

*"Materials-Cycle Optimisation in the
Production of Major Finished Materials"*
CHAPTER 6: SULFUR & SULFURIC ACID

by

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This chapter is part of a report made for the EC DGXII on a project entitled "*Materials-Cycle Optimisation in the Production of Major Finished Materials*". This project aims at facilitating the identification of longer-term R&D needs for materials-cycle optimisation, especially by using wastes, co-products, or by-products from one process as inputs to other processes. Book publication is envisaged. Following is the list of chapters:

- Chapter 1: Summary and Overview (*Insead ref N°: 95/05/EPS*)
- Chapter 2: Alumina, Aluminium and Gallium (*Insead ref N°: 95/06/EPS*)
- Chapter 3: Copper, Cobalt, Silver & Arsenic (*Insead ref N°: 95/07/EPS*)
- Chapter 4: Chromium Sources, Uses and Losses (*Insead ref N°: 95/08/EPS*)
- Chapter 5: Zinc and Cadmium (*Insead ref N°: 95/09/EPS*)
- Chapter 6: Sulfur and Sulfuric Acid (*Insead ref N°: 95/10/EPS*)
- Chapter 7: Phosphorus, Fluorine and Gypsum (*Insead ref N°: 95/11/EPS*)
- Chapter 8: Nitrogen-based Chemicals (*Insead ref N°: 95/12/EPS*)
- Chapter 9: The Chlor-Alkali Sector (*Insead ref: N°: 95/13/EPS*)
- Chapter 10: Electronic Grade Silicon (EGS) for Semiconductors (*Insead ref N°: 95/14/EPS*)
- Chapter 11: Packaging Wastes (*Insead ref N°: 95/15/EPS*)
- Chapter 12: Scrap Tires (*Insead ref N°: 95/16/EPS*)
- Chapter 13: Coal Ash: Sources and Possible Uses (*Insead ref N° 95/17/EPS*)

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CHAPTER 6. SULFUR AND SULFURIC ACID¹

6.1. Summary

Sulfur is biologically and environmentally important because it can exist in valence states from -2 (e.g. hydrogen sulfide, H_2S) to +6 (sulfuric acid, H_2SO_4). Like nitrogen and phosphorus, is essential to living organisms. It is a component of three of the 20 amino acids that, are the "building blocks" of all proteins, viz. cystine, cysteine and methionine. It seems to play a special part in cross-linking amino acid chains to give them their characteristic three-dimensional shapes (especially important for enzymes). On the other hand, a number of sulfur compounds are toxic, including hydrogen sulfide, sulfur dioxide and the mercaptans.

Sulfur is an important industrial substance. Sulfur is not intrinsically scarce; enormous quantities are theoretically available as a by-product of fossil fuels, as well as in deposits of sulfide ores, pyrites and elemental sulfur. Virtually all sulfur used by industry today comes from elemental sulfur deposits or from refining oil, gas and non-ferrous metals. In some sense, the availability of large reserves of reduced sulfur is the core of the problem, since it is much easier, hence cheaper, to obtain sulfur in forms useful to industry from reduced sources such as H_2S or S than it is to recover it from coal, or from oxides. Sulfur product-process flows for the U.S. in 1988 are shown in *Figure 5.1*.

Most industrial sulfur is converted initially to its most oxidized form, sulfuric acid. Sulfuric acid, because of low cost and its variety of uses as a powerful oxidizer and pH control in the chemical industry and other industries, is one of the most reliable indicators of general industrial activity. However, currently, the biggest and fastest growing single use of sulfuric acid, worldwide, is a specialized one: converting phosphate rock to phosphoric acid for fertilizer. In this case, the sulfur is combined with calcium as insoluble calcium sulfate (gypsum). (See *Chapter 7, Phosphorus & Fluorine* for a further discussion of gypsum). The majority of chemical processes end up with sulfur (from the acid) combined with calcium (from lime) or sodium (from caustic soda. In the latter case, the material is soluble and biologically available.

The major source of anthropogenic volatile sulfur oxide emissions, today, is the combustion of fossil fuels — especially coal — and the smelting and refining of non-ferrous metals (Cu, Zn, Pb). In these cases, the sulfur is oxidized to SO_2 or SO_3 . In the air, SO_2 and associated droplets of acid are irritating and harmful to the nasal passages and lungs. Sulfur dioxide was actually the first air pollutant to be subject to regulation, although its sharp and unpleasant odor may account for this early attention. The unreacted sulfur oxides remaining in the atmosphere are the major cause of a haze which reduces visibility and increases the reflectivity (albedo) of the earth to sunlight. Thus sulfur oxide emissions, other factors remaining equal, tend to cool the earth slightly.

The sulfur oxides are eventually deposited as dry sulfite/sulfate particulates, or dissolved in water droplets (producing sulfurous or sulfuric acid), or they react with ammonia, producing ammonium sulfite or sulfate. In any case, the sulfur is eventually deposited on land (or water) as sulfurous or sulfuric acid, or as sulfates. On the ground, ammonium sulfate is a fertilizer.

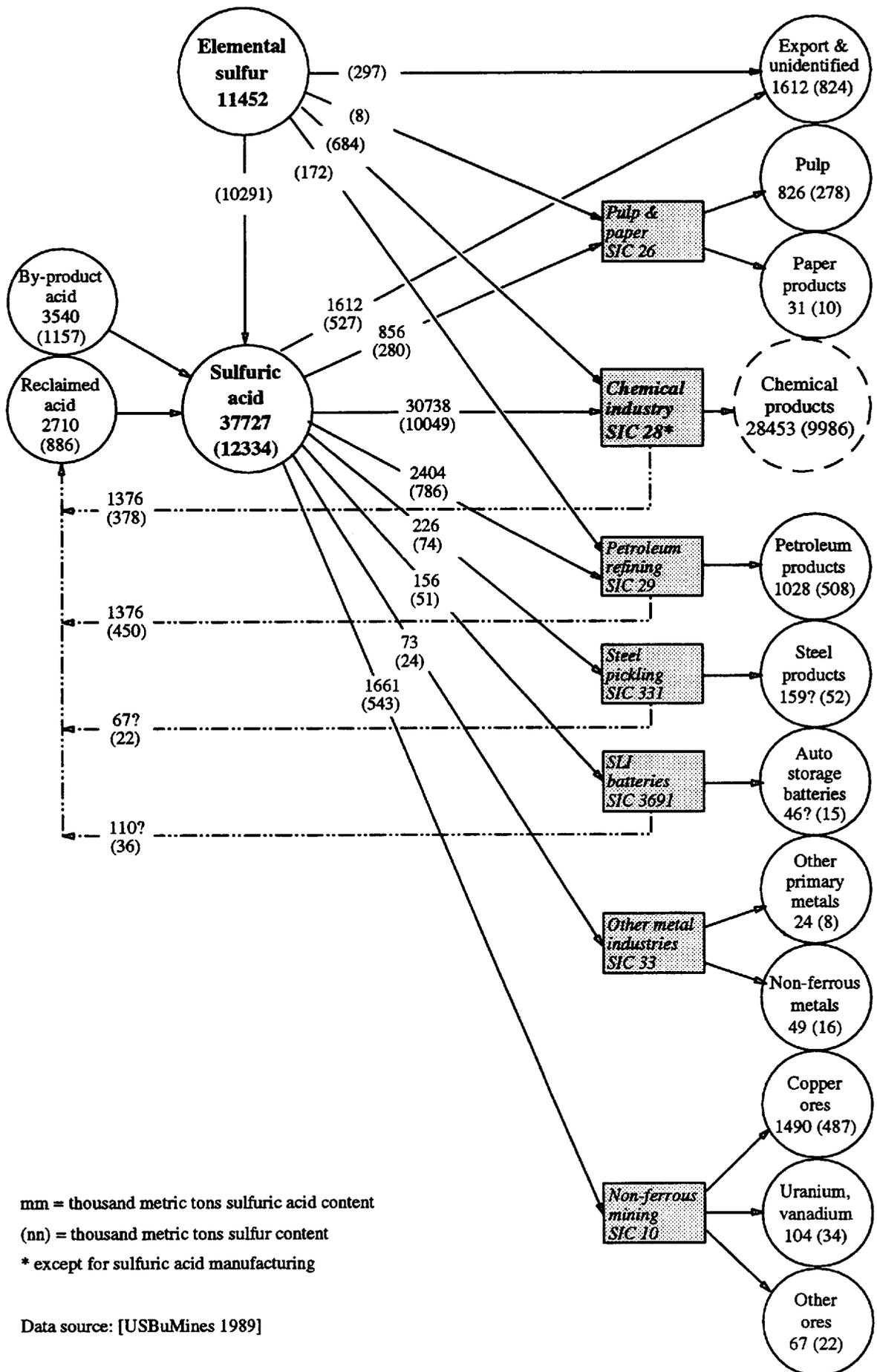


Figure 6.1. U.S. sulfur product flows, 1988

Sulfurous and sulfuric acids are also biologically active. In effect, the natural "sulfur cycle" has been significantly accelerated by industrial activity. One consequence is widespread acidification of forest soils, especially granitic soils in central and northern Europe. On the other hand, since many soils are sulfur deficient, there is also a general fertilization ("eutrophication") effect, especially in calcareous soils.

There are a few industrial processes where sulfur escapes in reduced forms. Reduced volatile forms of sulfur (H_2S and mercaptans) are particularly hazardous, although the quantities released in the industrialized countries (mainly from oil refineries and pulp mills) are comparatively minor. (The major source of reduced sulfur into the atmosphere is from volcanic eruptions, fumaroles, anaerobic decay in swamps, and vented natural gas).

Goals of Public Policy: to reduce unnecessary surface mining (of coal and gypsum, for instance); to reduce atmospheric emissions of sulfur oxides, especially in areas where increased acidification is a problem; to minimize emissions of toxic reduced forms of sulfur, such as H_2S ; to reduce the need for land disposal of wet fuel gas desulfurization (FGD) sludges; recover elemental sulfur or sulfuric acid for industrial use from fossil fuels and non-ferrous metals smelters.

6.2. Industrial Sulfur Sources

Worldwide, there are currently three major primary sources for elemental sulfur and sulfuric acid: (1) native sulfur found in the limestone caprock of salt domes, volcanic deposits, or bedded anhydrite, (2) hydrogen sulfide present in "sour" natural gas, refinery gas and other fuel gases, and (3) ferrous and nonferrous metallic sulfides.

Total world production of elemental sulfur in 1991 was 55.592 million metric tons (MMT). Production in Western Europe was 7.081 MMT. Much sulfur is still mined in pure form (native sulfur) or from underground deposits (by the Frasch process), though not in Western Europe. Poland produced 4.4 MMT by the Frasch process and another 0.5 MMT from native sulfur deposits. Sulfur is also mined as iron pyrites, and as gypsum (only in Poland, however). In Western Europe pyrites accounted for 2.215 MMT in 1989, about half from Spain.

Crude oil refined in the U.S. in 1980 averaged 1.5% S by weight. In the case of imported oil from Venezuela and Mexico, refined offshore, the average sulfur content was 5.5%. In the case of natural gas, the sulfur content was 0.003%. These percentages are rising, if anything, from decade to decade. The sulfur cannot be allowed to remain in the fuel, so it must be removed at the refinery, either as a waste or for beneficial use. Sulfur recovery from petroleum was negligible prior to the 1940s and is essentially a function of the complexity of the refinery. Much of the unrecovered sulfur — of which there is now relatively little in the industrialized world — was ultimately emitted as SO_x . This is still the case in some smaller refineries in less industrialized countries. Some so-called "sweetening" processes to eliminate odors from hydrogen sulfide and mercaptans leave odorless sulfur compounds dissolved in the fuel. These are ultimately burned, yielding SO_2 .²

Table 6.1. Sulfur production 1989 (kMT)

Country	Mined	Sulfur					Gypsum Mines (MMT)
		Gas	Oil	Metal	Unspec	Total	
Austria			36 ^(c)	12		48	625
Belgium						320	
Denmark			20			20	
Finland			45	240	320	585	
France	300		235			1051	5569
Germany (W)			210	315		1885	1850
Germany (E)					180	290	1850
Greece			5		310	180	500
Ireland	70	636			290		314
Italy		1050				820	1250
Netherlands	330		310 ^(d)			310	
Norway		105	10		500	260	
Portugal	170					125	300
Spain	120	330	8	225	80	1235	5500
Sweden	1000		50	125	5	400	
Switzerland	225		4		2 ^(e)	4	218
UK			130	55		185	3990
W. Europe	2215	1791	1063	1052	1607	7728	19426
Bulgaria	70					130	400
Czechoslovakia	60				60	77	775
Hungary	1				11	11	115
Poland	4920 ^(a)		20	150	10	5090	1090
Romania	150					270	1595
Yugoslavia	255		3	170	120	428	550
E. Europe	5462		23	320	201	6006	4515
Turkey	45					125	250
USSR	5050 ^(b)	2500	450	1350	80	9350	4800
US	3888	2537	3973	1190	4	11592	16000
World	24788	12191	7176	7521	6872	58348	100000
Source: [USBuMines 1991]			(c) Frasch 1100, native 1800, pyrites 2150				
(a) Frasch 4400, native 500, gypsum 20			(d) Includes 60 from Curaçao				
(b) Gas and oil			(e) From coal gasification				

In recent years, increasing amounts of refinery sulfur have been recovered for reuse. About 26% of the potential sulfur from crude oil refined in the U.S. was actually recovered in 1974, mostly by the catalytic hydrogen desulfurization process [USBuMines 1975]. About one third (33.9%) of US petroleum distillation capacity included hydro-treating facilities for sulfur recovery as of January 1, 1980 [Gaines & Wolsky 1981]. The sulfur recovery process itself is said to be 99% efficient. Petroleum refineries accounted for 28% of the domestic U.S. sulfur supply in 1983 [USBuMines 1985]. Natural gas accounted for 26% of the domestic

U.S. sulfur supply in 1983. These fractions are rising. Fuel processing accounted for 56% of the U.S. sulfur supply in 1990 and 61% in 1991 [USBuMines 1991]. Some sulfur is also recovered (as sulfuric acid) from copper, zinc, lead and nickel smelters. Western Europe now gets most of its sulfur from by-products. See *Table 6.1*.

Non-ferrous metals are almost exclusively obtained from sulfide ores. For instance, copper ore consists mostly of chalcopyrite (CuFeS_2) - which is the most common - followed by bornite (Cu_5FeS_4) and chalcocite (Cu_2S), although minor amounts of copper are also obtained from oxides and carbonates. Zinc and lead are obtained respectively from the minerals sphalerite (ZnS) and galena (PbS). Mercury ore is cinnabar (HgS). Nickel is also mined partly from sulfide ores (e.g. in Canada). *Table 6.2* gives the ratios of sulfur to metal in major non-ferrous ores.

Table 6.2. Ratio of copper, lead and zinc in ore, by weight

Copper	1.0 (a)
	1.47 (b)
Lead	0.15 (c)
Zinc	0.49 (d)

- (a) Preferred estimates. Based on chalcopyrite (CuFeS_2) as the ore. In the early 19th century a significant fraction of the copper mined was native (not combined with sulfur).
- (b) Implied by *Mineral Facts and Problems (1975)* estimate of potential by-product sulfur availability from copper ore.
- (c) Based on the mineral galena (PbS) as the ore. This is quite consistent with *Mineral Facts and Problems (1975)*.
- (d) Based on the mineral sphalerite (ZnS) as the ore. The coefficient implied by *Mineral Facts and Problems (1975)* is 0.43.

Sulfur recovery from copper and lead smelters is was still relatively incomplete until quite recently. It is motivated mainly by environmental concerns. As recently as 1974 the U.S. Bureau of Mines estimated a 30% sulfur recovery rate for copper smelting and 43% for lead smelting [USBuMines 1975]. However, the above estimate for copper assumes a sulfur content of copper ores equivalent to 1.47 tons of sulfur per ton of copper, which is inconsistent with the known composition of copper minerals and smelter feeds (*Table 6.2*). For this reason we suspect that the USBuMines recovery estimate for copper in that year was slightly too low. Using the lower figure for sulfur content, in *Table 6.2* the sulfur recovery rate for U.S. copper smelters in 1974 would also have been 43%. This is consistent with the fact that about 60% recovery was easily achievable at the convertor stage, but the remainder (40% or so) requires scrubbers or the equivalent. It is estimated that sulfur recovery from copper smelters in the U.S. has reached 95% [USBM 1994].

By contrast, complete sulfur recovery from zinc smelters in the U.S. was much easier to achieve (81% by 1974). This was apparently because the zinc retorting process itself makes sulfur recovery straightforward and economical. If all by-product sulfur recovery from copper and zinc smelters in 1911 (the first year for which we have data) is attributed to zinc smelting alone, the implied recovery rate would be 79% - close to the 1974 level. In 1983 copper smelting accounted for 6% of the U.S. sulfur supply, while zinc, lead and molybdenum

accounted for another 2% between them. In 1991 the non-ferrous metal smelters contributed 12% of domestic U.S. supply, entirely in the form of sulfuric acid.

The efficiency of sulfur recovery (as opposed to emissions control) from non-ferrous metal smelters is not easy to determine. One study [Chapman 1989, Table 3] estimated the sulfur control indices for a number of exporting countries for 1985 as follows: Chile (14%), Peru (0%), South Africa (39%), Zaire (76%), Zambia (70%), Philippines (0%), Australia (0%) and Canada (26%). It estimated the average control level for copper exporters as 32%, compared to an average of 89% for the major copper importing countries. A more recent study of 8 U.S. and 29 non-U.S. copper smelters around the world, commissioned by the U.S. Bureau of Mines, concluded that sulfur control (i.e. recovery) at U.S. smelters for the year 1988 was 90.4%, but that only 55% of the available sulfur was recovered by the non-U.S. group [Towle 1993]. However, of the non-U.S. smelters surveyed, three were located in Western Europe (Ronnskar, Sweden, Hamburg, Germany and Huelva, Spain). The first two, at least, are at the 90% recovery level.

In principle, all of the world's needs for elemental sulfur and sulfuric acid could easily be met by recovering the sulfur from metals, gas, oil and coal. Yet only a small proportion of the sulfur in coal is actually recovered, and most of that is disposed of as a semi-liquid sludge of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Virtually none of the sulfur in coal is used industrially. (As of 1989, only 2000 tonnes was recovered from coal in Europe, in a Spanish gasification plant). Most coal-bound sulfur is still emitted to the atmosphere as SO_x .

6.3. Potential Sulfur Recovery from Coal

Coal contains, on average, 0.5%-1.5% sulfur. Coal traded internationally must have a maximum sulfur content of 1%, though some coals being burned locally are significantly higher in sulfur [EU 1992]; [WEC 1992]. The sulfur oxidizes to SO_2 , which (if not removed) is the major source of environmental acidification. In turn "acid rain" from coal combustion (mainly in electric power plants) is largely blamed for forest die-back (*Waldsterben*) in many parts of Europe. Coal from the Saar and Ruhr areas ranges from 0.9% to 1% [WEC 1992]. British coal is 1.66% sulfur [ibid]. Some coals have much higher sulfur content. French sub-bituminous coal averages 5% sulfur [ibid]. Spanish coal has a high sulfur content. Hungarian coals are also high in sulfur (2.5-3.8%). (U.S. coal averages 1.85% S) [ibid]. Virtually none of the sulfur emitted from coal combustion in Europe is being recovered today, though there is some emissions control.

The total quantity of sulfur that could be potentially recovered worldwide from coal (assuming a conservative 1% sulfur content) approaches 40 MMT. In fact, this is a lower limit. This is more than enough to replace all the "mined" sulfur currently produced in the world (25 MMT). Since mining is itself an environmentally damaging activity, and uncontrolled emissions of SO_2 cause serious health hazards as well as acidification, it would be very beneficial to solve two problems at once by recovering the sulfur from coal in an industrially *useful* form, either as elemental sulfur, carbon disulfide or sulfuric acid.

The need to capture the sulfur from coal combustion is becoming clear, at least in Western Europe. Indeed, Western Europe will almost certainly be forced to subsidize Poland and the Czech Republic, and perhaps others, to reduce the sulfur emissions that would otherwise cross the border from east to west. But current means of flue gas desulfurization (FGD) are almost exclusively limited to variations of one theme: the use of lime (or limestone) "scrubbers" that capture the sulfur as wet calcium sulfite (CaSO_3). This is a material that has no market as such, and which is only convertible, with some difficulty, into hydrated calcium sulfate, essentially wet plaster-of-Paris. Synthetic gypsum for use in plaster-boards and building materials can be produced from wet FGD wastes from coal-burning plants. One viable approach seems to be the so-called lime-sinter process [Motley & Cosgrove 1978], although there are several variants. At least one such plant is already operational, on an experimental basis, in the Czech Republic, using German technology.

In general, the synthetic gypsum product is moderately costly to make and there is a limited market for it. In the more general case, wet FGD waste is difficult and costly to dispose of. Moreover, the limestone or lime used for the scrubber must itself be mined and shipped, at some cost to the environment. Finally, a typical wet scrubber installation consumes about 4% of the electric power produced by the plant.

Since disposal of wet FGD sludges from electric power plants will become increasingly costly, there will be strong incentives to extract a more useful and valuable by-product from the process. But, at present, the capital and energy cost of doing so, in the short term, is fairly high, but not entirely certain. In short, either capital subsidies or energy subsidies, or both, are needed. It is not entirely clear how big these subsidies need to be, nor who will provide them.

A number of dry FGD processes have been tested and some have been installed. Dry FGD systems require less equipment because there is no need for thickeners, centrifuges, slurry pumping and so on. They produce a dry solid waste that can be handled and disposed of in the same way that ash is normally handled and disposed of. They use less energy, for the same reason. The major disadvantage is that the sorbents are mostly sodium carbonates and bicarbonates, which are more expensive than limestone. Also, the sodium-based wastes have a greater potential for leaching than calcium-based wastes.

One dry process that has the advantages mentioned above, without the disadvantages, is the so-called "Trimex" process. A dry powder, consisting mainly of the clay known as calcium montmorillonite (bentonite), is injected into the firebox. The clay material has a very strong affinity for water and captures water vapor on its surface, where a catalytic reaction with SO_2 in the combustion product stream takes place. The sulfurous and sulfuric acids adhering to the clay particle surface, in turn, react immediately with the alkaline metals in the fly ash particulates. In other words, the fly ash becomes the sorbent for FGD in this case. The final product (collected by an electrostatic precipitator, would consist of dry metallic sulfites and sulfates. Certain additives, namely trisodium phosphate and borax, support or activate the catalytic function of the clay.

Recovery of elemental sulfur directly from flue gas is a further possibility [Kelly & Dickerman 198?]. As applied to coal gasification, this could utilize a variant of hydro-gasification technology, where the sulfur combines initially with hydrogen to form H_2S . The

latter is easily reduced to elemental sulfur by the Claus process. This is much less straightforward in an oxidizing environment, where solid coal is burned. The most useful product that can be extracted is probably a low-grade sulfuric acid.

An interesting process for co-producing sulfur, alumina and Portland cement was proposed by TRW Inc [Motley & Cosgrove 1978]. A plant utilizing this process would have to be co-located with a large coal-burning power plant fitted with a limestone scrubber. Inputs might be 1.365 million metric tons (MMT) of scrubber waste (50% solid), 317 kMT of kaolin, 250 kMT of coal, 12 kMT of soda ash and 5 kMT of lime. Direct outputs would be 70 kMT of alumina, 156 kMT of sulfur and 652 kMT of dicalcium silicate (input to a cement plant yielding 858 kMT of Portland cement. Unfortunately, the process chemistry involved in the process was non-standard and partially hypothetical at the time of the Motley-Cosgrove study. In particular, there are unresolved questions about the reaction rates of soda, alumina, calcium and silica to form dicalcium silicate and sodium aluminate under reducing conditions, and the likely percentage of completion. Further laboratory work and bench testing was needed (and may still be needed).³ A variant of the above scheme was also suggested, in which the kaolin input is replaced by silica and the product is tricalcium silicate (cement) rather than dicalcium silicate.

In summary, there is a need for more research on FGD, not just as an "add on" process for existing coal-fired power plants, but in the context of an integrated system, such as "coalplex". For more detailed discussion see (*Chapter 13, Fly Ash*). The need is for sulfur recovery, not just for emissions control by itself. This need can best be met by treating the combustion unit as a source of raw materials, of which sulfur (in some form) is one, and integrating several down-stream processes in such a way as to take advantage of synergistic mutual interactions.

6.4. Sulfuric Acid and Sulfur-based Chemicals

Sulfuric acid is by far the most important sulfur-based chemical. It accounts for 92% of total U.S. sulfur use, and 77% of non-fertilizer sulfur use. In the U.S. (the largest consumer) phosphates alone account for 66% of the total demand for sulfuric acid. However, the U.S. is a major exporter of phosphates, whereas Europe is a major importer. For W. Europe non-fertilizer consumption of sulfuric acid dominates in percentage terms (58.5 %). This is because there are virtually no sources of phosphate rock in W. Europe; a great deal of the phosphoric acid consumed in Europe is imported, from a variety of places, including the U.S., Israel, South Africa and N. Africa. Quite a lot of the processing is done outside Europe⁴. For the world as a whole, fertilizer accounts for 61.7% of total sulfuric acid consumption, mostly for phosphates.

The primary product is wet-process phosphoric acid, which is the source of phosphate fertilizers. The sulfur in this case ends up as hydrated calcium sulfate ("phospho-gypsum") and is discarded as waste. See *Chapter 7, Phosphates* for a further discussion. The waste from phosphate rock processing is, essentially, a somewhat contaminated form of the mineral gypsum. Similarly, the waste from flue gas desulfurization (FGD) is also gypsum. Yet, most by-product gypsum is a waste that poses a disposal problem. At the same time, approximately

100 million metric tons (MMT) of natural gypsum is mined, each year. Uncalcined gypsum is used in the manufacture of Portland cement and in agriculture as a soil conditioner for alkaline and saline soils. Calcined gypsum is used for conversion into plaster-of-paris and plasterboard products.

Production and consumption statistics for sulfuric acid are summarized in *Tables 6.3 & 6.4*. Elemental sulfur (23% of non-fertilizer use) is used to manufacture carbon disulfide, an intermediate in the production of fluorocarbons. It is also used in petroleum refineries (see below), to vulcanize rubber⁵ and in a number of unspecified uses, mostly agricultural [USBuMines 1989 "sulfur" Table 12]. The latter include traditional soil conditioners such as "lime-sulfur" mixture.

Sulfuric acid is not only used for phosphatic fertilizers. It is also used in the manufacture of ammonium sulfate. See *Table 6.4, sulfuric acid end-uses*. There are no detailed statistics on non-fertilizer sulfuric acid use in Europe. However, non-fertilizer use in Europe is very similar in absolute magnitude to non-fertilizer consumption in the U.S. It is reasonable to assume that the sectoral breakdown of non-fertilizer use of sulfuric acid in Europe would also be similar. A detailed sulfur balance accounting for most sulfur uses in the U.S. was summarized in *Figure 6.1*.

Sulfuric acid (H_2SO_4) is produced from elemental sulfur or by-product SO_2 from gas processing, petroleum refining or non-ferrous metal smelting. It is the starting point for most sulfur based chemicals. What is recovered in petroleum refineries is mostly also consumed there. Sulfur is used in refineries for several purposes, both as

Table 6.3. Sulfuric acid 1989/1990 (kMT)

Country	Production	Consumption	Consumption in fertilizer
Belgium	1957	2704	2070
Finland	1375	1286	706
France	4064	4009	1689
Germany (W)	3725	3342	460
Germany (E)	1070 ^(a)	1068 ^(a)	368 ^(a)
Greece	1025	1016	957
Italy	2212	1972	722
Netherlands	1387	2004	1234
Norway	636		
Portugal	267	300	213
Spain	3146	3014	2184
Sweden	905	899	339
UK	2148	2404	56
Others	783 ^(b)	1030 ^(c)	261 ^(d)
W. Europe	23629^(e)	23893	6492^(e)
Albania ^(b)	65	65	53
Bulgaria ^(b)	522	576	216
Czechoslovakia ^(b)	1090	1152	402
Hungary ^(b)	244	250	115
Poland ^(b)	2000	1815	1515
Romania ^(b)	1170	1170	510
Yugoslavia ^(b)	1350	1337	566
E. Europe^(b)	6441	6365	3377
Turkey		869	704
USSR ^(b)	645	27144	16644
US ^(b)	27300	41999	28999
World	158201	161431	99879^(b)
<i>Source: Kemira</i>			
<i>(a) 1990</i>			
<i>(b) Ireland, Denmark, Luxembourg & Switzerland</i>			
<i>(c) Ireland, Denmark, Luxembourg, Norway & Switzerland</i>			
<i>(d) Austria, Ireland, Denmark, Luxembourg, Norway & Switzerland</i>			
<i>(e) Does not include East Germany</i>			

Table 6.4. Sulfuric acid end-uses 1990 (kMT)

	Fertilizer				Non-Fertilizer	Total
	N (NH ₄) ₂ SO ₄	P ₂ O ₅	Other Fertilizer	Total		
W. Europe	2312 (10%)	6295 (27.3%)	953 (4.1%)	9560 (41.5%)	13,454 (58.5%)	23,014 (100%)
E. Europe	873 (13.6%)	2504 (39.4%)	-	3377 (53%)	2988 (47%)	6365 (100%)
USSR	2579 (9.9%)	14,065 (51.6%)	-	16,644 (61.5%)	10,500 (38.5%)	27,144 (100%)
US	1653 (3.9%)	27,347 (66%)	-	28,999 (69.9%)	12,500 (30.1%)	41,999 (100%)
World				97,787 (61.7)	60,696 (38.3%)	158,482 (100%)

Source: Kemira

elemental sulfur and as acid [Gaines & Wolsky 1981 p. 76]. Refinery uses as S include solvent extraction with liquid SO₂, and as an additive to high sulfur metal-cutting oils. Acid is used especially as a catalyst for alkylation of iso-and normal butane to produce high octane blending stock, and for polymerization of cracking-still gases to produce so-called "poly-gasoline". These uses accounted for about 14.7% of elemental sulfur and 16.7% of non-fuel consumption of sulfuric acid, in the U.S. in 1988. Over half of the "spent" acid from U.S. refineries is reclaimed, however and sold in the market [USBuMines 1991].

Similarly, acid recovered from U.S. copper smelters is mostly used for the so-called hydro-metallurgical process of copper and other non-ferrous ore leaching (e.g. uranium, vanadium). This use accounted for 16.3% of non-fuel consumption of sulfuric acid in the U.S. in 1988. This use is much less important in Europe. Crude copper sulfate is recovered from the leach piles, and this is recycled, but some of the leaching acid remains in the ore heaps where it presumably reacts with other minerals and remains as insoluble sulfates. In Europe, acid from smelters not co-located with mines (i.e. those not in Finland) is presumably sold on the market.

Inorganic chemicals manufacturing accounted for 10.75% of U.S. sulfuric acid consumption in 1988. Major quantity uses included production of titanium dioxide from ilmenite, chromic acid hydrofluoric acid from flourspar, copper sulfate, lead sulfate, zinc sulfate and other pigments.

The next largest use of sulfuric acid in the U.S. (9.85%) is in the manufacture of synthetic rubber, plastics and synthetics. Since very few organic chemicals actually contain any sulfur, it is likely that the most important contribution of sulfur (i.e. sulfuric acid) is to maintain reaction pH. In general, it is not embodied in products. Wastes are discharged, mostly as dilute or insoluble sulfates.

A further 1.3% of sulfuric acid consumption was used to make cellulosic fibers (e.g. rayon) yielding sodium sulfate as a by-product. Detergents — sulfonated fatty acid esters — accounted for another 2.5% of n.f sulfuric acid. This is virtually the only category of products (apart from vulcanized rubber) in which sulfur is actually embodied. Minor amounts of sulfuric acid are used in other chemicals manufacturing processes, adding up to 9.3%. Agricultural and water treatment chemicals are the biggest categories.

Another important non-fertilizer use of sulfuric acid — about 12.2% of U.S. consumption — is in the sulfate (Kraft) pulp bleaching process. Sulfuric acid is used to convert sodium chlorate to chlorine dioxide, with sodium sulfate as a by-product. The by-product sodium sulfate is used in the dominant Kraft pulping process. Sulfuric acid may also be used to produce sodium sulfate by direct reaction with sodium hydroxide. In the case of Kraft pulp mills there are increasing efforts to recover sodium sulfate and other chemicals from the waste stream ("black liquor") by using electrostatic precipitators at recovery furnaces. But the annual makeup requirements represent that which is discharged, either into the air as H_2S and other non-condensable gases (mercaptans, DMS, DMDS), or into streams and rivers as complex lignin-sulfonates (from the sulfite process).

The "pickling" process for cleaning rolled steel prior to galvanizing or tin-plating uses a small amount of sulfuric acid (1.5%). In this case the waste is mostly ferrous sulfate, which is easily recoverable but has few markets. Sulfuric acid is used in small amounts by other metallurgical processes (such as plating). Automotive storage (lead-acid) batteries accounted for 1.3% of n.f. uses. All the above items add up to 92.7% of the total. Unidentified uses, including exports, account for the rest (7.3%). The unidentified uses are probably distributed more less in proportion to the identified uses. Summarizing, 77% of non-fertilizer uses of sulfur are based on sulfuric acid. The remainder is diverse. Other starting points are SO_2 (used in the sulfite pulp process), and carbon disulfide (CS_2) which is used in the manufacture of chlorinated methanes. Elemental sulfur is used as such in agriculture (as noted preciously) and in rubber processing (as a vulcanizing agent). Sulfur is also used in the manufacture of some pesticides. In most cases, the sulfur is eventually oxidized and released or neutralized. However, when organic sulfur compounds enter anaerobic environments, trouble (i.e. reduced sulfur gases) can ensue. In particular, this is a problem that has been associated with paper pulping, for instance.

Virtually all uses of sulfur are dissipative. Most of the dissipative losses occur in agriculture (as elemental sulfur or ammonium sulfate), within the chemical industry itself, or in the petroleum refining or pulp and paper sectors. The final form of production waste is normally either insoluble calcium sulfite/sulfate, soluble (dilute) sodium sulfate, organic sulfonates, or SO_2 or reduced sulfur gases (H_2S , mercaptans, etc) emitted to the air. Consumption wastes include sulfur cutting oils and sulfonated detergents. Only a small amount of sulfuric acid is recycled (about 0.864 MMT S, or 7.3%), also mostly from petroleum refineries and synthetic materials. It is likely that the non-fertilizer sulfur consumption pattern for Europe is very similar to that for the U.S.

6.5. Atmospheric Emissions of Sulfur Oxides (SO_x)

Aggregate emissions of sulfur dioxide can be best estimated by using a materials balance calculation. Sulfur emitted (as SO₂) can be estimated fairly accurately as the *difference* between sulfur associated with ores and the sulfur recovered at refineries or smelters, with appropriate adjustments for imports or exports of sulfur containing fuels or minerals.

Table 6.5. Sources of anthropogenic sulfur in 1980 (kilotonnes of sulfur)

Country	Atmospheric emissions ^a			Sulfuric acid consumption ^b	Industrial sulfur consumption ^c	Ratio: industrial S to total S
	Combustion	In dust	Industrial /total			
Austria	147	30	17%	101	119	45%
Belgium-Lux	375	73	16%	792	932	71%
Denmark	226	1	0%	94	111	4%
Finland	170	122	42%	373	439	
France	1434	343	19%	1631	1919	57%
Germany, East	1377	223	14%	1337	1573	53%
Greece	333	15	4%	305	359	52%
Ireland	105	3	2%	24	28	21%
Italy	15112	293	16%	908	1068	41%
Netherlands	139	86	38%	619	729	84%
Norway	36	33	48%	87	103	74%
Portugal	130	19	13%	203	239	65%
Spain	1020	609	37%	1025	1206	54%
Sweden	157	86	35%	267	314	67%
Switzerland	63	1	1%	32	37	37%
United Kingdom	2089	250	11%	1049	1234	37%
Western Europe	9310	2183	19%	8763	10310	53%

^a Data from IIASA Transboundary Air Pollution Project. Combustion includes combustion from power plants, district heat generation, domestic and service sectors, transportation and industry. Industrial sulfur includes non-combustion industrial process emissions and all emissions (combustion and non-combustion) from the conversion of fossil fuels (refinery coke production). It was not possible to divide the data from this project into combustion and non-combustion emissions for this sector.

^b Data from UNIDO Trade Statistics.

^c Assumes 85% of industrial sulfur is sulfuric acid.

^d Total sulfur is the industrial sulfur plus combustion emissions.

The sulfur mobilized by the industrial economy in Western Europe for non-combustion uses is compared to the atmospheric sulfur emissions from combustion and the total anthropogenic sulfur budget in *Table 6.5*. The percentage of sulfur metabolized by the European and U.S. industrial economy (non-combustion uses) is much higher than the global average. For

Western Europe as a whole, industrial uses account for just over half of the total sulfur budget. Numbers for the U.S. are comparable.

6.6. Emissions to Other Media

Much has been written about the sources of atmospheric sulfur emissions and their detrimental environmental effects. Less information is available on industrial sulfur waste disposal in water and on land. It is important to emphasize here that the majority of the sulfur used in industrial processes is used for processing and is not embodied in the end product. That which is not recycled becomes a waste.

Having concluded that the industrial use of sulfur is a significant portion of the Western European anthropogenic sulfur budget, two new questions arise: in what form is the emission? And, is it an environmental hazard? Currently, sulfur does not appear to be a problem pollutant in large international rivers. However, humans have had an impact on the sulfur concentration in rivers. It is estimated that, globally, man-induced sulfur runoff is roughly equal to the natural flow [Schlesinger 1991]. In industrialized regions, such as the eastern U.S. or Western Europe, the ratio of anthropogenic to natural sulfate in runoff is much higher (up to 8) [Husar & Husar 1985].

The common opinion about non-atmospheric sulfur wastes from industry is described in a passage from Meyer (1977).

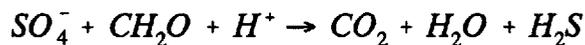
"...Industrial sulfur is almost totally converted to sulfate, is used as an acid, and promptly returns to the sediment as sulfate. So far, only comparatively little sulfur enters industrial products. It is possible that in the future a much larger fraction of sulfur will be incorporated into industrial products. If this becomes the case, it will be mainly in elemental form or in the form of sulfite, both of which readily biodegrade to sulfate, which reenters the sedimentary cycle. We need not dwell here on the use of gypsum, which is mixed and used as such, because in it sulfur does not change oxidation state." [Meyer 1977, pp. 161-162]

This reassuring view leaves several questions unanswered. Much of the sulfuric acid used in industry which is not recycled (and not discharged to the atmosphere) is eventually converted to calcium sulfite or calcium sulfate. Clues about the potential problems caused by the disposal of calcium sulfate and calcium sulfite wastes can be found in the extensive literature on flue gas desulfurization and other methods used for the control of sulfur dioxide emissions from fuel combustion [Ellison & Luckevich 1984; Morrison 1982]. These sulfate wastes pose three potential problems.

One problem is disposal *per se*. The calcium sulfite and sulfate wastes are often in a sludge form which is difficult to dewater. In addition, the disposal of these materials on land makes the site unusable for other purposes for an indefinite period. The sheer magnitude of such wastes over the long term, can create serious disposal problems, at least locally.

The second concern is the possibility of environmental mobilization and secondary damages. The pathway for environmental mobilization is through leaching. The leachate from these dumps can contain concentrations of sulphate, chloride, calcium and magnesium several orders of magnitude greater than natural background concentrations. In addition, in the case of wastes from fuel emissions (and possibly some industrial processes) the leachate may also contain traces of heavy metals.

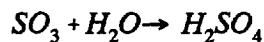
The third, and perhaps the most serious, concern has to do with the fate of concentrations of sulfates in anaerobic environments rich in organic materials. In the absence of oxygen, nitrates or manganese or iron oxides, but given the availability of organic materials, decay bacteria can extract oxygen from the sulfate (SO_4) radical for their own metabolic purposes, releasing toxic hydrogen sulfide. The basic (equivalent) reaction is



Concern over the long term accumulation of solid or liquid sulfate wastes is of particular importance due to the trend (prompted by environmental regulation) toward reduced atmospheric emissions of sulfur. This trend means that increasingly the anthropogenic sulfur wastes are being disposed of on land or waterways. We can expect this trend to continue and possibly accelerate.

6.7. The Global Sulfur Cycle

Biologically available sulfur is apparently "scarce" on land, because its commonest forms (calcium and magnesium sulfates) are extremely insoluble. Unfortunately, soluble (i.e. bio-available) forms of sulfur like ammonium sulfate are continuously depleted by erosion and runoff to the oceans, where sulfur accumulates. To close the cycle, sulfur is recycled back to the land by atmospheric flows of volatile sulfur compounds such as hydrogen sulfide, mercaptans, dimethylsulfide (DMS) or dimethyldisulfide (DMDS), produced by marine organisms.



Dissolved in water, sulfurous and sulfuric acids then react with ammonia, derived from the decay of nitrogenous organic materials (e.g. animal manure) forming ammonium sulfate. Thus, the natural sulfur cycle interacts strongly with the natural nitrogen cycle here.

The global sulfur cycle (*Figure 6.2.*) consists of a set of oxidation reactions balanced by reduction reactions. Reduced forms of sulfur (S, H_2S) are gradually oxidized by atmospheric oxygen, ending in sulfur oxides (SO_2 , SO_3) and finally sulfate SO_4^{++} . Sulfate is deposited on the earth's surface in wet or dry form (e.g. as ammonium sulfate). The reverse part of the cycle, which converts sulfur back to reduced forms — states of higher thermodynamic potential — is accomplished either by biological activity or possibly by high temperature magmatic reactions in the earth's mantle.

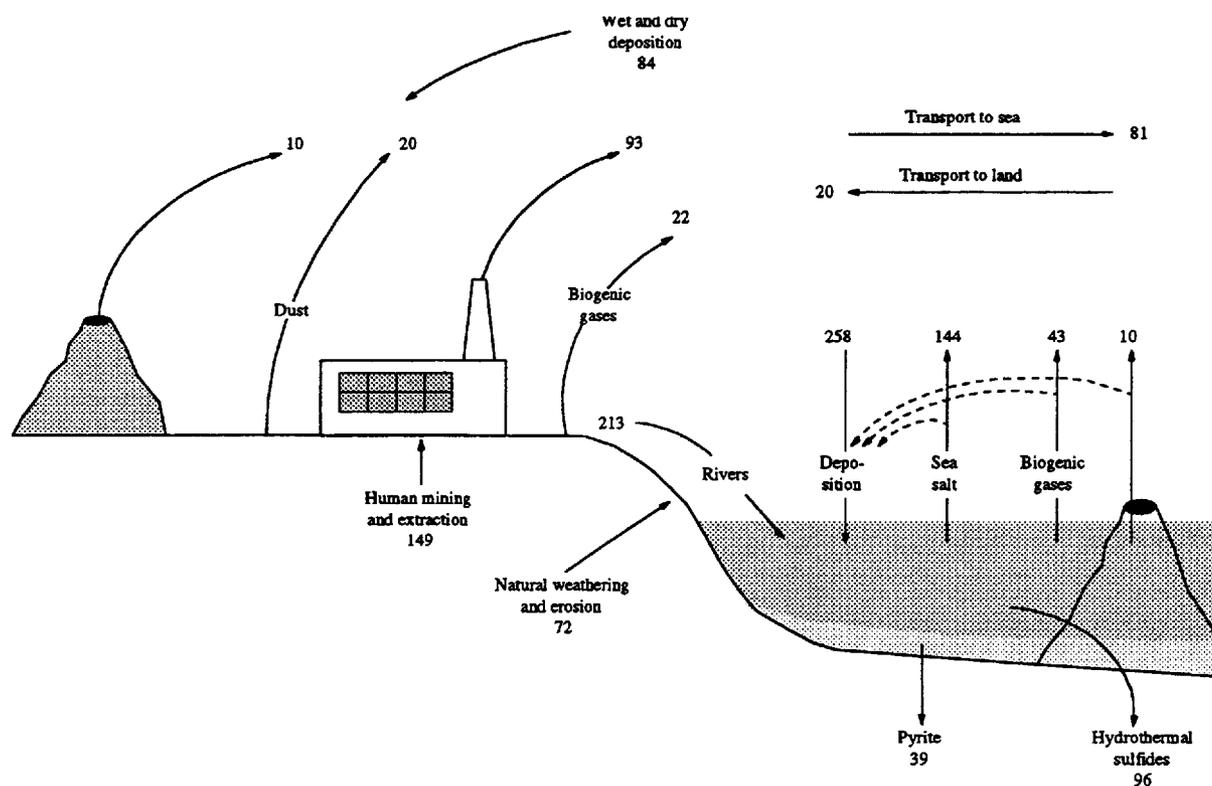


Figure 6.2. Global sulfur cycle (teragrams/year). Source: [Schlesinger 1991]

From another perspective, of course, it can be seen as a cycle in which insoluble and biologically unavailable forms of sulfur — notably sulfides (pyrites) and calcium and magnesium sulfates — are converted to biologically available forms, utilized, and finally returned once again to unavailable forms. From this perspective, the cycle can also be seen as a complex set of transfers between air, land and sea (Figure 6.2.). Assuming the pre-industrial version of the cycle was really balanced, the controlling rate, or "bottleneck" in the system must have been the rate at which insoluble sulfides or sulfates were deposited in oceanic sediments. In the very long run (on the average) this deposition rate must have been equal to the rate at which sulfur was re-mobilized by pre-industrial geo-chemical processes, with or without biological assistance. It must also equal the pre-industrial net rate of deposition of sulfur compounds on the ocean surface, plus the pre-industrial runoff from rivers, abrasion of shores, etc.

Various estimates of sulfur fluxes are shown in Table 6.6. Estimates of the impact of human activity are most explicit in the work of Ivanov and Freney [Ivanov & Freney 1983]. These authors estimated that globally 113 teragrams of sulfur was emitted to the atmosphere (as SO_2) through the combustion of fossil fuels and the smelting of ores. By comparison, 28 teragrams was used for phosphate fertilizer production, and 28 teragrams was used in other chemical industries. Thus, around one third of the sulfur extracted from the lithosphere is used in industrial processes, half of this being used in the manufacture of phosphate fertilizer. In this connection, it is important to emphasize that relatively little sulfur is embodied in final products. In the case of fertilizer, just mentioned, the sulfuric acid is used to convert insoluble calcium phosphate into soluble phosphoric acid, leaving calcium sulfate as a by-(waste)-product.

Ivanov & Freney's estimate of current industrial atmospheric inputs and outputs is 342 Tg/yr. Removing the anthropogenic emissions (113 Tg/yr) from the input side (from land) should be compensated by a corresponding reduction in wet/dry deposition on the output side during the pre-industrial period. Assuming the anthropogenic contribution falls disproportionately on land (58 Tg/yr vs. 65 Tg/yr), the overall current ratio of oceanic to terrestrial deposition (258:84) implies that sulfate deposition from natural sources is allocated between oceans and land in the ratio 193:26. In other words, the pre-industrial inputs to the land surface must have been about 26 Tg/yr, as compared to 84 Tg/yr from atmospheric deposition (c. 1980) and a further 28 Tg/yr as fertilizer. In short, the sulfur flux to land has more than quadrupled since the beginning of industrialization.

The pre-industrial situation with regard to both sulfur and nitrogen has changed radically in the last two centuries. The net impact is not clear. The original cycle was presumably stable. It is not clear how the system will react to anthropogenic disturbances, mainly in terms of increased availability of sulfur to the terrestrial biosphere. (See also *Chapter 8, Nitrogen*).

6.8. Reducing Global Sulfur Flux

Sulfur dioxide pollution is sufficiently hazardous to health to warrant the imposition of pollution controls at the local level. In addition, acid rain appears to be sufficiently harmful to some forests and lakes to warrant controls at the regional level. However, the problem of anthropogenic disturbance of the global sulfur cycle, still largely unrecognized, may be even more serious in the long run. Unfortunately one cannot pinpoint any specific ecological consequences. It is only possible to point out that humans appropriate most of the surplus productivity of the entire biosphere, a system that has reached a stable evolutionary balance over eons. To disturb such a balanced system is inherently risky, especially to humans, who are the most vulnerable to any change in the balance. The chances are great that any changes will be adverse rather than beneficial in human terms.

By far the most effective way of reducing the excess flux of biologically available sulfur in the biosphere is to stop burning coal. This does not seem to be a realistic option for decades to come, however. The best alternative is to permanently immobilize sulfur oxides at the point of combustion (by fuel gas desulfurization) or — still better — to recover the sulfur oxides and convert them to reduced sulfur or to industrially useful sulfuric acid. It is evidently environmentally beneficial to recover and use sulfur from petroleum, natural gas and from the smelting of non-ferrous metals, as long as the latter are to be exploited in any case. The sulfur recovery activities should be encouraged still further. On the other hand, it is extremely undesirable from an environmental standpoint to extract large amounts of reduced sulfur from the earth's crust (by mining pyrites and elemental sulfur) while simultaneously allowing large amounts of fuel-bound sulfur to escape into the atmosphere in oxidized form without recovery.

The technologies for doing these things are relatively straightforward, but the economics are unfavorable — as long as reduced forms of sulfur are commercially available and inexpensive.

There is no need to comment further on the technology of recovery. To alter the economics will require government intervention. An obvious possibility would be to tax sulfur dioxide emissions on a progressive scale. At the same time it would be sensible to tax sulfur mined from underground deposits (Frasch process) and sulfur recovered from pyrites, but *not* sulfur recovered from oil and gas refineries or non-ferrous smelters. Taxes of this kind would fit into a program of shifting the major source of government revenues from taxes on labor to taxes on resources and pollution.

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Endnotes(6)

1. We wish to acknowledge the some of the material in this chapter has appeared previously in a 1988 summer study performed at IIASA [Ayres *et al* 1989]. Further work on the industrial metabolism of sulfur was carried out in 1991 with support by the Stockholm Environment Institute. See Ayres, Robert U. and Vicki Norberg-Bohm *Industrial Metabolism of Sulfur* Working Paper 93/23/EPS, INSEAD, Sept. 8 1993. We wish to thank Michael Chadwick and Paul Raskin.
2. However some other refinery processes leave the sulfur in liquid wastes or in asphalt and road oils.
3. Actually, much of the proposed testing could probably be by-passed by computer simulation, using software (e.g. ASPEN+®) that has become relatively standard since 1978.
4. It is noteworthy that in 1988 Morocco produced 8.085 MMT of sulfuric acid, which was consumed entirely for phosphate rock processing. (In 1989, Moroccan production and consumption both dropped to 3.965 MMT, of which only 15 KMT were used for non-fertilizer applications.)
5. Sulfur constitutes about 1.5% of the weight of tires (see # 12). Data on this specific use is not published. However, in the U.S. 1988 tire production amounted to about 3 MMT, of which about 50,000 tonnes was presumably sulfur, equivalent to 5% of the total use of elemental sulfur (i.e. sulfur not converted to acid).