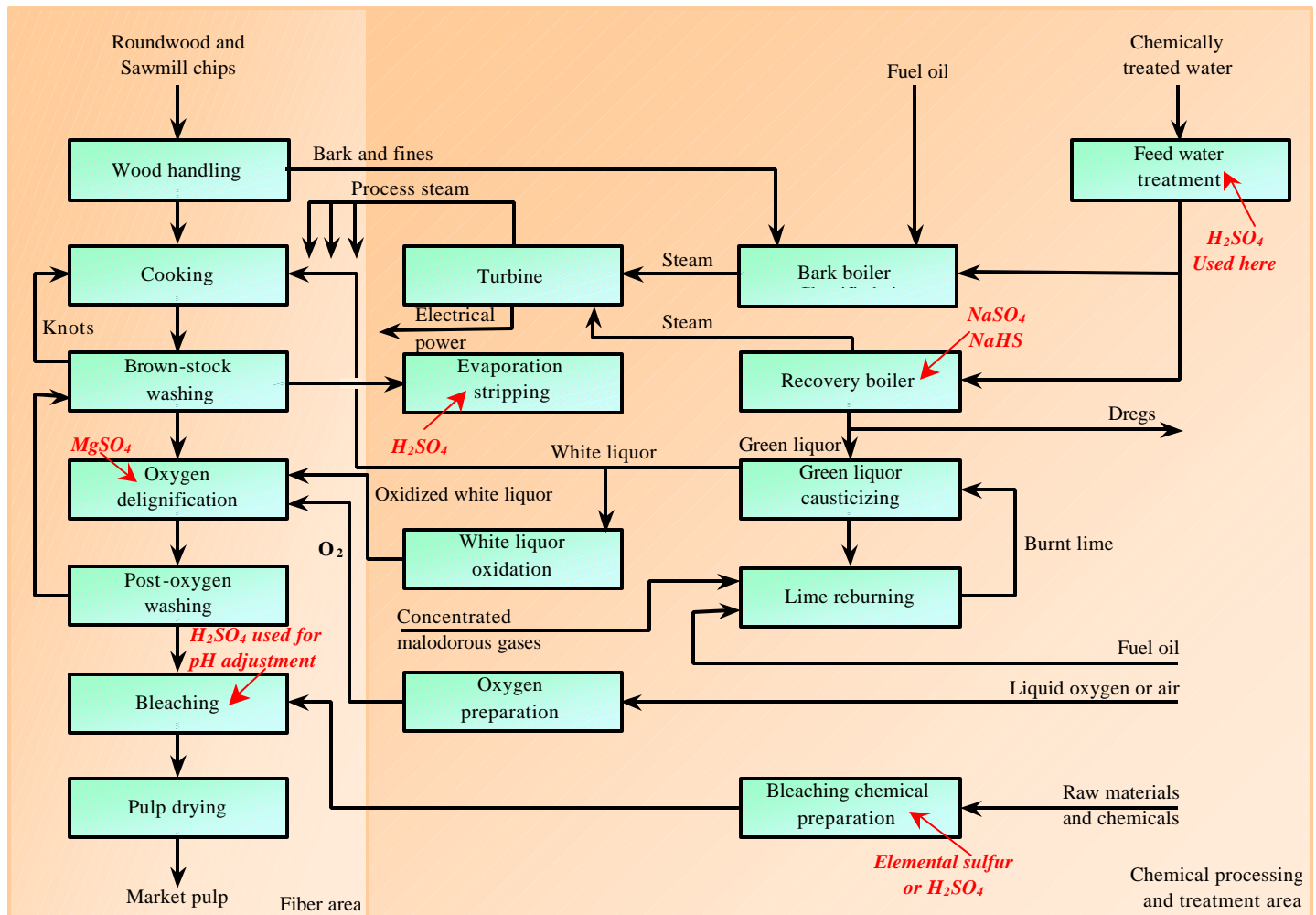


Figure 30. Chart that shows the steps in the Kraft pulp and paper process that use sulfur chemicals.

byproducts and wastes. These events, coupled with the increasing availability and decreasing costs of recovered sulfur have made sulfur-extended asphalt cements a more attractive alternative to the traditional asphalt paving materials.

Tests initiated in 1975 showed that sulfur-extended asphalt was at least comparable with traditional asphalt concrete, with some properties being superior as shown in table 7. Sulfur-extended asphalt was stiffer, making it more resistant to rutting damage in warm climates. Transverse cracking was also a lesser problem than in more traditional asphalt paving. The addition of sulfur to the asphalt mix just prior to pouring the roadway reduces the viscosity of the hot paving material, making the pavement easier to install. Equipment for preparing traditional asphalt requires little or no adaptation to handle sulfur-extended asphalt, an important factor in the acceptance of sulfur-extended asphalts on a large scale (Weber and McBee, 2000, p. 10-11).

Even with the demonstrated advantages of sulfur-extended asphalt over more traditional paving materials, no large-scale highway projects have used sulfur-extended asphalt. A period of elevated sulfur prices in the late 1980s eliminated the financial incentives for substitution (Weber and McBee, 2000, p. 13). Recent increases in low-cost sulfur availability have reinvigorated interest, and large-scale testing of sulfur-extended sulfur as a viable, economic alternative to more traditional asphalt formulations are underway.

The main competitor to asphalt pavements is concrete made with portland cement and aggregates. Sulfur can substitute for portland cement in roads and other construction uses. The 7 percent of U.S. roads not made with asphalt cement use portland cement concrete, representing a significant market for sulfur. Elemental sulfur incorporating a small quantity of polymer modifiers, which stabilize the sulfur structure especially during thermal and hydraulic cycling, has replaced portland cement very effectively in industrial applications exposed to corrosive environments. Comparisons of the effects of common liquids on portland cement concrete and STARcrete Technologies Inc.'s sulfur polymer concrete are shown in table 8. A comparison of the performance of the two construction materials in a corrosive environment is illustrated in figure 31.

Several companies and researchers have developed slightly different formulations for polymer sulfur concretes, but all share the improved properties of extremely high resistance to corrosion, high physical strength, high resistance to fatigue, low water permeability, and fast curing time, which are listed in more detail in table 9. Molten sulfur is the binder that holds the aggregates together to form the pavement or other concrete forms when it cools and solidifies. Additives contribute special properties to the

Table 7. Influence of Sulfur Substitution on Material Properties of Asphalt Concrete

Composition				Properties						
Sulfur		Asphalt		Specific Gravity	Voids (%) (percentage)	Marshall		Flow (0.254 millimeter; 0.01 inch)	Dynamic Stiffness	
Volume percent <sup>1</sup>	Weight percent <sup>2</sup>	Volume percent <sup>1</sup>	Weight percent <sup>2</sup>			Stability			Million kilopascals	Million pounds per square inch
						Kilograms	Pounds			
0	0.0	100	7.0	2.288	2.4	1,161	2,580	12	4.499	0.653
15	2.0	85	5.9	2.300	2.8	1,004	2,230	10	6.752	0.980
25	3.4	75	5.2	2.307	3.2	1,388	3,085	11	10.624	1.542
35	4.7	65	4.4	2.321	3.2	2,484	5,520	10	14.056	2.040
50	6.7	50	3.4	2.320	4.4	4,322	9,605	12	--	--
75	9.9	25	1.7	2.343	4.9	4,460	9,910	6	--	--

<sup>1</sup>Volume percent of the binder.

<sup>2</sup>Weight percent of the total mix.

Source: Weber and McBee, 2000

Table 8. Effects of Some Common Liquids and Other Influences on STARcrete™ Sulfur Polymer Concrete as Compared with Portland Cement Concrete

Exposure	STARcrete™	Portland cement concrete
Fuel oils .....	None .....	None.
Silicates .....	.do .....	Do.
Fluorides.....	.do .....	Do.
Volatile oils .....	.do .....	Do.
Alcohol.....	.do .....	Do.
Wood pulp.....	.do .....	Do.
Mineral oils .....	.do .....	Slight.
Vegetable oils.....	.do .....	Do.
Grain oils.....	.do .....	Do.
Syrup glucose .....	.do .....	Do.
Chlorides of magnesium, iron, mercury, copper, and ammonia .....	.do .....	Do.
Phenol.....	.do .....	Slow.
Cresol .....	.do .....	Do.
Lysol.....	.do .....	Do.
Carbonic acid.....	.do .....	Do.
Tannic acid .....	.do .....	Do.
Juices .....	.do .....	Do.
Acid sulfates .....	.do .....	Very active.
Sulfates of calcium, potassium, sodium, magnesium, copper, zinc, aluminum, manganese, iron, nickel, and cobalt .....	.do .....	Do.
Chlorides of potassium, sodium, and calcium .....	.do .....	Do.
Acetic acid.....	.do .....	Do.
Sulfuric acid .....	.do .....	Do.
Hydrochloric acid .....	.do .....	Do.
Nitric acid.....	.do .....	Do.
Ammonium sulfate .....	.do .....	Do.
Ammonium nitrate .....	.do .....	Do.
Moisture penetration.....	Very slight.....	Slow.
Freeze/thaw damage .....	.do .....	Do.
Corrosion expansion on reinforcing steel .....	.do .....	Do.
Fatigue through repetitive loading.....	None/very slight....	Severe.

Source: STARcrete™ Technologies Inc., 2000.



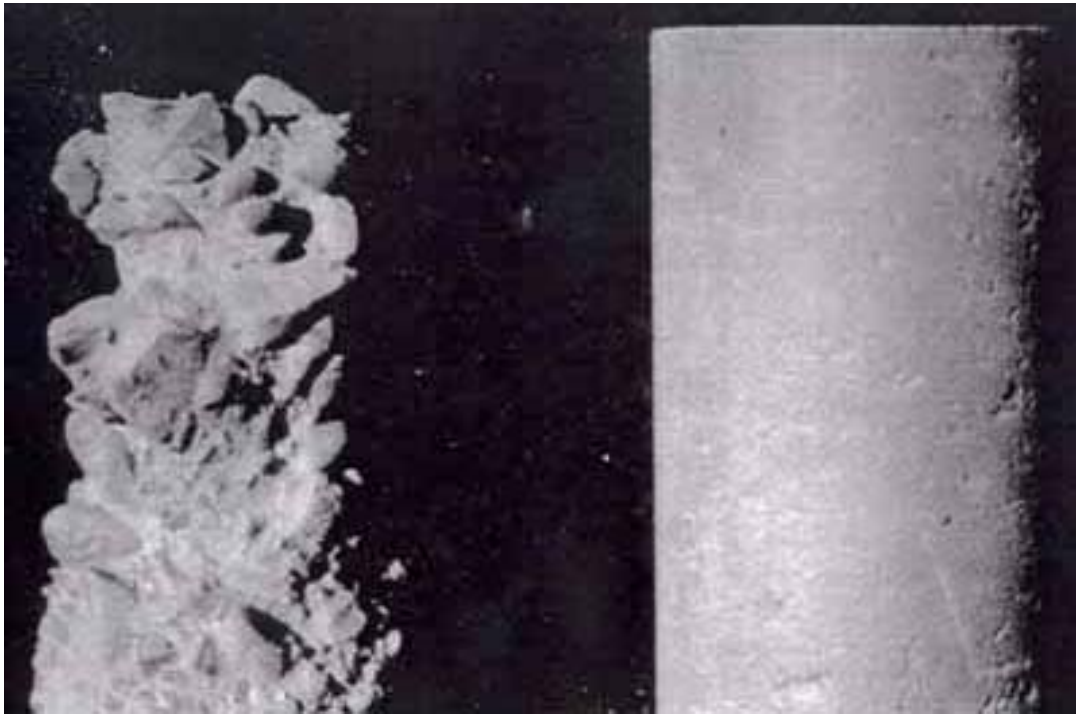


Figure 31. Photograph that illustrates the corrosion rates of sulfate-resistant portland cement concrete and sulfur polymer concrete (STARCrete™). The sample on the left is sulfate-resistant portland cement concrete that was immersed in 20% sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) for 3 weeks. The sample on the right is sulfur polymer concrete that was immersed in 20% H<sub>2</sub>SO<sub>4</sub> for 3 years. *Photo courtesy of STARCrete™ Technologies Inc.*

Table 9. STARCrete™ Sulfur Polymer Concrete Properties Compared with Those of Portland Cement Concrete

Property	Compared with 62.0 megapascal (5,000 pounds per square inch) portland cement concrete
Compressive strength .....	Greater.
Flexural strength.....	Greater.
Splitting tensile strength .....	Greater.
Modulus of elasticity .....	Greater.
Compressive creep .....	Less.
Bond strength to reinforcing steel.....	Greater.
Bond strength to concrete .....	Much greater.
Coefficient of linear expansion.....	Equivalent.
Thermal conductivity.....	Less.
Durability under thermal cycling.....	Equivalent or higher.
Corrosion resistance .....	Much greater.
Fire resistance.....	Slightly less.
Fatigue resistance .....	Much greater.
Water permeability .....	Much less.
Abrasion resistance.....	Much greater.

Source: STARCrete™ Technologies Inc., 2000.

sulfur binder, the most important of which is to produce a protective char surface when exposed directly to a flame. The char surface, when combined with the naturally low thermal conductivity of elemental sulfur, result in a slow penetration of heat. In the event of a fire near any form of sulfur concrete, tests have shown zero flame spread, zero fuel contribution, and zero smoke density. Because sulfur concrete sets on cooling, extreme weather conditions do not hamper its installation. Recycling is simply accomplished by crushing and reheating with no loss in strength.

Sulfur concrete can be precast easily into various shapes, such as construction blocks and slabs, railway ties, sewer pipes, support beams, tanks for holding corrosive liquids, and any number of other items. Sulfur concrete can be extruded to form bricks and paving

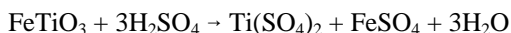
stones, roofing tiles, and street curbs and gutters. In most uses, such as agricultural effluent systems, bridge decks, drilling platforms, and fertilizer plants, sulfur concrete can replace cast-in-place portland cement. Sulfur concrete has found its greatest acceptance in facilities that must withstand corrosion from process acids, although it could be used in many other applications including road construction (STARcrete Technologies Inc., 2000).

Sulfur concrete can be precast easily into various shapes, such as construction blocks and slabs, railway ties, sewer pipes, support beams, tanks for holding corrosive liquids, and any number of other items. Sulfur concrete can be extruded to form bricks and paving stones, roofing tiles, and street curbs and gutters. In most uses, such as agricultural effluent systems, bridge decks, drilling platforms, and fertilizer plants, sulfur concrete can replace cast-in-place portland cement. Sulfur concrete has found its greatest acceptance in facilities that must withstand corrosion from process acids, although it could be used in many other applications including road construction (STARcrete Technologies Inc., 2000).

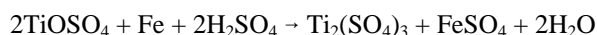
**Titanium Dioxide.**—Titanium is most well known as a high-tech metal, used in aerospace equipment and 21st century sporting goods. The most common use of titanium, however, is in the form of titanium dioxide (TiO<sub>2</sub>) pigment, which is used in paints, paper, plastics, and other materials. TiO<sub>2</sub> is widely used because of its whiteness, high refractive index, and light scattering ability. Ilmenite (FeTiO<sub>3</sub>) and rutile (TiO<sub>2</sub>) are ores used for producing pigment-grade TiO<sub>2</sub> through the sulfate and chloride processes. As the name suggests, the sulfate process requires sulfur on the form of H<sub>2</sub>SO<sub>4</sub>, and so, this process is of more interest in the context of this report. The sulfate process has been in use longer than the chloride process and uses the lower cost ilmenite, which contains 35 to 54 percent TiO<sub>2</sub>, or titanium slag with 75 to 79 percent TiO<sub>2</sub> as raw materials. Most chloride process plants require a high TiO<sub>2</sub>-content ilmenite with about 64 percent TiO<sub>2</sub>, slag containing 85 percent or greater TiO<sub>2</sub>, rutile, and synthetic rutile. The chloride process, however, has become preferred by most TiO<sub>2</sub> producers because technical and environmental considerations of the sulfate process are more complicated and expensive.

To produce TiO<sub>2</sub> via the sulfate process, finely-ground ilmenite or high-TiO<sub>2</sub> slag is mixed with concentrated H<sub>2</sub>SO<sub>4</sub>, forming a solid porous cake. The cake is dissolved with dilute acid to make a titanyl sulfate and iron sulfate solution. Scrap iron is added to ensure that the iron present in the solution is in the proper chemical state. Following the reduction, settling and filtration clarify the solution. Some of the iron may be crystallized and removed from the solution as ferrous sulfate heptahydrate. The remaining solution is concentrated and the TiO<sub>2</sub> is precipitated through hydrolysis, filtered, washed, and calcined at 900° C to 1,000° C to remove the water from the hydrolysis. Further milling and surface treatment of the TiO<sub>2</sub> particles produces pigment of the desired grade and type (Lynd and Lefond, 1983, p. 1310).

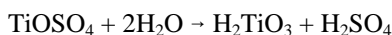
Several reactions occur during the process and are listed as follows (Roskill Information Services Ltd., 1991):



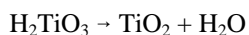
The initial reactions of ilmenite and H<sub>2</sub>SO<sub>4</sub> are exothermic, raising the temperature from 125° C to 200° C. The second reaction listed occurs more often. Scrap iron turnings are then added to precipitate ferrous sulfate.



Titanium sulfates are converted to metatitanic acid and precipitated through hydrolysis.



The precipitate is then calcined to remove water and residual SO<sub>3</sub>. Different calcine temperatures produce TiO<sub>2</sub> with the desired crystal structure.



Estimates of raw material requirements for TiO<sub>2</sub> production through the sulfate process and its waste products are listed in table 10. Figure 32 shows a diagram of the sulfate TiO<sub>2</sub> process and its waste acid recycling circuit.

Although the sulfate process remains a significant source of TiO<sub>2</sub> production, byproducts and the waste products that result from the sulfate process are part of the reason it has been losing favor. Significant quantities of byproduct iron sulfate are produced and frequently sold in water treatment markets. Most of the other solids must be disposed of in an environmentally sound method. The dilute acid can be neutralized for disposal, recycled, or treated with calcium carbonate to produce a byproduct gypsum product and liquid carbon dioxide.

Because the preferred chloride process for TiO<sub>2</sub> production requires high-TiO<sub>2</sub> feed materials, ilmenite is frequently converted to synthetic rutile or high-TiO<sub>2</sub> slag. Several different processes are used to produce synthetic rutile, but one is of interest here because it uses elemental sulfur. The Becher process, used mostly in Western Australia, heats ilmenite in a high-temperature kiln with coal and sulfur to remove iron and manganese (ACTED Consultants, 1997). The quantity of sulfur used in this application is not known.

**Other Uses.**—Elemental sulfur is essential for the vulcanization of natural and synthetic rubber tires. Vulcanization keeps rubber usable at temperature extremes, preventing it from becoming brittle in extreme cold and from becoming sticky or melting at high temperatures. H<sub>2</sub>SO<sub>4</sub> is used to make explosives and other organic and inorganic chemicals. It is used in steelmaking and in the

Table 10. Raw Material Requirements and Waste Produced During Titanium Dioxide Production via the Sulfate Process  
(Per metric ton of product)

Material	Quantity required (metric tons)
Raw materials:	
Ilmenite or titanium slag .....	1.5-2.8
Sulfuric acid.....	3.0-4.0
Iron scrap .....	0.1-0.2
Byproducts and waste products:	
Iron sulfate .....	2.0-3.0
Other solids.....	0.7-1.0
Dilute sulfuric acid (3-4%) .....	80

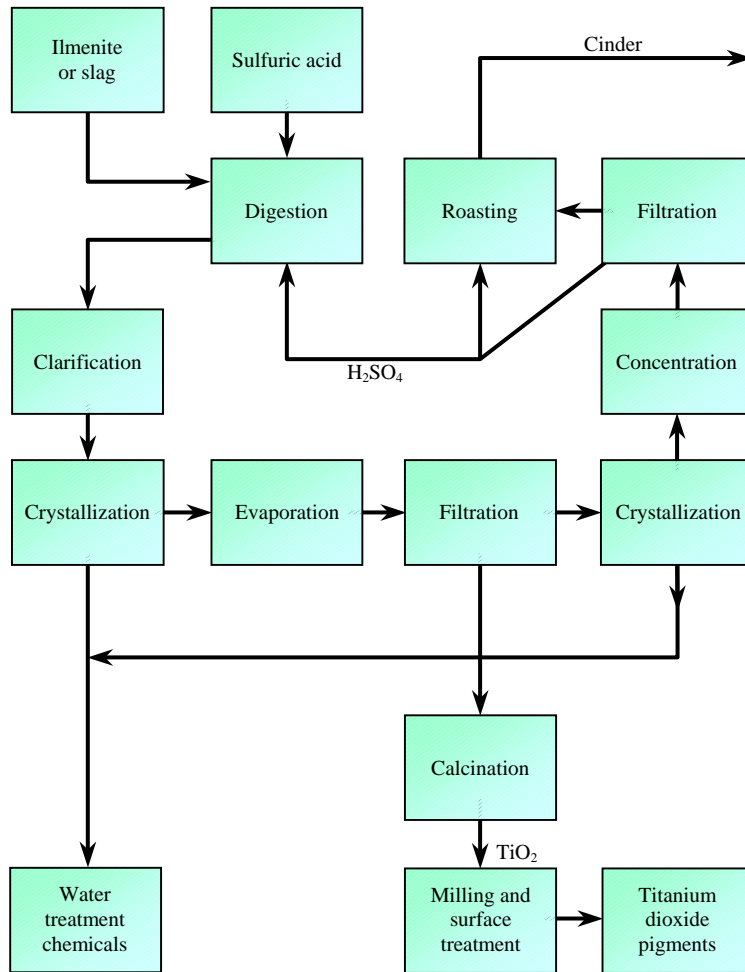


Figure 32. Flow diagram that shows the sulfate process for producing titanium dioxide and its waste acid recycling circuit. H<sub>2</sub>SO<sub>4</sub> is sulfuric acid. production of the synthetic fiber rayon. The electrolyte in lead-acid batteries is H<sub>2</sub>SO<sub>4</sub>. Many other processes use sulfur and H<sub>2</sub>SO<sub>4</sub>, but listing all of them would be nearly impossible.

**Trade**

Early in the 20th century, the United States was the world’s largest sulfur exporting country. Because of its production dominance owing to the development of the Frasch process and the relative abundance of sulfur deposits that were amenable to the process, few countries came close to matching U.S. production until recovered sulfur overtook Frasch as the leading source of domestic sulfur

production. For at least the last 20 years, Canada has been the world's leading sulfur exporter, exporting sulfur recovered at natural gas and oil sands purification operations concentrated in Alberta, British Columbia, and Saskatchewan.

The United States has been a net importer of elemental sulfur since 1977. Exports of elemental sulfur represent about 7 percent of domestic sulfur production. Sulfur imports to the United States are usually about three to four times higher than exports and represent about 20 percent of domestic consumption. Most of the U.S. exported sulfur is produced on the West Coast, where it is easier to export it in solid form by ocean-going vessel than it is to transport molten sulfur to eastern markets via rail or truck. Nearly all of the sulfur imported to the United States comes from Canada and Mexico, with a small but steady quantity imported from Venezuela.

Sulfur has become an important internationally traded commodity. It has become more widely traded since recovered sulfur production increased. The importance of the United States as an elemental sulfur exporting country has decreased significantly in recent years. The ascendancy of many countries in the petroleum and natural gas industries and increased environmental awareness and regulations around the world have created a tremendous increase in recovered sulfur production throughout the world.

An example of a country with large production and limited consumption is Canada. As in other developed countries, Canada limits the level of sulfur allowable in gasoline and other automotive fuels and SO<sub>2</sub> emissions at petroleum refineries. Canada's major contribution to the world sulfur supply, however, comes from its large sour natural gas deposits in western Canada, especially in Alberta. Many operating gas wells contain large quantities of H<sub>2</sub>S, some as high as 45 percent, which must be removed prior to selling the natural gas. Canada is the world's largest producer of recovered sulfur; it is also the largest exporter of elemental sulfur. Although Canada exports an average 7 Mt/yr, supply exceeds demand to the extent that more than 15 Mt of elemental sulfur has been stockpiled in Alberta. Canadian companies are actively exploring methods for long-term storage and disposal of sulfur, such as reinjection and underground storage. In some operations, it can no longer be considered a valuable byproduct but rather a waste material with costs attributed to its storage or disposal. The processing of heavy crude oil associated with tar sands extraction is also a significant and growing source of sulfur—almost 2 Mt in 2001 and expected to rise to more than 3 Mt by 2005.

In contrast to Canada, Morocco is a large consumer of sulfur with little domestic supply, necessitating the import of about 2.5 Mt/yr. Morocco possesses huge deposits of phosphate rock from which it produces phosphoric acid and phosphate fertilizers. Because the demand in Morocco significantly exceeds domestic supply, the Moroccan phosphate producers import sulfur from many different countries.

Even with the huge global sulfur market, production exceeds consumption worldwide. The global sulfur market has become quite competitive, resulting in a trend to ever lower prices. Regional supply constraints have caused brief price increases, but overall, prices have been on a downward trend, especially in constant dollars for the past 20 years, as shown in figure 33.

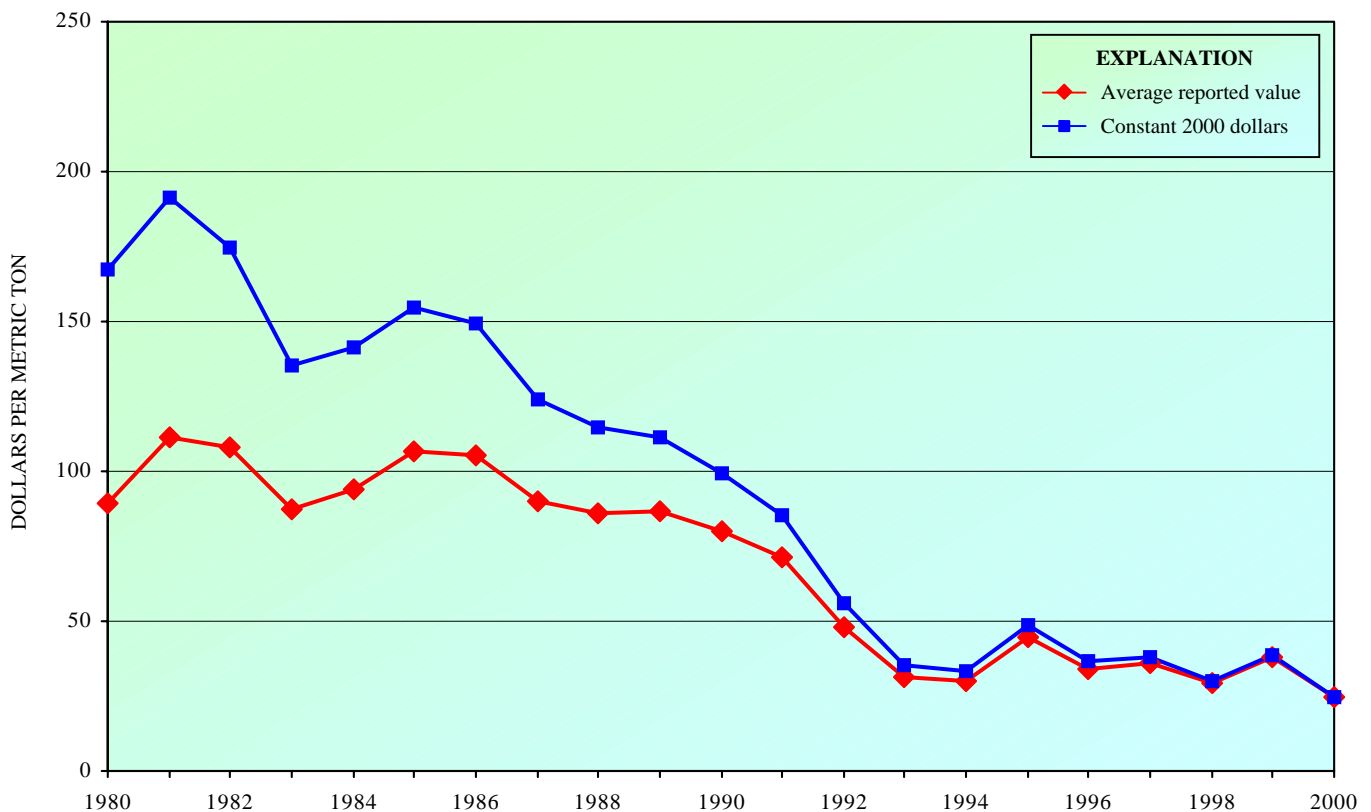


Figure 33. Chart that shows the prices of sulfur in the United States from 1980 through 2000. Sulfur prices generally have been in decline in the United States for the past 20 years. The data represented are the average value per metric ton of elemental sulfur as reported by domestic producers and those values translated to constant 2000 dollars.

Because many of the countries that produce sulfur are not large consumers and many of the large consumers do not have large sulfur production capabilities, a large global sulfur market has emerged. Figures 33 and 34 illustrate how the global sulfur trade has changed since 1981. Perhaps the most striking change in sulfur trade since 1981 is the number of countries that have entered the market. In 1981, six countries that exported a total of 15 Mt dominated sulfur trade. They were, in descending order, Canada, Poland, the United States, Mexico, France, and the Federal Republic of Germany. By 1990, Saudi Arabia joined the leaders, and the United States was decreasing in importance. By 2000, 16 countries were exporting more than 100,000 t of sulfur, and even more were exporting small quantities for a global total of about 21 Mt. Canada was the leader throughout the period, and Saudi Arabia became more important. Mexico, Poland, and the United States became less important as the Frasch industry in each of those countries dwindled and operations closed. Of these three countries, only Poland continues to mine sulfur. Russia, as part of the Soviet Union, was a major importer of sulfur for use in its fertilizer industry and has become a major exporter of sulfur. This dramatic change is due in part to increased recovered sulfur from large sour natural gas operations in Russia, the downturn of the Russian economy, and the subsequent cutbacks at fertilizer operations that resulted from the break-up of the Soviet Union in 1991.

1981

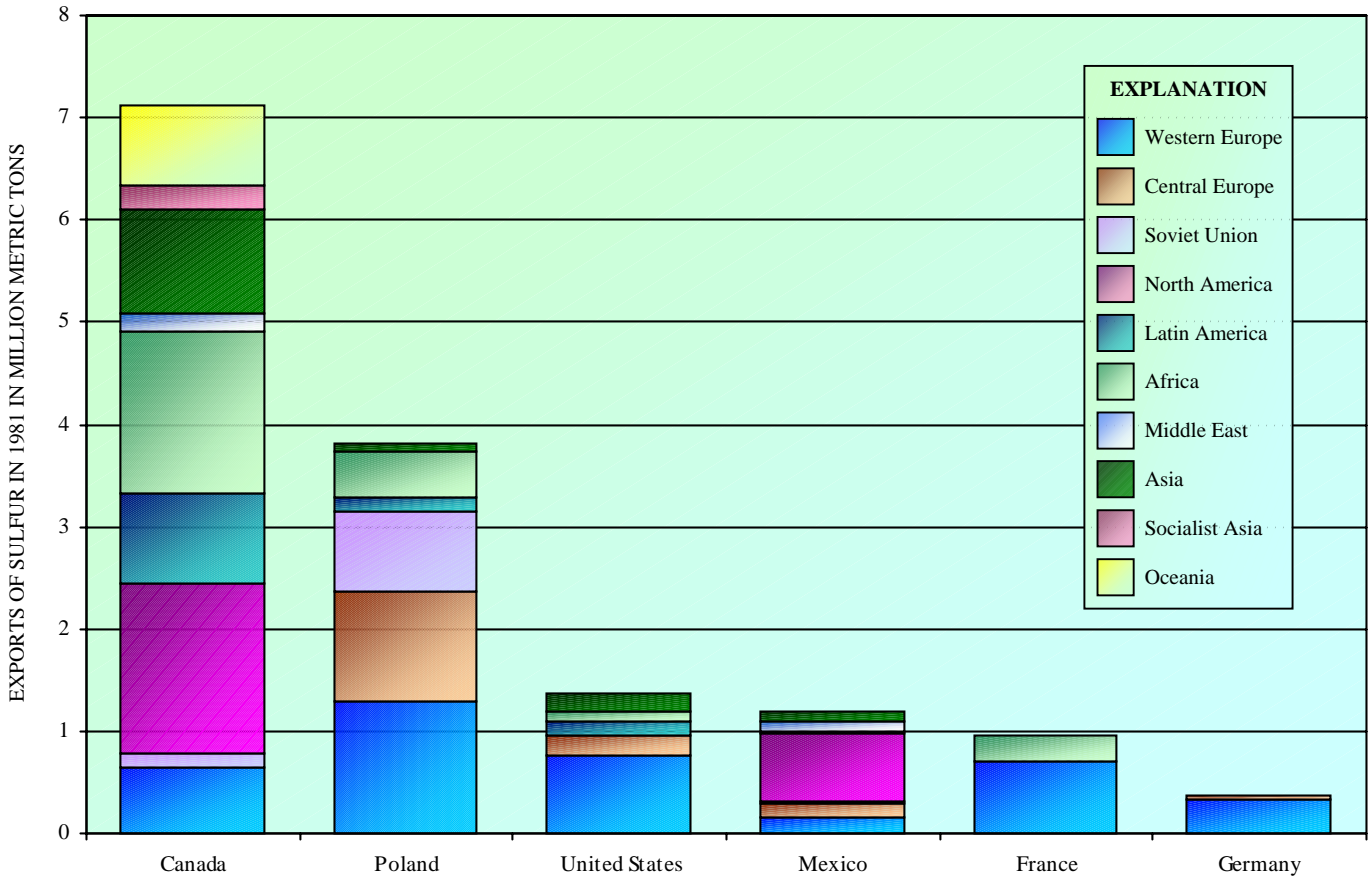
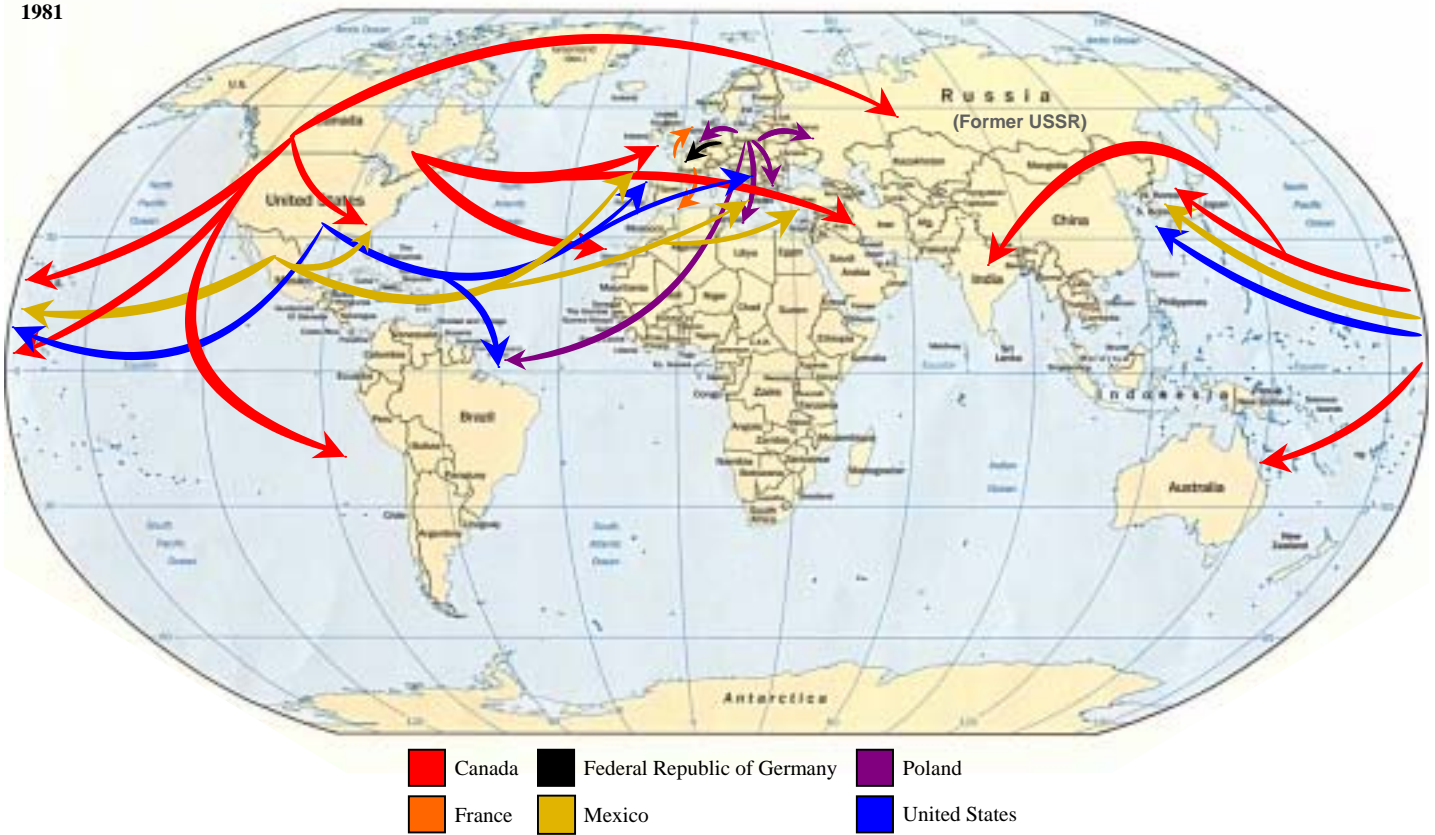


Figure 34. Map and chart that show worldwide sulfur trade in 1981. Sulfur trade in 1981 was characterized by six dominant producers exporting about 15 million metric tons of elemental sulfur around the world.

2000

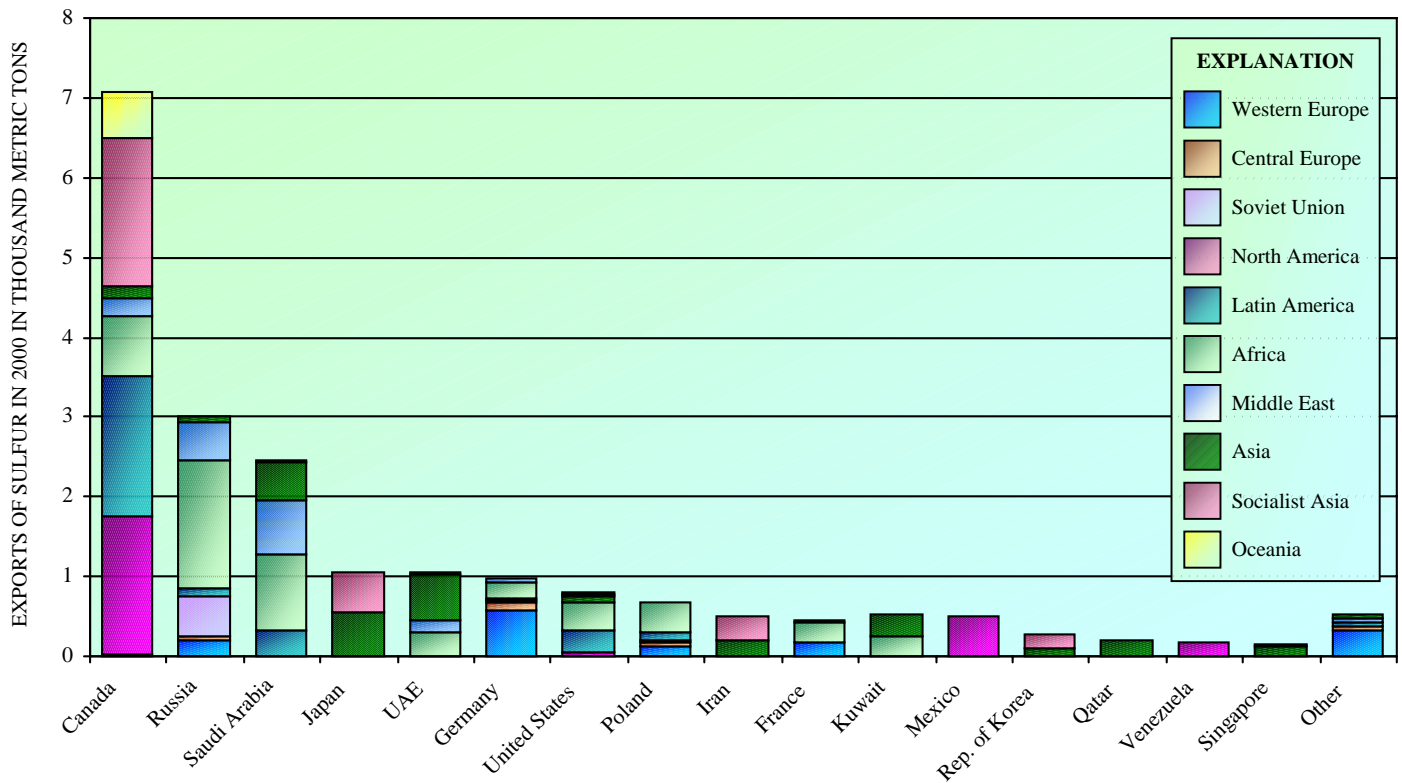
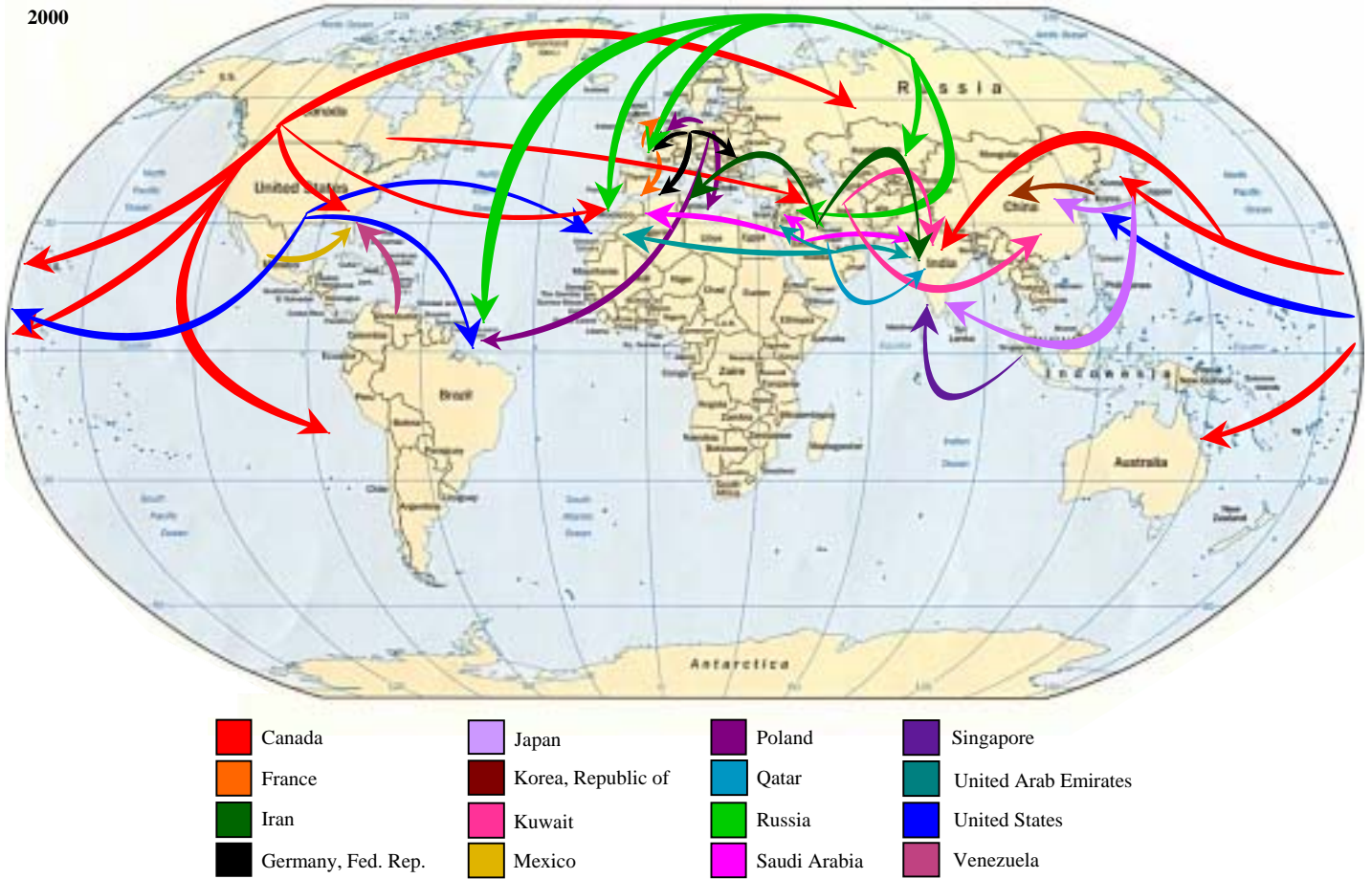


Figure 35. Map and chart that show worldwide sulfur trade in 2000. Sixteen countries each exported more than 100,000 metric tons of elemental sulfur. Exports totaled about 21 million tons.

## MATERIALS FLOW OF SULFUR

### Losses From Production and Processing

In any industrial endeavor, attempts are made to minimize losses during production and processing in order to maximize the economic benefit of the operations. This is certainly the case in sulfur mining where producers strive to optimize sulfur extraction. The nature of sulfur mining differs from more conventional mining methods in ways that reduce losses during the Frasch mining process. Because ores are not processed by mechanical methods to obtain the elemental sulfur product, virtually no product is lost during handling. Sulfur leaks may occur at various locations at Frasch operations, but in very small quantities and insignificant in relation to the total sulfur production and environmental considerations at those locations. With the demise of the Frasch industry in the United States and its serious decline in other countries, these losses are inconsequential to the sulfur industry.

In petroleum refining and natural gas processing, recovery of sulfur can be an economic liability rather than an asset. Sulfur recovery equipment and operations add significantly to the cost of oil and gas processing. Costs vary considerably by location, size of operation, and type of equipment that must be installed. For example, a relatively small petroleum refinery in Oklahoma contracted an engineering firm to double its sulfur recovery capacity at a cost of \$22 million in 2000 (Sulphur, 2000d). In the same year, a deal to build a new desulfurization unit in Kuwait was estimated to cost \$125 million (Cunningham, 2000). Environmental concerns related to sulfur and SO<sub>2</sub> emissions, however, prohibit virtually all losses to the atmosphere, making these kinds of installations necessary. Although recovered sulfur sales can be profitable to producers in some locations, others producers incur expenses in order to have sulfur removed from their premises. Discontinuing sulfur recovery operations while continuing to process oil and gas, however, is never an option. If a refinery or natural gas operation cannot recover sulfur, for whatever reason, then that facility must close, at least temporarily, until the situation has been resolved and sulfur recovery is again possible. In the United States during 1999, losses through emissions from a category of industries defined by the EPA to include oil and gas production, petroleum refineries, and other related industries totaled 314,000 t of SO<sub>2</sub>, equivalent to 157,000 t of sulfur. These losses represent less than 2 percent of total domestic sulfur production. Few mineral industries can match that recovery rate. SO<sub>2</sub> emissions from electric powerplants were 11.98 Mt in 1999, 38 times higher than those from oil and gas operations (U.S. Energy Information Administration, 2001, p. 327).

Environmental protection legislation also is a more influential factor to H<sub>2</sub>SO<sub>4</sub> byproduct production than economics. Regulations mandate that smelter operators recover the majority of SO<sub>2</sub> liberated during the smelting process. These mandates include monitoring programs to ensure that the emissions regulations are not violated. If excess SO<sub>2</sub> emissions are detected, then fines may be imposed. H<sub>2</sub>SO<sub>4</sub> plants that burn elemental sulfur to produce acid for their own use or for sale also must meet environmental regulations limiting SO<sub>2</sub> emissions, significantly reducing sulfur losses at these operations.

Actual regulatory limits for SO<sub>2</sub> vary considerably by location. States are able to set emissions limits with the approval of the EPA. Some factors influencing specifications set are the type of facility, its proximity to population centers, the age of the facility and whether it is an existing or a new operation, available technology for SO<sub>2</sub> recovery, and the cost of implementing new technology. Many regulations specify the quantity of allowable SO<sub>2</sub> emissions in relation to the quantity of sulfur in the raw materials being processed or in the finished products.

Because SO<sub>2</sub> emissions were identified as a major source of pollution when environmental regulations were first instituted, much of the regulation focuses on limiting and eliminating SO<sub>2</sub> emissions. The Clean Air Act Amendments of 1990 concentrated specifically on limiting and eliminating emissions from coal-fired powerplants where SO<sub>2</sub> emissions are from burning fuels that contain significant quantities of sulfur, sometimes up to 3.5 percent sulfur by weight. Significant improvement in air quality has been demonstrated as a result of these regulations; SO<sub>2</sub> emissions decreased 23 percent from 1989 to 1999 (U.S. Energy Information Administration, 2001, p. 327). Reductions in SO<sub>2</sub> emissions have resulted in increased recovered elemental and byproduct H<sub>2</sub>SO<sub>4</sub>. Reduced emissions at powerplants, however, have not resulted in additional supply for the industrial sulfur market. Of the operators who chose to install equipment to bring their facilities into compliance, the majority opted for some form of scrubbing that produces a byproduct or waste gypsum material that is not part of the commercial sulfur market.

Losses during handling and shipping solid bulk sulfur have been significant in the past, although difficult to quantify. When sulfur was poured to block in the early days of the industry, the solid material was broken up and moved with bulldozers, creating a tremendous problem with fine sulfur dust. The fine particles were difficult to contain and could be blown great distances on the wind. In addition to contaminating the area adjacent to the production locations, contamination was a problem along rail lines and at port facilities. Of even more concern than the dust contamination was the hazardous nature of the sulfur dust. Finely divided sulfur presents explosive and fire hazards, and the SO<sub>2</sub> generated by such a fire is toxic (West, 1966).

Because of these issues, regulations were established to limit shipments of crushed and broken sulfur. Several processes have been developed to minimize the loss and lessen the hazards in handling solid sulfur. Domestically, nearly all sulfur is shipped molten, avoiding any of the dusting problems associated with bulk sulfur. If sulfur is poured to block in the U.S. Gulf Coast area, then it is mechanically broken and passed through a melter before it is shipped from the storage site in molten form. During this processing, dust is kept to a minimum by containing dust inside the outer walls of the sulfur block. Most sulfur produced in California and Washington is shipped overseas. To make this material acceptable for bulk transport, the molten sulfur is processed in forming apparatus that solidifies the sulfur into distinct particles, such as granules, pastilles, prills, and slates, that resist breakage, significantly reducing the fines problems during handling. Additional dust suppression techniques include covered conveyors systems, dust collectors, and enclosed railcar unloading facilities with water sprays. These innovations have reduced losses during handling to a minimum.



## Disposition After Consumption

Because of the wide range of uses for sulfur and its compounds, identifying the ultimate disposition of every ton of sulfur consumed is extremely difficult. Quantifying the amount of material that is dispersed through the atmosphere or disposed of in landfills is even more challenging. The tremendous variety of industrial processes that use sulfur and sulfuric acid makes it virtually impossible to identify every operation where they are consumed. In addition, the quantity of sulfuric acid required in many of its applications varies considerably according to the quality and type used, the raw materials used, and by the exact process employed. An attempt to illustrate the flow of sulfur after consumption is made in figure 36.

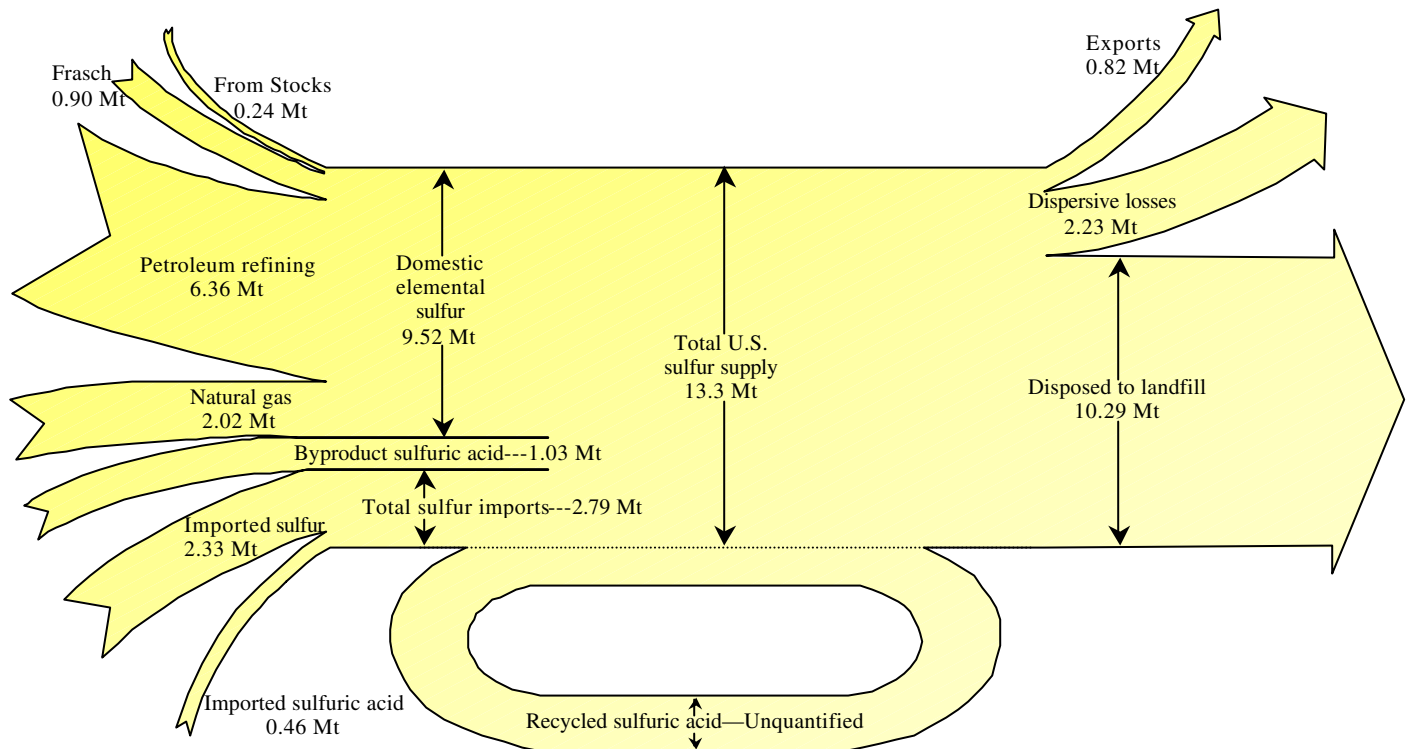


Figure 36. Flow diagram that estimates where sulfur ends up after it is used in end-use industries. Landfilled material is dominated by waste phosphogypsum from phosphate fertilizer production. Dispersive uses are mostly other agricultural uses. A significant quantity of sulfuric acid is constantly recirculated at solvent extraction operations, and acid from petroleum alkylation facilities is reconstituted and purified. The actual amount that is recycled, however is unquantified. Quantities are measured in million metric tons (Mt).

The production of phosphate fertilizers results in a phosphogypsum material that, in almost all circumstances, is a high-volume waste. Synthetic gypsum is also a byproduct or waste from other industrial processes that use sulfur in the form of  $H_2SO_4$ . Some end uses result in dispersive losses to the environment via different routes, and sulfur as  $H_2SO_4$  is continually recycled through some applications.

**Dispersive Losses.**—Most agricultural uses of sulfur (except for that used in the manufacture of phosphate fertilizers) where it is applied for crop nutrition or pest and fungus control disperse excess sulfur through the environment via different routes. In the simplest dispersal process, such sulfur materials as ammonium sulfate or elemental sulfur can be washed away by rain into surface water, contributing no value to the area in which it was applied.

Good agricultural practices are designed to avoid this outcome. Sulfur applied to the cropland mixes into the soil where it reacts with bacteria, forming new sulfur compounds that can be absorbed by plants. If it is absorbed by grass or grain, then it may become part of the food chain and pass through several other organisms before it finally returns to the environment as a waste material. This animal waste could cycle once more through the food chain if it again is absorbed into plant matter after being distributed onto crop land. Portions of sulfur-containing plant residues that are not consumed as food decay to enrich soils and undergo similar processes. Even agricultural sulfur that is used in animal feeds and pest control often is deposited eventually in soil where it undergoes the same reactions and transfers as sulfur nutrient materials.

Where sulfur materials are used in construction, the materials undergo slow dispersive losses during use as some portion of it is worn away. For example, as vehicles drive along a highway made of sulfur-extended asphalt, minute particles of the paving material could be loosened from the road and washed by rain water or blown by wind into soil or water. At the same time as traffic creates wear on the road materials, the road surfaces abrade tires that contain small percentages of elemental sulfur, which also is dispersed into the environment. Dispersion from these processes is negligible. Roads and tires are engineered to withstand heavy wear and abrasive action as much as possible.

Although  $\text{H}_2\text{SO}_4$  is constantly cycled through copper leaching operations, portions of the acid are lost. The  $\text{H}_2\text{SO}_4$  dissolves the copper oxides, and the copper-laden acid drains into collection ponds. The  $\text{H}_2\text{SO}_4$ , however, can react with other minerals and rocks in the leach beds, forming insoluble compounds that remain in the leach beds, removing that portion of sulfur from the SX-EW cycle and requiring additional acid to be added to the system. The quantity of sulfur compounds dispersed in this way is dependent on the type of rocks and minerals included with the copper oxide ores that are targeted by the leach process.

**Disposed to Landfill.**—As the largest end use for sulfur, phosphoric acid and phosphate fertilizer production generates huge quantities of phosphogypsum. Depending on the source of the phosphate rock that is used, the gypsum may be considered a byproduct of the process, but more often, it is treated as waste. Purified phosphogypsum may substitute for mined gypsum, but because much of the phosphate rock produced in the United States, especially that from central Florida, contains uranium and radium, the resultant phosphogypsum is slightly radioactive. For this reason, domestic uses of phosphogypsum are extremely limited. Most phosphogypsum produced in the United States is treated as hazardous waste that must be stored in stacks or piles. Another problem common to phosphogypsum stacks is the entrainment of small quantities of acidic liquids in this waste. Neutralization or extensive washing of the material is required before it is stabilized for use in construction.

Tremendous quantities of phosphogypsum have accumulated during the history of the domestic phosphate fertilizer industry. More than 1 billion metric tons has accumulated in stacks in several States, the majority of which is in Florida. The ratio of phosphogypsum produced per ton of  $\text{H}_3\text{PO}_4$  varies according to the quality of phosphate rock processed. Estimates vary between 3 and 5.5 t of phosphogypsum per 1 t of  $\text{H}_3\text{PO}_4$  produced. In the United States, an average of about 40 Mt/yr of phosphogypsum has been produced since the mid-1980s, nearly all of which has been deposited onto stacks for long-term storage. Some producers, such as the one in Morocco, dispose of the material at sea. Only about 1 percent of the phosphogypsum produced domestically is used in such applications as agricultural soil conditioners, road base construction, and research activities (U.S. Environmental Protection Agency, 2000).

HF production also results in waste gypsum production. About 4 t of waste gypsum is produced for every 1 t of HF produced. Dilute  $\text{H}_2\text{SO}_4$  resulting from  $\text{TiO}_2$  production is sometimes neutralized to form byproduct gypsum. Some  $\text{TiO}_2$  producers substitute their byproduct gypsum for natural gypsum in certain applications; others treat it as waste and dispose of it in landfills.

Sulfur used in pulp and paper processing results in waste compounds. Owing to the variety of compounds used, however, it is difficult to identify the ultimate disposition of the sulfur.

**Recycling.**—Because  $\text{H}_2\text{SO}_4$  is a catalyst in the alkylation process, it should, theoretically, circulate through the process continuously. In practice this is not the case. Over time, the acid becomes diluted to the point that it is not effective in this application. It also becomes contaminated with impurities from the petroleum products being processed. When the  $\text{H}_2\text{SO}_4$  becomes too diluted, portions of it are withdrawn from the process to be replaced with more concentrated acid. The diluted, contaminated material is treated at a regeneration facility for purification and reconcentration. As a result of the  $\text{H}_2\text{SO}_4$  reacting with impurities, some of it cannot be purified to the point that it can be returned to its original use.

Many processes can be used to reconcentrate or reclaim spent  $\text{H}_2\text{SO}_4$  depending on the concentration of the acid and the amount and kind of impurities in it. Because so many processes are available and a dominating preferred technology cannot be identified, no specific details will be discussed here. The goal of all the processes, however, is to remove excess water by evaporation and to dehydrate the acid as well as eliminate impurities. The common denominator at all locations is the need to use materials of construction, which can withstand the corrosive effects of hot, dilute  $\text{H}_2\text{SO}_4$ . Depending on the processes used and the uses for which the recycled acid is intended, varying quantities of impurities are removed from the acid. An example of acid recycling unit is shown in figure 37.

Like so many other aspects of the sulfur industry, economics are not the driving force behind recycling  $\text{H}_2\text{SO}_4$ . In the past, spent acid was disposed of by dumping into the oceans or neutralizing it with lime and treating the resulting gypsum material as a waste and placing it in a landfill. These disposal methods are no longer acceptable in most of the world, necessitating the development of reclamation processes, even when costly (Sander and others, 1984, p. 350-351).

The vast majority of sulfur construction materials that are not dispersed into the atmosphere can be recycled more easily than more conventional construction materials. Separation of the aggregate from the binding material is not necessary. Sulfur concrete material, which has been crushed to a size to facilitate handling, can simply be reheated in the same equipment used for the original installation to melt the sulfur. The recycled material does not suffer any degradation of properties.

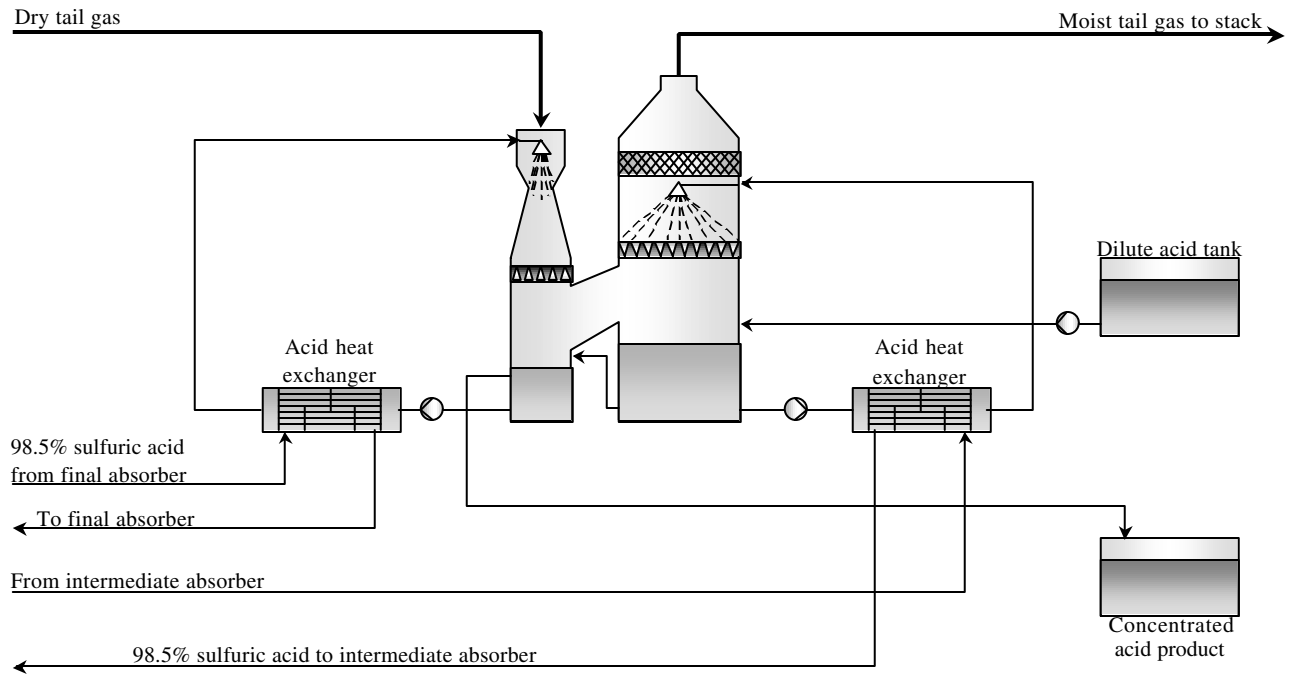


Figure 37. Flow diagram that illustrates a spent sulfuric acid recycling process.

## CUMULATIVE EFFECT OF SULFUR PRODUCTION AND CONSUMPTION

### Effects of Production

Years of sulfur production have had a less profound physical effect on the environment than many other mineral operations. Because the Frasch process does not require large disturbances on the Earth's surface, long-term operations have more subtle impacts. As the sulfur is extracted from underground sulfur deposits, the ground subsides. At some locations, ponds or lakes form in the area that subsided. In other places, as the formations collapse after the underground sulfur has been removed, the only surface evidence is a ground depression in the mined area. These operations typically have been developed in locations away from large population centers. Some of the first domestic on-shore operations were so remote that the companies built residential areas for the workers and their families. Although the operators of the last Frasch operation in western Texas, which closed in 1999, did not support a company town, the workers at that mine were bused from the closest towns—about 64 km away—for their daily work shifts. There were no buildings in the area except those directly related to the mining operation, and these were built in stable areas under which no sulfur extraction took place. Off-shore operations have even less surface impact because any alterations are underwater. Mine platforms were designed to withstand subsidence, with little or no effect on the total mining process. Measures were implemented to avoid any accidental discharges that might have a negative effect on the marine environment around the mining operation.

The cumulative effect of recovered sulfur and byproduct sulfuric acid production is more important for what has not occurred in the environment than what has. The impetus for sulfur recovery is environmental protection, which has resulted in better air quality than would have been the case if no recovered sulfur had been produced. If sulfur was not recovered at oil refineries and natural gas processing plants, then it would be emitted into the atmosphere as  $\text{H}_2\text{S}$  or  $\text{SO}_2$ . Byproduct  $\text{H}_2\text{SO}_4$  recovered at smelters dramatically limits the quantity of  $\text{SO}_2$  emitted at those facilities. Thus, production of environmental sulfur products has reduced acid rain, although the phenomenon has not been eliminated. An interesting effect of reduced atmospheric sulfur emissions is that soils in agricultural areas around the world are becoming deficient in sulfur. Unregulated  $\text{SO}_2$  emissions were large contributors to acid rain, which, in turn, deposited sulfates into the soil. As the air quality has improved and agricultural production has become more intense, crops are beginning to show the effect of sulfur deficits. Plant nutrient sulfur applications have become necessary because acid deposition has been significantly reduced.

Unlike some mineral commodities, there is no concern that supplies of sulfur will decrease. The concern is what to do with the increasing quantities of sulfur produced as a result of regulations limiting and eliminating sulfur emissions from all types of industries. In other countries, especially Canada, producers of recovered sulfur have accumulated tremendous stockpiles because production exceeds domestic and worldwide demand. During the 1970s, stocks in Canada approached 20 Mt. That quantity was almost eliminated in the 1990s before it began to expand again to reach 13 Mt in 2000. The stocks of sulfur in Canada and other countries are expected to expand further because world production continues to grow as consumption stagnates.

### Effects of Consumption

After centuries of using sulfur in a multitude of industrial processes, the most obvious cumulative effect of this consumption are the mountains of phosphogypsum accumulated in Florida. Indeed, the phosphogypsum stacks are higher in elevation than many natural land formations in Florida and Louisiana. As discussed earlier, the concerns about radioactive materials contained in the stacks have made it difficult to find approved uses that could reduce the volume of waste and treat it as a useful byproduct. In areas other than Florida, where radioactivity is not a problem, the material has been used to backfill depleted phosphate mines, as road base material, and to improve soils. These are the exceptions rather than the norm, however, and phosphogypsum stacks continue to grow.

Synthetic materials resulting from industrial uses of  $\text{H}_2\text{SO}_4$  can be treated in a number of different ways. Like the reaction of phosphate rock, other minerals, such as fluor spar, react with  $\text{H}_2\text{SO}_4$  to form byproduct or waste gypsum. When acidic process effluents are neutralized with lime, gypsum of varying purities results. The gypsum may be usable in the production of wallboard or other products traditionally made from mined gypsum. Often, however, these products are of insufficient quality for further use and must be landfilled, adding to the waste problems of the United States. Quantifying how much is produced and where the material ultimately resides is extremely difficult.

Other industrial processes result in byproducts that are useful in other applications. As previously mentioned in the discussion of caprolactam and titanium dioxide production, ammonium sulfate and ferrous sulfate, respectively, are byproducts. Ammonium sulfate is a major source of plant nutrient sulfur and can be dispersed into the environment to become part of the natural sulfur cycle. Ferrous sulfate is an important water treatment chemical, but the quantity of byproduct production may exceed that required for water treatment. The excess must be disposed of in an environmentally sound manner, again adding to difficult waste disposal issues. Most other sulfur end uses that result in waste material contribute to national waste-disposal issues.

Where sulfur is dispersed into the environment in reasonable quantities, little cumulative effect is discernable. The dispersed sulfur becomes part of the robust natural sulfur cycle, migrating through the environment. Except in areas where large quantities of sulfur dust from solid sulfur storage and reclamation sites or  $\text{SO}_2$  is emitted into the atmosphere by such industrial facilities as coal-fired electric utilities and unimproved smelters, sulfur does not tend to accumulate in the soil. Where acid precipitation is a problem, forests and other vegetation can be severely damaged or killed, lakes and streams can become too acidic causing aquatic plants and animals to die, buildings experience corrosion, and excess sulfur can collect in the soil. This is caused, however, by  $\text{SO}_2$  emissions, not by sulfur production or consumption.

## SUMMARY

Sulfur is different than other minerals with respect to mining issues and supply concerns. The sustainable production of necessary sulfur supplies is not in question as long as the world economy is petroleum-driven. Sulfur mining has stopped, not because sulfur resources have become depleted, but because sufficient sulfur can be recovered as a byproduct at petroleum refineries and natural gas processing plants to more than meet the demand for sulfur worldwide. Byproduct  $\text{H}_2\text{SO}_4$  from metal smelters contributes additional supplies.

While the production of recovered sulfur has been increasing around the world as a result of growing environmental awareness and concerns, the use of sulfur in a multitude of end uses has increased at a slower pace. Huge quantities of sulfur and  $\text{H}_2\text{SO}_4$  are consumed in many industries, but not as much as is produced. Expansive world trade transfers large quantities of sulfur from the large producing areas to the large consumers. Stocks, however, are accumulating at recovery operations in remote locations where the distances to the market make its transportation prohibitively expensive. In such countries as Kazakhstan, the infrastructure is inadequate for transporting the large volumes of sulfur produced.

The cumulative effects of sulfur production also differ from the results of other mineral production. Modern sulfur production actually results in improved environmental conditions rather than mining processes and outcomes that must be repaired. Sulfur recovery prevents the emissions of  $\text{SO}_2$  and other harmful compounds into the atmosphere, avoiding the detrimental effects of those emissions.

The challenges facing the sulfur industry are unique. In other mineral industries, the major concerns are how to continue to produce necessary materials and protect the environment as much as possible at the same time. The sulfur industry is confronting the question of what to do with all the sulfur it produces. Current production exceeds consumption by a relatively small percentage, but environmental regulations continue to increase with little growth in sulfur uses. The 21st century sulfur industry will need to expand sulfur consumption in nontraditional markets and find acceptable ways to dispose of unneeded sulfur without compromising environmental protection.

## REFERENCES CITED

- ACTED Consultants, 1997, Rutile and ilmenite—Australian production and potential profile, web site at <http://www.chemlink.com.au/rutile.htm>. Accessed April 4, 2002.
- Albright, L.F., 1990a, Alkylation will be key process in reformulated gasoline: *Oil & Gas Journal*, v. 88, no. 45, November 12, p. 79-92.
- 1990b, H<sub>2</sub>SO<sub>4</sub>, HF processes compared, and new technologies revealed: *Oil & Gas Journal*, v. 88, no. 47, November 26, p. 70-77.
- Barker, J.M., Cochran, D.E., and Semrad, Robert, 1979, Economic geology of the Mishraq native sulfur deposit, northern Iraq: *Economic Geology*, v. 74, no. 2, p. 484-495.
- Bernar, Rodger, 2000, Pulp & paper manufacturing & sulfur—Future challenges: *Sulphur Markets Today and Tomorrow—Biennial International Symposium*, 7th, Washington, DC, March 26-28, 2000, Presentation, 10 p.
- BHP Copper Inc., [undated], From rock to rod—Producing copper at San Manuel: San Manuel, Ariz., BHP Copper Inc. brochure, 13 p.
- Bilbrey, J.H., and Long, E.R., 1960, Nickel, *in* *Metals and minerals: U.S. Bureau of Mines Minerals Yearbook 1961: v. I*, p. 801-816.
- Bixby, D.W., Rucker, D.L., and Tisdale, S.L., 1966, Phosphatic fertilizers properties and processes—A study of technological, economic, and agronomic considerations: Washington, D.C., The Sulphur Institute, Technical Bulletin No. 8, 64 p.
- Blossom, J.W., 1985, Molybdenum, *in* *Mineral facts and problems: U.S. Bureau of Mines Bulletin 667*, p. 521-534.
- Bodenlos, A.J., and Nelson, C.P., 1979, Sulfur: *Economic Geology*, v. 74, no. 2, p. 459-461.
- Bolton, G.L., Berezowsky, R.M., and Day, M.D., 1997, Hydrometallurgy—Nickel now and next century: International Nickel Study Group, The Hague, Netherlands, April, 1997, Presentation, 18 p.
- Bush, W.R., and Semrad, R., 1996, Sulfur—Native occurrence and extraction, *in* McKetta, J.J., and Weismantel, G.E., eds., *Encyclopedia of chemical processing and design*: New York, Marcel Dekker, Inc., p. 269-295.
- Butcher, S.S., 1992, Global geochemical cycles: San Diego, Calif., Academic Press Inc., p. 290-291.
- Cobalt News, 1999, The Bulong nickel/cobalt project: *Cobalt News*, no. 99/4, October, p. 8.
- Connock, Lisa, 1998, Approaching the limit—99.9+% sulphur recovery: *Sulphur*, no. 257, July-August, p. 34-55.
- 1999a, A new generation of pressure leach projects: *Sulphur*, no. 262, May-June, p. 47-56.
- 1999b, Maximizing energy savings in sulphuric acid plants: *Sulphur*, no. 262, May-June, p. 33-41.
- Cunningham, Chris, 1999, Chinese demand more refined: *Sulphur*, no. 262, May-June, p. 16-22.
- 2000, Oil price underpins gulf brimstone output: *Sulphur*, no. 267, March-April, p. 13-18.
- Day, D.T., 1885, Sulphur, *in* *Mineral resources of the United States: U.S. Geological Survey Professional Paper 820*, p. 864-905.
- Delahanty, T.W., 1931, Sulphur in Italy: U.S. Department of Commerce Chem. No. 353, 8 p.
- Donovan, J.R., and Salamone, J.M., 1983, Sulfuric acid and sulfur trioxide, *in* Grayson, Martin, ed., *Kirk-Othmer encyclopedia of chemical technology* (3d ed.): New York, John Wiley & Sons, v. 4, p. 190-232.
- Doorebus, 1977, The fluorocarbon-hydrogen fluoride industry, chap 16 *of* *Industrial process profiles for environmental use: Cincinnati, Ohio, U.S. Environmental Protection Agency, EPA-600/2-77-023*, 89 p.
- Edelstein, D.L., 1996, Copper, *in* *Metals and materials: U.S. Bureau of Mines Minerals Yearbook 1994, v. I*, p. 247-266.
- 2002, Copper, *in* *Metals and minerals: U.S. Geological Survey Minerals Yearbook 2000, v. I*, p. 23.1-23.26.
- 2002, Copper: *U.S. Geological Survey Mineral Commodity Summaries 2002*, p. 54-55.
- Energetics Inc., 1998, Alkylation, *in* *Energy and the environmental profile of the U.S. petroleum refining industry: U.S. Department of Energy, Office of Industrial Technologies*, December, p. 75-82.
- Eriksson, E., 1960, The yearly circulation of chloride and sulfur in nature—Meteorological, geochemical, and pedological implication: *Stockholm, Sweden, Tellus*, pt. II, v. 12, p. 63-109.
- Fertilizer Markets, 1999, Decline in Chinese pyrites aids Canadian S exports: *Fertilizer Markets*, v. 10, no. 9, September 13, p. 2-3.
- Fischer, H., 1984, Sulphur, *in* Sander, U.H.F., Fischer, H., Rothe, U., and Kola, R., *Sulphur, sulphur dioxide and sulphuric acid*: London, The British Sulphur Corp. Ltd., 415 p.
- Fisher, W.B., and Crescentini, L., 1992, Caprolactam, *in* Kroschwitz, J.I., ed., *Kirk-Othmer encyclopedia of chemical technology* (4th ed.): New York, John Wiley & Sons, v. 4, p. 827-839.
- ForestSweden, [undated], Pulp/paper, web site at [http://www.skogssverige.se/default\\_eng.cfm](http://www.skogssverige.se/default_eng.cfm). Accessed September 4, 2001.
- Freeport Sulphur Co., [undated], Freeport Sulphur Co.: Freeport Sulphur Co. brochure, 17 p.
- Friend, J.P., 1973, The global sulfur cycle, *in* Rasool, P., ed., *Chemistry of the lower atmosphere*: New York, Plenum Press, p. 177-201.
- Georgia Gulf Sulfur Corp., 2000, Products, web site at <http://www.georgiagulfssulfur.com/products.htm>. Accessed August 27, 2001.
- Gillen, G.P., 1996, Copper leaching with sulfuric acid—Past, present, future: *Sulphur Markets Today and Tomorrow—Biennial International Symposium*, 5th, Washington, DC, March 27-29, 1996, Presentation, 7 p.
- Granat, L., Hallberg, R.O., and Rodhe, H., 1976, Sulfur, *in* Svensson, B.H., and Söderlund, R., eds., *Nitrogen, phosphorus, and sulphur—Global cycles: Stockholm, Ecological Bulletins*, v. 22, p. 89-134.
- Hachmuth, H.K., 1994, The alkylation process: *Sulphur Markets Today and Tomorrow—Biennial International Symposium*, 4th, Washington, D.C., March 23-25, 1994, Presentation, 13 p.
- Haynes, Williams, 1959, Brimstone—The stone that burns: Princeton, N.J., D. Van Nostrand Co., Inc., 293 p.

- H.J. Baker & Bro., Inc., 2001, DakSul45—Achieve maximum yields with sulphur and nitrogen, web site at <http://www.bakerbro.com/daksulpg.htm>. Accessed August 27, 2001.
- Hedrick, J.B., 1995, The global rare-earth cycle: *Journal of Alloys and Compounds*, no. 225, p. 612.
- International Copper Study Group, 2002, Directory of copper mines and plants: Lisbon, Portugal, International Copper Study Group, January, 87 p.
- Ivanov, M.V., and Freney, J.R., 1983, The global geochemical sulfur cycle: New York, John Wiley & Sons, 470 p.
- Jolly, J.H., 1985, Zinc, *in* Mineral facts and problems: U.S. Bureau of Mines Bulletin 667, p. 923-940.
- Jolly, J.L.W., 1985, Copper, *in* Mineral facts and problems: U.S. Bureau of Mines Bulletin 667, p. 197-221.
- Kalyoncu, R.S., 2002, Coal combustion products, *in* Metals and minerals: U.S. Geological Survey Minerals Yearbook 2000, v. I, p. 20.1-20.14.
- Karolak, Jozef, 1997, The Polish sulfur industry *in* International Fertilizer Industry Association Production and International Trade Committee Meeting, Warsaw, October 14-15, 1997, Proceedings: Paris, International Fertilizer Industry Association, v. III, p. 85-92.
- Kellogg, W.W., Cadle, R.D., Allen, E.R., Lazrus, A.L., and Martell, E.A., 1972, The sulfur cycle: *Science*, v. 175, no. 4022, February 11, p. 587-595.
- Kennecott Utah Copper Corp., 2000, Sulfuric acid, web site at <http://www.odyssey-web.com/kennecott/sulfuricacid.html>. Accessed August 22, 2001.
- Klein, Jack, 1996, Gypsum finds ecological concerns stacked against it: *The Business Journal*, December 9, p. 1.
- Kordosky, G.A., 1992, Copper solvent extraction—The state of the art: *Journal of Metals*, v. 44, no. 5, May, p. 40-45.
- Kramer, D.A., 2002, Nitrogen, *in* Metals and minerals: U.S. Geological Survey Minerals Yearbook 2000, v. I, p. 55.1-55.22.
- Kuck, P.H., [undated], Nickel statistics and information, web site at URL <http://minerals.usgs.gov/minerals/pubs/commodity/nickel/>. Accessed August 22, 2001.
- Kyhle, O., 1983, The outlook for pyrites: Sulphur-Phosphate Symposium, 9th, Tarpon Springs, Fla., January 16-19, 1983, Presentation, 13 p.
- Larson, L.P., and Marks, A.L., 1955, Sulfur, *in* Metals and minerals: U.S. Bureau of Mines Minerals Yearbook 1954, v. I, p. 1136-1137.
- Leffler, W.L., 2000, Petroleum refining in nontechnical language (3d ed.): Tulsa, Okla., Pennwell Corp., 310 p.
- Liolios, G.C., 1989, Alkylation—Past, present and future: National Petroleum Refiners Association Annual Meeting, San Francisco, Calif., March 19-21, 1989, Presentation, 11 p.
- Lynd, L.E., and Lefond, S.J., 1983, Titanium minerals, *in* Lefond, S.J. ed., *Industrial minerals and rocks*: New York, Society of Mining Engineers of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., p. 1303-1362.
- Merwin, R.W., 1974, Sulfur and pyrites, *in* Metals and minerals: U.S. Bureau of Mines Minerals Yearbook 1972, v. I, p. 1175-1190.
- Merwin, R.W., and Keyes, W.F., 1976, Sulfur and pyrites, *in* Minerals and metals: U.S. Bureau of Mines Minerals Yearbook 1974, v. I, p. 1235-1259.
- Monsanto Chemical Co., [undated], Monsanto designed contact sulfuric acid plants: St. Louis, Mo., Monsanto Chemical Co. brochure, 39 p.
- Morse, D.E., 1983, Sulfur, *in* Metals and minerals: U.S. Bureau of Mines Minerals Yearbook 1982, v. I, p. 799-818.
- 1985, Sulfur, *in* Mineral facts and problems: U.S. Bureau of Mines Bulletin 667, p. 783-797.
- 1987, Sulfur, *in* Metals and minerals: U.S. Bureau of Mines Minerals Yearbook 1986, v. I, p. 895-915.
- Moss, M.R., 1978, Sources of sulfur in the environment—The global sulfur cycle, *in* Nriagu, J.O., ed., *Sulfur in the environment—Part 1—The atmospheric cycle*: New York, John Wiley & Sons, p. 23-50.
- North American Sulphur Service Sulphur Newsletter, 2000a, News and developments: North America Sulphur Service Sulphur Newsletter, v. 11, no. 2, February, p. 2-3.
- 2000b, News and developments: North America Sulphur Service Sulphur Newsletter, v. 11, no. 7, July, p. 4.
- Ober, J.A., 1994, Sulfur, *in* Metals and minerals; U.S. Bureau of Mines Minerals Yearbook 1993, v. I, p. 1165-1193.
- 2002, Sulfur, *in* Metals and minerals: U.S. Geological Survey Minerals Yearbook 2000, v. I, p. 76.1-76.24.
- Occupational Safety & Health Administration, 1999, Section IV—Chapter 2—Petroleum refining processes, OSHA Technical Manual, web site at [http://www.osha-slc.gov/dts/osta/otm/otm\\_iv/otm\\_iv\\_2.html](http://www.osha-slc.gov/dts/osta/otm/otm_iv/otm_iv_2.html). Accessed November, 27, 2001.
- Oil & Gas Journal, 1999, A description of Canadian oilsands characteristics: *Oil & Gas Journal*, v. 97, no. 26, June 28, p. 48.
- Olson, D.W., 2002, Gypsum, *in* Metals and minerals: U.S. Geological Survey Minerals Yearbook 2000, v. I, p. 36.1-36.9.
- Phelps Dodge Mining Co., [undated], Phelps Dodge Morenci Inc.: Phoenix, Ariz., Phelps Dodge Mining Co. brochure, 20 p.
- Ramey, D.S., 1995, The production of SX-EW copper at Magma Copper Company: International Fertilizer Industry Association Production and International Trade Committee Meeting, Tampa, Fla., September 14-15, 1995, Presentation, 15 p.
- Roskill Information Services Ltd., 1991, The economics of titanium: London, Roskill Information Services Ltd., p. 29.
- Sander, U.H.F., Rothe, U., and Kola, R., 1984, Sulphuric acid, *in* Sulphur, sulphur dioxide and sulfuric acid: London, The British Sulphur Corp. Ltd., p. 257-399.
- Schmerling, Louis, 1981, Organic and petroleum chemistry for nonchemists: Tulsa, Okla., PennWell Publishing Co., 109 p.
- STARcrete Technologies Inc., 2000, STARcrete—The first commercial sulfur concrete, web site at <http://www.starcrete.com/>. Accessed September 10, 2001.
- Stevens, Jason, 1998, Oil sands projects gather pace: *Sulphur*, no. 254, January-February, p. 27-30.
- Stowasser, W.F., 1985, Phosphate rock, *in* Mineral facts and problems: U.S. Bureau of Mines Bulletin 667, p. 579-593.

- Sulfuric Acid Today, 2000, Alkylation is the wave of the future for cleaner burning fuels: *Sulfuric Acid Today*, v. 6, no. 2, fall/winter, p. 29.
- Sulphur, 1991, The aftermath: *Sulphur*, no. 215, July-August, p. 5.
- 2000a, Acid leach supply contract for Kennecott: *Sulphur*, no. 279, September-October, p. 14.
- 2000b, JPMC cuts costs with Iraqi imports: *Sulphur*, no. 271, November-December, p. 10-11.
- 2000c, Latest developments in leaching technology for metal ores: *Sulphur*, no. 269, July-August, p. 31-40.
- 2000d, Sulphur removal JV to handle cheaper crude: *Sulphur*, no. 270, September-October, p. 52.
- 2001, Poland's leading sulphur mine forced to close: *Sulphur*, no. 277, November-December, p. 13-14.
- Tiger Industries Ltd., 1999, Run with the leader—New Tiger 90CR, quicker breakdown, season-long sulphur nutrition: Calgary, Canada, Tiger Industries Ltd. brochure, 8 p.
- Toon, Steve, 1986, Sulphur—A sweet or sour future?: *Industrial Minerals*, no. 221, February, p. 16-37.
- U.S. Census Bureau, 2001, Inorganic fertilizer materials and related products: U.S. Census Bureau MQ325B(00), July, 6 p.
- U.S. Energy Information Administration, 1997, The effects of title IV of the Clean Air Act Amendments of 1990 on the electric utilities—An update: U.S. Energy Information Administration, March, 118 p.
- 2001, Annual energy review 2000: U.S. Energy Information Administration, DOE/EIA-0384(00), August, 379 p.
- U.S. Environmental Protection Agency, 2000, National emission standards for hazardous air pollutants—Subpart R—Radon from phosphogypsum stacks, web site at <http://www.epa.gov/radiation/neshaps/subpartr>. Accessed May 10, 2001.
- Weber, H.H., and McBee, W.C., 2000, New market opportunities for sulphur asphalt: *Sulphur Markets Today and Tomorrow—Biennial International Symposium*, 7th, Washington, D.C., March 26-28, 2000, Presentation, 24 p.
- West, J.R., 1966, Safety in handling liquid and dry sulfur: *Commercial Fertilizer*, v. 112, no. 1, January, p. 15-20.
- Whelpdale, D.M., 1992, An overview of the atmospheric sulphur cycle, in Howarth, R.W., Stewart, J.W.B., and Ivanov, M.V., eds., *SCOPE 48—Sulphur cycling on the continents—Wetlands, terrestrial ecosystems and associated water bodies*: New York, John Wiley & Sons, p. 5-26.
- Will, Ray, 2000, The outlook for hydrofluoric acid—Effects on the sulphur industry: *Sulphur Markets Today and Tomorrow—Biennial International Symposium*, 7th, Washington, D.C., March 26-28, 2000, Presentation, unpaginated.
- Woodbury, W.D., 1985, Lead, in *Mineral facts and problems*: U.S. Bureau of Mines Bulletin 667, p. 433-451.
- Zwicker, D.A., 1990, Bright future for brimstone: *The Lamp* (Exxon Corp.) Fall, p. 10-15.