INDUSTRIAL METABOLISM, THE ENVIRONMENT, AND APPLICATION OF MATERIALS-BALANCE PRINCIPLES FOR SELECTED CHEMICALS

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Foreword

One of the objectives of IIASA's study *The Future Environments for Europe: Some Implications of Alternative Development Paths* is to characterize the major environmental transformations that might beset Europe in the 21st century. From a purely chemical perspective, environmental changes may be understood in terms of changes in the flows of environmentally-relevant chemicals through the biosphere. Such relevant chemicals include those that affect the regulation of natural processes such as climate, acidification, major nutrient cycling, and those that are biologically active.

Despite the obvious linkages between chemical flows and the environment, industrial societies often possess little detailed knowledge of how major chemicals flow through the industrial economy after the production phase. They are, in fact, embodied in numerous products that are ultimately dissipated into the environment during use, disposed of in landfills, or burned as refuse. In most cases, detailed quantitative information regarding the spread or accumulation of these chemicals in the environment is nonexistent, and chemical monitoring is totally inadequate to fill this gap. What is urgently needed is a thorough *bookkeeping*, that tracks the flows from mining, processing and manufacturing, consumer use, and disposal. This report provides an important step in our understanding of material flows for four widely used inorganic chemicals, bromine, chlorine, sulfur, and nitrogen.

Also, by invoking the concept of *industrial metabolism*, the authors provide a new vision for understanding how industrial societies produce, process, use, and dispose of materials, and how these actvities, taken as a whole, are linked to environmental change.

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CHAPTER 1

Industrial Metabolism

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1.1. The Analogy between Biology and Industry

The use of matter and energy in our economic system – that part of the sum total of human activities that is concerned with the production and consumption of material goods and services generated thereby – displays certain parallels with the use of matter and energy by biological organisms and ecosystems. The term ***industrial metabolism*** used in this report deliberately invokes this analogy.

The industrial system that exists today is actually more similar in one key respect to the unsustainable bio-system that existed on earth before the "invention" of photosynthesis. It seems that the first living cells obtained their energy by fermentation from an organic "soup" formed in the atmosphere and oceans by natural processes (such as electrical storms). The most familiar example of a fermentation process is the breaking up of sugar molecules by yeast cells to yield carbon-dioxide and ethanol plus energy, which the yeast cell uses to synthesize its own biomass (anabolism). Fermentation-based life forms lived quite happily in the presence of what we regard as toxic compounds such as carbon monoxide, hydrocyanic acid, and hydrogen sulfide. Carbon-dioxide was simply a waste product that began to build up in the earth's primitive atmosphere.

The second great evolutionary invention was anaerobic photosynthesis (probably by cyanobacteria). This process utilized sunlight as a source of energy and the "waste" carbon-dioxide from the atmosphere as a source of carbon. Cyanobacteria were able to co-exist with fermentation organisms and could replenish the supply of organic molecules the latter required to survive. This dependence of one organism on another was the first linkage of the complex web of life that began to evolve. Photosynthesizers produced oxygen as a waste product, however, whence oxygen also began to build up in the atmosphere.

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[*] This chapter was expanded and published in substantially similar form, under the same title, in a symposium volume (Ayres, 1989).

This set the stage for the third great evolutionary invention: aerobic respiration (or catabolism) which obtains energy from the oxidation of organic molecules. The fermenters could no longer compete with the respirators, at least in the presence of oxygen, because respiration is far more efficient (by a factor of 35) than fermentation. The latter have found a niche in the remaining anaerobic environments of the earth, primarily sediments.

Since the evolutionary invention of respiration, the cyanobacteria have been displaced by more highly evolved photosynthesizers, the green plants. Similarly, evolution has created more efficient and specialized oxygen-breathing respirators, the animals. Each major category of organism utilized the biomass or waste-products of the other, and the closed carbon-dioxide cycle (and the associated nitrogen cycle) was born.

The industrial analog of the original fermentation organisms is the combustion and carbothermic reduction-based system that exists today. Like the fermentation organisms, we currently depend upon relatively inefficient processes to convert an inherited primordial stockpile of energy-rich compounds (fossil fuels) into industrial materials analogous to *biomass*. In so doing, we are also creating waste products, mainly carbon-dioxide, on a very large scale.

Indeed, the industrial analogs of biological catabolism/anabolism are close. In the biological case energy is "carried" by specialized molecules – notably adenosine diphosphate and adenosine triphosphate (ADP and ATP) – whereas in the industrial case the energy carriers are more various: process steam, electricity or high-energy chemical intermediates like acetylene, hydrogen, or ethylene. The synthetic processes whereby macro-molecules are built up from simple chemical building blocks such as sugars and amino-acids also have industrial parallels.

On the other hand, not every biological process has an industrial analog. In particular, the process of digestion in animals breaks down complex macromolecules into their component parts for efficient re-use. The corresponding function in natural ecosystems is carried out by the specialized decay organisms. In the modern industrial world, by contrast, this key function is underdeveloped. Unlike the biological system, the industrial system has not evolved largely into a closed cycle that exists on renewable resources ultimately derived from the sun.

1.2. Mass Flows and Waste Emissions

As shown in *Figure 1.1* our economic system at present depends on the extraction of large quantities of matter from the environment. Extraction is followed by processing and conversion into various forms, culminating in final products for consumption. *Table 1.1* shows the mass of *active* raw materials extracted for processing within the boundaries of the USA for the years 1960, 1965, 1970, and 1975.

Evidently, more than 10 tons of *active* mass per person (excluding atmospheric oxygen and fresh water) are extracted by the US economy from its own territory each year. The amount processed is somewhat larger, since the US is

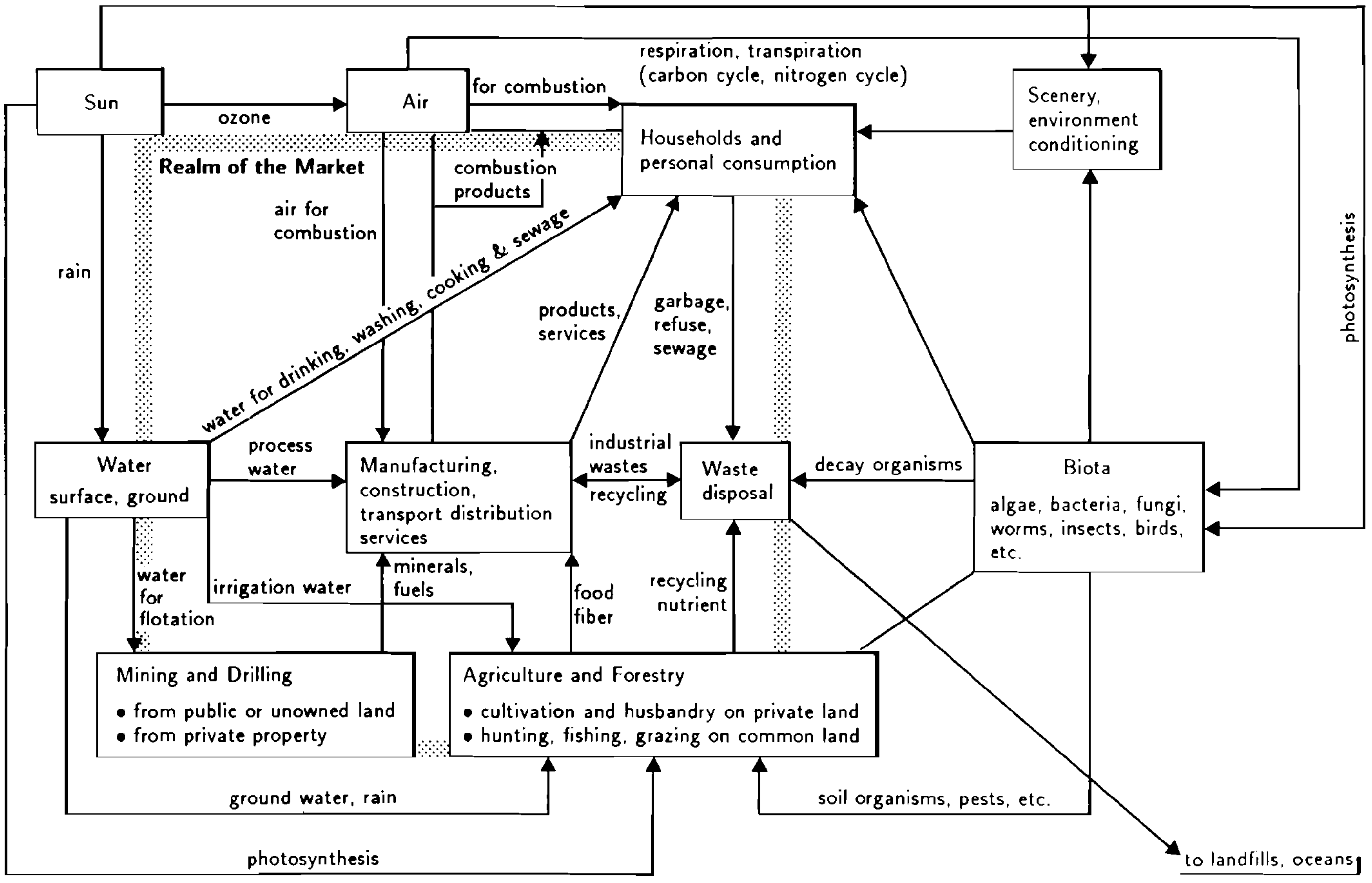

Figure 1.1. **Interactions between the market economy and the environment.**

Table 1.1. Mass of active materials extracted commercially, US (1960–1975).

	(Millions of tons)			
Material	*1960*	*1965*	*1970*	*1975*
Food and feed crops (excluding hay)	267	295	314	403
Meat, fish, and dairy products	82	85	85	84
Cotton, wool, hides, and tobacco	5	5	4	4
Timber (15% moisture basis)	256	267	271	249
Fuels (coal, lignite, oil, gas)	990	1176	1458	1392
Ores (Fe, Al, Cu, Pb, Zn)	400	435	528	460
Non-metallics	200	240	266	255
Total	2200	2500	2926	2847

Vegetable material harvested directly by animals has been omitted for lack of data, along with some obviously minor agricultural and horticultural products. Figures for metal ores exclude mine tailings and gangue removed to uncover ore bodies. Inert construction materials such as stone, sand and gravel have also been omitted. Inert materials account for enormous tonnages, but undergo no chemical or physical change except to the extent they are incorporated in concrete or paved surfaces. We also exclude soil and subsoil shifted during construction projects or lost by erosion.
(Source: US Bureau of Mines, 1960–1975)

now a net importer of many minerals and petroleum. Of course, quite a lot of the grain harvested in the US is exported, which balances the international accounts to some degree. Of the active mass processed each year, roughly 75 percent is mineral and non-renewable while 25 percent is, in principle, from renewable, i.e., biological sources. Of the latter, most is ultimately discarded as waste, although most of it could (in principle) be utilized for energy recovery.

It is difficult to estimate the fraction of the total mass of processed active materials that is annually embodied in long-lived products and capital goods (durables). None of the food or fuel is physically embodied in durable goods. Most timber is burned as fuel or made into pulp and paper products. At least 80 percent of the mass of *ores* is unwanted impurities (more than 99 percent in the case of copper). Of the final products made from metals, a large fraction is converted into consumption goods, such as bottles, cans, chemical products, and throw-away products such as batteries, light-bulbs, and so on. Only in the case of non-metallic minerals (ignoring inert materials, as before) is as much as 50 percent of the mass embodied in durable goods (mainly portland cement used for concrete, and clays used for bricks and ceramics). The annual accumulation of active materials embodied in durables, after some allowance for discard and demolition, is probably not above 150 million tons, or six percent of the total. The other 94 percent is converted into waste residuals (more or less) as fast as it is extracted. In addition to raw materials, large amounts of energy in a high quality (available) form are also needed to drive the system. This energy is also degraded and finally discarded as low temperature heat.

1.3. The Impact of Waste Residuals

Referring again to *Figure 1.1*, one can observe that materials do not disappear after they are "used up" in the economic sense. They become waste residuals that must be disposed of because they can cause harm. In fact, it is not difficult to show that the tonnages of waste residuals are actually greater than the tonnages of crops, timber, fuels, and minerals recorded by economic statistics. While usually unpriced and unmeasured, both air and water are major inputs to industrial processes and they contribute mass to the residuals – especially combustion products. Residuals tend to disappear from the market domain, where everything has a price, but not from the real world in which the economic system is embedded.

Many services provided by the environment are inherently from common property – including the air, the oceans, the genetic pool of the biosphere, and the sun itself. Distortions in the market (i.e., prices) are unavoidably associated with the use of common property resources. Clearly, environmental resources such as air and water have been unpriced, or (at best) significantly underpriced in the past. For this reason, such resources have been generally over-used.

An important corollary is that the underpricing of environmental resources corresponds to an underpricing of those exhaustible mineral resources whose subsequent disposal as waste residuals causes harm to the environment. This is because of the lack of any link between the market price paid (for coal, oil, etc.) and the subsequent cost of waste disposal or – more important – of uncompensated environmental or health damages such as bronchitis, asthma, emphysema, cancer, soil acidification, the greenhouse effect, and so on. Again, resource underpricing has resulted in excessive use. (Here the distinction between renewable and non-renewable resources is critical: while renewable resources can obviously create pollution problems, such as sewage, they are almost invariably localized in nature and can be abated at moderate cost. This is emphatically not the case for combustion products of fossil fuels or dispersion of toxic heavy metals, etc.)

1.4. Implications for Industrial Metabolism, Past, Present and Future

As noted above, the total mass of waste residuals produced each year far exceeds the mass of active inputs derived from economic activities. This is because nearly half of the inputs accounted for in economic statistics are fossil fuels (hydrocarbons), which combine with atmospheric oxygen and form carbon dioxide and water vapor. The carbon fraction of hydrocarbons ranges from 75 percent in methane to about 90 percent in coal. Petroleum is intermediate. The average for all fossil fuels consumed in the US cannot be less than 82 percent, which translates into around 1,200 million tons of carbon in 1970 (imported oil increases this figure somewhat). In inefficient combustion processes, up to 10 percent of fuel carbon is converted into carbon monoxide (CO), while carbothermic reduction of iron ore and other metals, generates even more. However, the average percentage over all processes is much smaller. Actual emissions of CO to the atmosphere in the US were about 110 million tons in 1970 (mostly from automobiles and trucks), with a carbon-content of 47 million tons, or about 3.5 percent of the total. Emission controls reduced this to about 85 million tons net output in 1980 [Environmental Protection Agency (EPA), 1986].

Carbon monoxide is, or course, quite toxic to humans and has been implicated in health problems among urban populations. It is less well known that carbon monoxide plays an active, and not necessarily benign, role in a number of atmospheric chemical reactions. Eventually, of course, most carbon monoxide oxidizes to carbon dioxide unless it is taken up by photosynthetic reactions.

Roughly, one billion tons of fuel carbon is converted into 3.67 billion tons of carbon dioxide emitted to the atmosphere. Not all of this remains in the atmosphere, but enough to raise very serious concerns about the long-term climatic impact of continued fossil fuel combustion. The problem is the *greenhouse effect*. It appears that the carbon dioxide level of the earth's atmosphere has risen over the last century from about 290 parts per million (ppm) to around 340 ppm at present. While the baseline and the climatic impacts of the rising level of carbon dioxide are both still uncertain, it is already clear that *industrial metabolism* is influencing the natural environment in ways that appear increasingly adverse. For example, in the Worldwatch Institute's latest *State of the World* report it is projected that the mean temperature of the earth will rise by 1.5–4.5°C by the year 2050 (Brown *et al.*, 1988). Climatic effects are still quite uncertain, but a number of models have suggested a warming and drying of the North American grain-belt. The record drought in the summer of 1988 could be the first of many. Another likely consequence of global warming is a rise in the mean sea-level of 1.4–2.2 meters by the year 2100. This would flood low-lying rice paddies in delta areas of South East Asia, not to mention sharply increasing flood control costs (and losses) in other low areas such as the Netherlands, Norfolk (UK), Long Island (New York, USA), and the Eastern Shore of Maryland, (USA).

The discovery of chlorofluorocarbon (CFC) gases in the stratosphere has raised an even more frightening prospect: ozone depletion. In apparent confirmation of this phenomenon, an *ozone hole* has recently appeared in the stratosphere over Antarctica. This hole has reappeared each spring for several years and seems to be growing. Chlorofluorocarbons are industrial gases, discovered in 1928 and produced since the 1930s. They are used commercially as refrigerants, solvents, and for "blowing" plastic foams. The major use is for refrigeration and air-conditioning. In most cases they are not released deliberately, but losses and leakage are inevitable.

Their inertness, once thought to be a great virtue, is the source of the difficulty. Precisely because they do not break down in the presence of oxygen, they have now dispersed throughout the atmosphere, including the stratosphere. At very high altitudes they can be ionized and decomposed by the ultra-violet (UV) radiation of the sun. The resulting chlorine radicals efficiently destroy stratospheric ozone by a catalytic reaction. The problems revealed so far may only be the beginning. If (perhaps it might be better to say *when*) the ozone level in the stratosphere is depleted, the effect will be to let more of the sun's UV radiation through to the earth's surface. One likely impact on humans is a sharp increase in the incidence of skin cancer, especially among whites. The ecological impact on vulnerable species is incalculable, at present, but could be extremely severe. Already it is estimated that several thousand species are becoming extinct each year, and up to 20 percent of all species could disappear wihin the next twenty years. Increased UV flux would increase the stress levels that already exist.

Methane, oxides of nitrogen, and sulfur oxides are other residuals that have been seriously implicated in climatic and/or ecological effects. All three are generated by fossil fuel combustion, as well as other industrial processes. Like carbon monoxide, carbon dioxide and the chlorofluorocarbons, they can be considered as metabolic products of economic activity. Methane is lost in natural gas pipelines, petroleum drilling, coal mining, and several kinds of intensive agriculture (especially rice cultivation and sheep farming). Sulfur oxides are generated by the combustion of sulfur-containing fuels, especially bituminuous coal, and by the smelting of sulfide ores. Most copper, lead, zinc, and nickel ores are of this kind. In principle, sulfur can be recovered for use from all of these activities, and the recovery rate is rising. But the costs of recovery, especially from coal-burning electric power plants, are still far higher than the market value of the potential products (e.g., dilute sulfuric acid). Hence, for the present, calcium sulfites and sulfates, as well as SO_x *per se*, constitute a waste residual that needs to be disposed. This will only change if (or when) the economic value of sulfur rises very sharply above its present low level. This in turn, depends on the discovery of new uses.

Nitrogen oxides are also coproducts of combustion. In effect, at high temperatures, some of the atmospheric nitrogen is literally "burned". Again, in principle, recovery for use (e.g., as nitric acid) is possible. But in comparison with the commercially dominant processes of nitrogen fixation based on natural gas (the *Haber-Bosch* process), there is no economic justification for such recovery. It is only because dispersion of oxides of nitrogen is implicated in smog and acid rain that recovery technology is even being explored. Only a spectacular rise in the economic value of nitric acid would change this picture. The discovery of some unexpected new technology, or a much tougher regulatory environment, could lead to such a change.

Fly-ash is yet another by-product of combustion. At present it is being recovered quite efficiently (80–99 percent) from stack gases of large utility boilers and industrial furnaces, by means of electrostatic precipitators. But the ash itself has become a large-scale nuisance because there is no use or market for it (as in the United States). The amounts are large: over 50 million tons are generated per year in the United States alone. At least two possible remedies exist, however. Fly-ash is a potential "ore" for several metals, especially iron, aluminium, and silicon. These could probably be recovered commercially if, for example, bauxite became unavailable (Ayres, 1982). Alternatively, fly-ash can be used as a substitute, or more likely as a supplement, for portland cement in the manufacture of concrete and concrete-like products, as is already being done in the UK and Belgium. Its major disadvantage in this application is that concrete made with fly-ash does not harden and set as rapidly as the commercial variety. This has obvious economic costs, but so does the disposal of fly-ash into landfills. A final possibility worth mentioning is that fly-ash could be used as a medium for the disposal of toxic liquid wastes, yielding a hard, impermeable substance suitable for long term storage. (This technology is already being utilized in France.)

Combustion and carbo-thermic reduction processes are the major sources of atmospheric pollutants today, but by no means the only important ones. Nor is the atmosphere the only vulnerable part of the environment. From a broader environmental perspective, the production and dispersal of thousands of synthetic chemicals – many new to nature, and some highly toxic, carcinogenic or mutagenic – and the mobilization of large tonnages of toxic heavy metals are of equally great concern. The complexity of the problem is too great to permit any kind of short summary.

However, two points are worthy of emphasis. First, as noted above, most materials *pass through* the economic system rather quickly, i.e., the transformation from raw material to waste residual takes only a few months to a few years in most cases. Long-lived structures are the exception, and the more biologically *potent* materials are least likely to be embodied in a long-lived form.

The second point, emphasized strongly some years ago (Ayres, 1978) but still worth repeating, is that many materials uses are inherently dissipative, i.e., the materials are degraded, dispersed, and lost in the course of a single normal usage. In addition to food and fuels (and additives such as preservatives), this applies to packaging materials, lubricants, solvents, flocculants, anti-freezes, detergents, soaps, bleaches and cleaning agents, dyes, paints and pigments, most paper, cosmetics, pharmaceuticals, fertilizers, pesticides, herbicides and germicides, and so on. Many of the current consumptive uses of toxic heavy metals such as arsenic, cadmium, chromium, copper, lead, mercury, silver, and zinc are dissipative in the above strict sense. Other uses are dissipative in practice because of the difficulty of recycling such items as batteries and electronic devices. In some cases the dissipation is slow and almost invisible. For instance, paints (often containing lead, zinc or chromium) gradually crack, weather and turn to powder, which is washed or blown away. Tires, containing zinc (and cadmium) are gradually worn away during use, leaving a residue on the roads and highways. Similarly, shoe-leather, containing up to two percent pentavalent chromium (the most toxic form) is gradually worn away to powder during use. Incinerator ashes contain fairly high concentrations of heavy metals from a variety of miscellaneous sources, ranging from used motor oil to plastics, pigments and so forth.

On reflection, many dissipative uses (food and fuel again excepted) are generally seen to be non-essential in the sense that, theoretically, technologies are available, or imaginable, that could eliminate the need for them. To take one example only: hydroponic agriculture in enclosed, atmospherically controlled greenhouses, with genetically engineered pest controls, would eliminate all losses of fertilizers and pesticides to water-courses by way of surface runoff.

Speculations about substitutes for current uses of materials, and new uses of today's wastes are not as extreme as industrialists might believe. Several of the most valuable products of the present day chemical industry began as unwanted by-products. Coal tar was one of the first. It became a valuable source of chemicals such as aniline dyes in the 19th century. Coke oven gas became not only a valuable fuel, but also the first commercial source of ammonia. Slag from blast furnaces was once a nuisance. Today it has a number of major uses and old slag heaps are even being *mined* in some locations. Natural gas was once an unwanted by-product of petroleum drilling – but not for long. Chlorine is a less well-known example, being originally a by-product of the manufacture of caustic soda (lye) by electrolysis of brine. Today chlorine is the primary product. Much of the petro-chemical industry is built on by-products of the natural gas industry: ethane, propane, and butane. Helium is also taken from natural gas. Hydrochloric acid and sulfuric acid are increasingly being obtained as by-products, and many other examples could be given.

It is probably safe to say the industrial metabolism of the next century will recycle a number of the major tonnage waste products of today, notably sulfur, fly-ash and lignin wastes from the paper industry. The latter may yet turn out to be a useful growth medium for single-cell organisms providing high-protein supplements for food products. By the same token, inherently dissipative uses of biologically active materials will have to begin to decline, as the mistakes of the past are rectified. In particular, the underpricing of environmental and exhaustible resources must be reduced or even (temporarily) reversed.

1.5. Applications of Materials-Balance Principles

The *materials-balance* principle, a straightforward application of the first law of thermodynamics (widely used in the design of chemical engineering systems, for instance), is a potentially valuable and underutilized tool for using economic data in environmental analysis. Frequently a combination of input data (obtainable from economic statistics), together with technical process data available from engineering analysis, gives a more reliable estimate of waste residual outputs than direct measurements alone could be expected to do. This is particularly true in situations where the pollutant of concern is produced in relatively small quantities and is emitted together with large amounts of combustion products or process wastewater.

One good example of this has been taken from a study of environmental problems in the aluminum industry. One of the major environmental problems associated with aluminum smelting in the past was the emission of gaseous fluorides from the smelter. The source of the fluorine is the electrolytes (molten cryolite and aluminum fluoride) used as a solvent for alumina in the electrolytic cell. An unavoidable side reaction in the cell breaks down these eletrolytes and releases some of the fluorine at the anode. Exact recipes for the production of aluminum are only known by the aluminum companies. However, a materials-balance analysis for the year 1973 suggested that for each 100 kilograms (kg) of aluminum produced, 2.1 kg of cryolite and 3 kg of aluminum fluoride were consumed as inputs (Ayres, 1978). Based on these estimates and straightforward chemistry, the aluminum industry would have accounted for 40 percent of the known production of hydrofluoric acid in that year, consistent with both official and unofficial estimates. In the absence of fluorine recovery facilities, all of the fluorine consumed by the industry must have been eventually emitted to the environment. In other words, the total amount of cryolite and aluminum fluoride consumed by the aluminum industry was (and is) exclusively for replacement of fluorine losses.

It is interesting to note that the fluoride emissions calculated using materials-balance principles were about twice as high as the Environmental Protection Agency's (EPA) published estimates at the time. The latter were based on direct (but unreliable and difficult to verify) measurements taken at a few smelter sites. Assuming the production and use statistics for hydrofluoric acid were correct, one would have to believe that the indirect estimate based on materials-balance considerations was probably more reliable than the estimate based on direct measurements.

Another application of the materials-balance methodology is in the reconstruction of historical emissions data. This is a problem of some importance to basic environmental science, since the cumulative impact of air or water pollution over long periods can only be evaluated in relation to a baseline of some sort. In this context it becomes important to know more about emissions in the past, when no measurements were made. To be sure, peat bogs, guano deposits, sediments, ice-cores, tree rings, and even museum specimens offer some help, but not enough. The picture can be clarified considerably, however, with the help of synthetic models utilizing production and consumption data (which is often imperfect, but better known than emissions) together with engineering analysis of processes. Sometimes process information is not even needed, as when emissions are linked directly to inputs.

For example, fairly good historical estimates of sulfur oxide emissions (SO_x) – needed to analyze the long term impact of acid rain, among other things – can be reconstructed quite easily form historical statistics on coal consumption and copper, lead, and zinc smelting (e.g., Gschwandtner *et al.*, 1983). This is because the sulfur content of coal and metal ores can be assumed to be the same in the past as it is today, and until recently all of that sulfur was emitted straight to the atmosphere. Reconstruction in the case of NO_x is slightly more complicated, but the approach is basically similar.

More complex reconstructions of historical emissions have been undertaken recently, e.g., for the Hudson-Raritan estuary (Ayres *et al.*, 1985). Two examples of material process-product flows, taken from this study, are shown in *Figure 1.2* (cadmium) and *Figure 1.3* (chromium). Other examples of "element-by-element" materials-balance analyses, relevant to forecasting future emissions as well as reconstructing past ones, are provided in Chapters 2 through 5 of this report. They show the industrial metabolic pathways for bromine, chlorine, sulfur, and nitrogen. These elements were chosen to exemplify biologically active materials that are utilized largely in the chemical industry, many of whose compounds are toxic. They are chosen, in part, because the major toxic metals (arsenic, cadmium, chromium, copper, lead, mercury, silver, and zinc) were analyzed in a similar manner in Ayres *et al.* (1985).

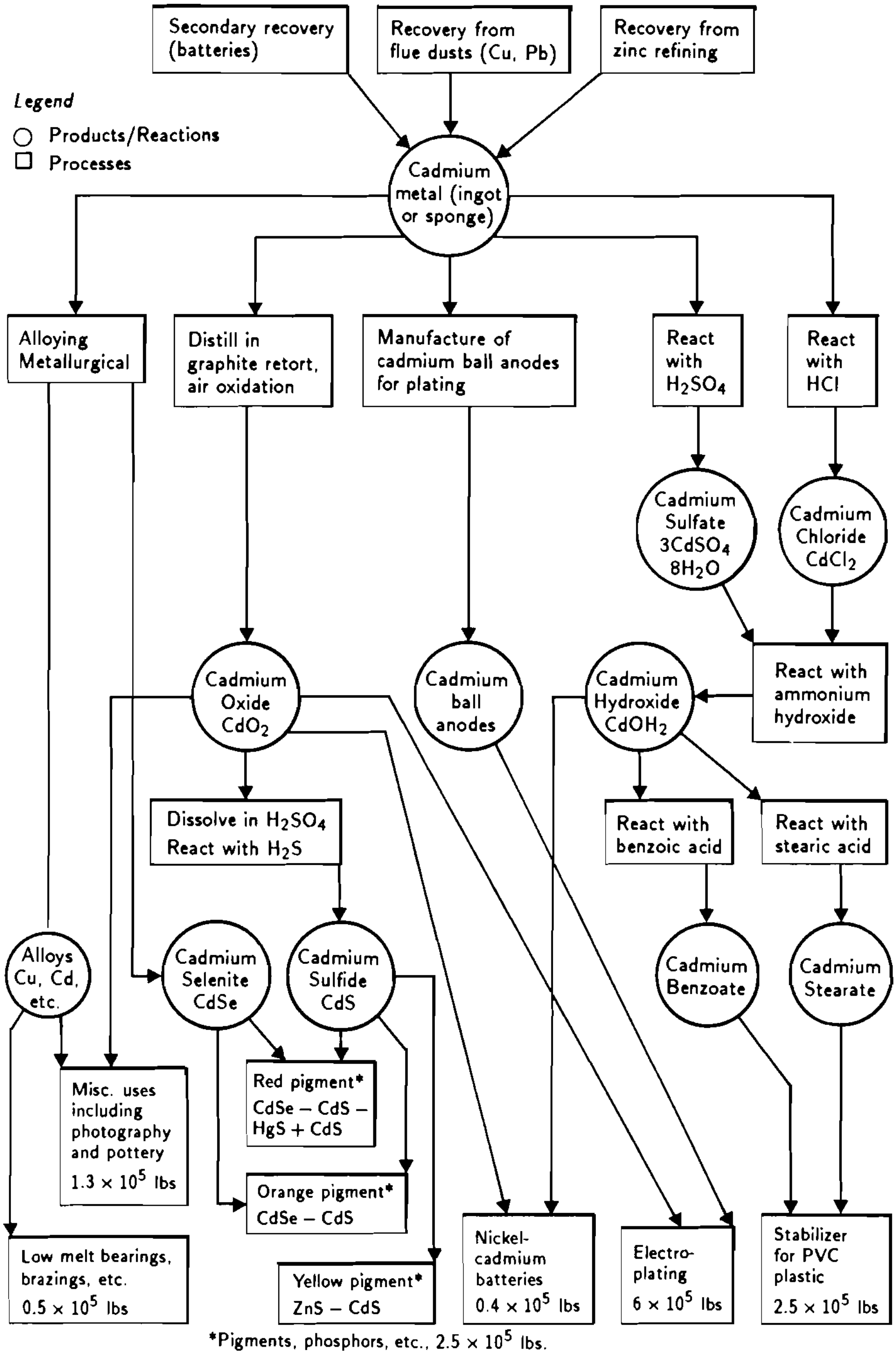

Figure 1.2. **Process-product flows for cadmium in an industrial economy.**

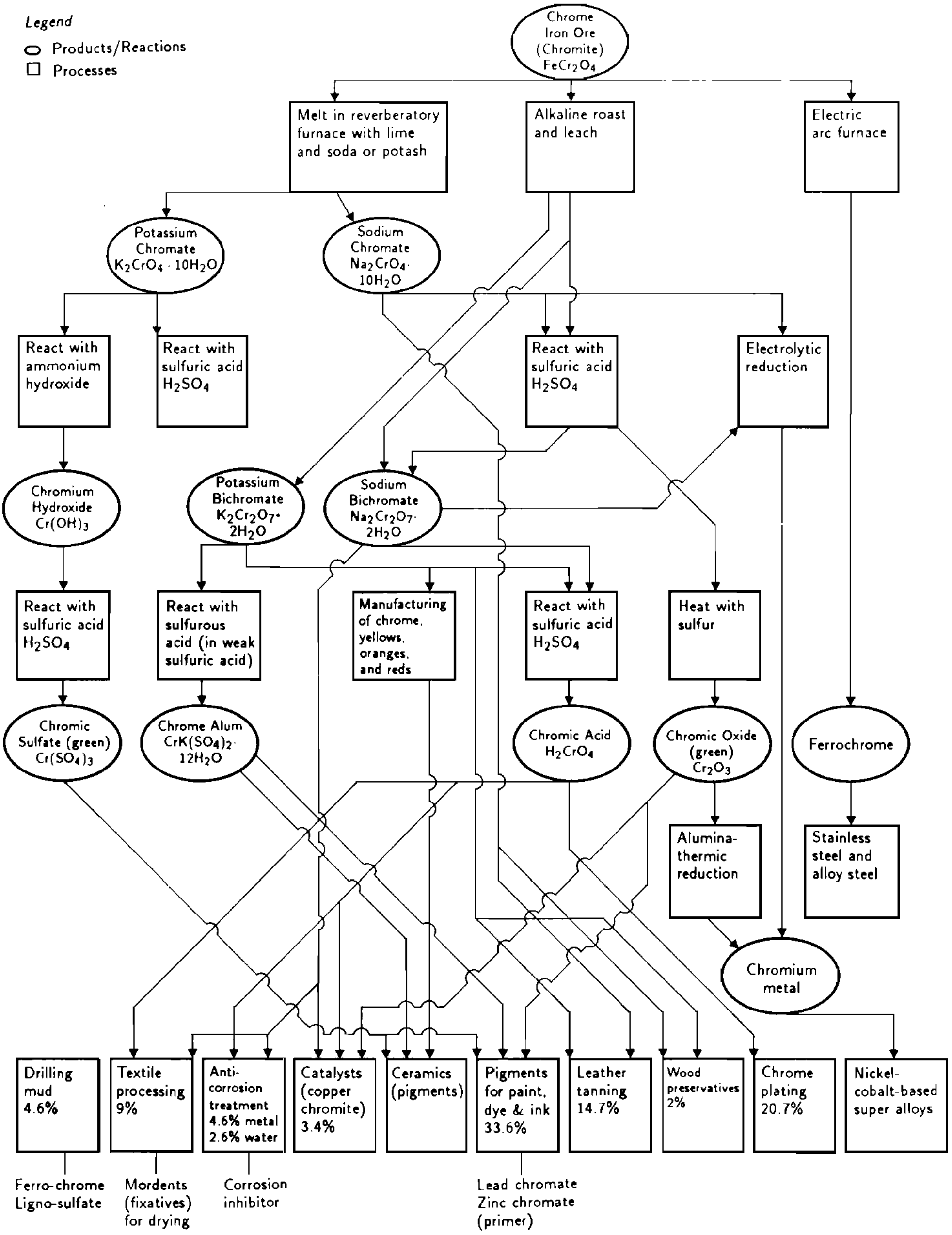

Figure 1.3. **Process-product flows for chromium in an industrial economy.**

Another way of using the materials-balance approach is in the analysis of material "cycles". The water cycle, the carbon cycle (*Figure 1.4*) and the nitrogen cycle are familiar examples. The concept is also applicable, of course, to flows which are not really cyclic, as in the case of arsenic (*Figure 1.5*). These have been widely used by geochemists, hydrologists, ecologists, and environmental scientists to organize and systematize their work. Such a presentation obviously specifies the geographical scale of the analysis. It also facilitates such comparisons as the relative importance of natural and anthropogenic sources. Finally, and potentially most important, it provides a starting point for detailed analysis of the effect of anthropogenic emissions on natural processes.*

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* We are grateful to a Reviewer for pointing out to us that a somewhat similar approach has been utilized by Denaeyer and Duvigneaud (1980).

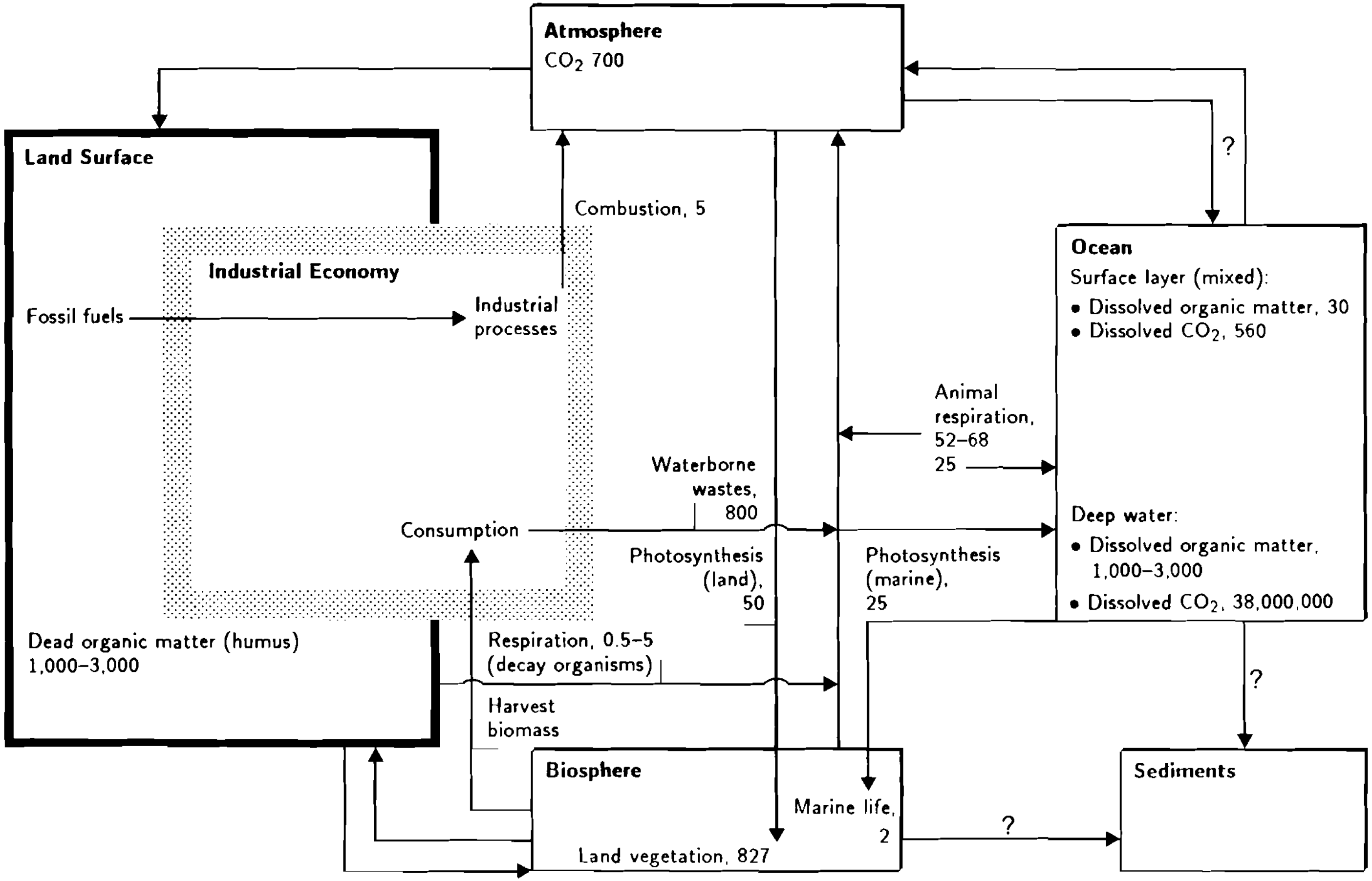


Figure 1.4. The carbon cycle (units = 10^9 metric tons carbon).

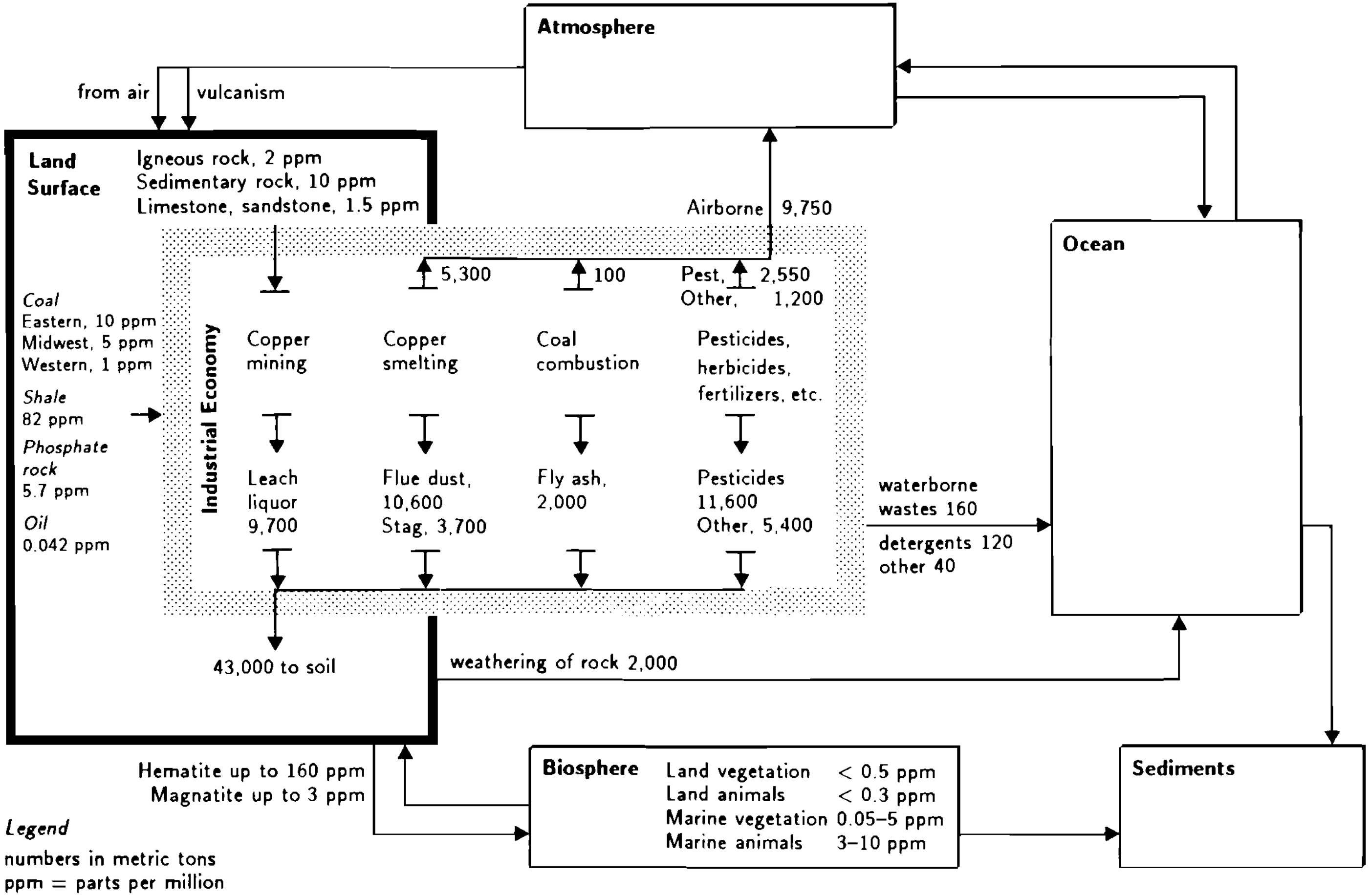


Figure 1.5. **Arsenic cycles, in the United States of America (units = metric tons).**

CHAPTER 2

Bromine: Anthropogenic Sources and Flows

Jackie Prince

2.1. Introduction

The first step in constructing a materials-balance analysis of bromine is to create process-product diagrams. The second step is to apply available data on sources, production and processing, consumption, and disposal of bromine in order to quantify its flows, as delineated in the process-product diagrams. At points in the flow where data is lacking, it is sometimes possible to infer quantities by application of the conservation of mass principle.

Quantitative data on bromine flows in Europe is limited, and therefore, the analysis in this chapter is incomplete. However, detailed quantitative information is available for the Netherlands and the United States (US), and a comparison of the bromine flows is given. The discussion is also extended to other Western European countries where data is available.

2.1.1. Sources

Bromine is a halogen element with reactive properties intermediate between chlorine and iodine. It is found in natural brines, salt deposits, salt lakes, and seawater in the form of sodium or calcium bromide (NaBr or $CaBr_2$). For the first 40 years of commercial production, bromine was derived primarily from seawater, which contains an average of 65 parts per million (ppm) of bromine. Approximately one ton of elemental bromine (Br_2) can be extracted from 17,000 tons of processed seawater. Seawater continues to be a major source of bromine in Western Europe, but since the late 1960s the primary source of bromine in the world has been natural brines. Brines contain a more concentrated source of bromine with an average bromine content of 1,000 ppm. Furthermore, bromine can be produced as a by-product of alkali metal salt production [e.g., magnesium chloride ($MgCl_2$), potassium chloride (KCl), sodium chloride (NaCl), and calcium chloride ($CaCl_2$)] by first extracting bromine from the brines. In this case, 1,000 tons of brine release approximately one ton of bromine. Other bromine sources include inland lakes and seas, with the Dead Sea being an especially rich source (5,000 ppm bromine on average).

2.2. Bromine Production

Bromine was first produced in the United States in Freeport, Pennsylvania in 1846 from brines. Commercial production from seawater began about 1924 and quickly became the primary source of bromine. European bromine production began about 1865 from the waste liquors of salt production in Stassfurt, Germany (Shreeve, 1967).

Bromine production has been increasing steadily since 1900 when the world (mainly the US) produced roughly 300 metric tons (Lyday, 1985). The changes from 1900 to 1985 are shown in *Table 2.1* for selected European countries and the United States.

The US continues to be the primary producer worldwide accounting for approximately 70 percent of total production during the 1960s and 1970s and roughly 45 percent at the present time. US production has remained steady, but the increases in output of the USSR and Israel have shifted the relative market shares (Roskill Information Service, Ltd., 1986). The major Western European producers are the United Kingdom (UK) (*circa* 10 percent), France (*circa* six percent), Federal Republic of Germany (*circa* one percent), Italy (*circa* one percent), and Spain (Anzion and Feenstra, 1980). The UK, Italy, and Spain mainly produce bromine from seawater. France produces over 50 percent of its bromine from seawater, but the Alsace deposits are also an important source. The Stassfurt potash deposits and the Bergmannssegen-Hugo and Salzdetfurth mines are major sources in the Federal Republic of Germany. Italy produces bromine from waste bitterns and inland lakes. Despite the fact that since 1970, Western Europe has produced roughly 16–18 percent of the total world production, with the UK and France as the two leading producers, Western Europe continues to consume more than it produces. Other major world producers are the USSR, Israel (from the Dead Sea), and Japan.

In the Netherlands, bromine compounds are manufactured and exported (often to the US), although the bromine raw material is imported from Israel, France, the UK, and the Federal Republic of Germany. In 1977, the Netherlands imported 3,286 tons of bromine for use in the manufacture of bromine compounds.

Table 2.1. Bromine production in Western Europe (metric tons).

	1900[b]	*1950*[b]	*1960*[b]	*1965*[b]	*1970*[c]	*1973*[b]	*1978*[a,e]	*1980*[d]	*1983*[d]	*1985*[e]
USA	236	44,691	77,132	124,578	158,600	189,769	202,586	170,347	166,670	158,800
UK					24,700	30,595	25,100	26,220	28,830	22,700
France		1,060	2,009	2,800	14,700	14,060	16,200	16,370	9,910	11,300
Germany, F.R.				2,945	2,500	2,900	3,900	3,980	3,018	3,200
Italy		391	1,278	2,060	3,300	5,215	600	586	495	500
Spain						399	400	405	315	300
Others	64	4,258	23,081	17,617	21,000	27,262	112,680	122,680	149,230	184,500
Total	300	50,400	103,500	150,000	224,800	270,200	361,207	340,588	358,468	381,300

Sources:

[a] Lyday, 1985, p. 4;

[b] Kirk and Othmer, 1978, p. 238;

[c] Anzion and Feenstra, 1980, p. 11;

[d] US Bureau of Mines, 1984, p. 177;

[e] Roskill Information Services, Ltd., 1986, p. 6.

2.2.1. Production processes

Two techniques are used in the commercial production of bromine, depending on the bromine concentration in the raw material. A blowing-out process is used for seawater with dilute bromine concentrations, while a more expensive steaming-out process is used for concentrated brines (1,000 ppm and above). Both processes involve the following four basic steps:

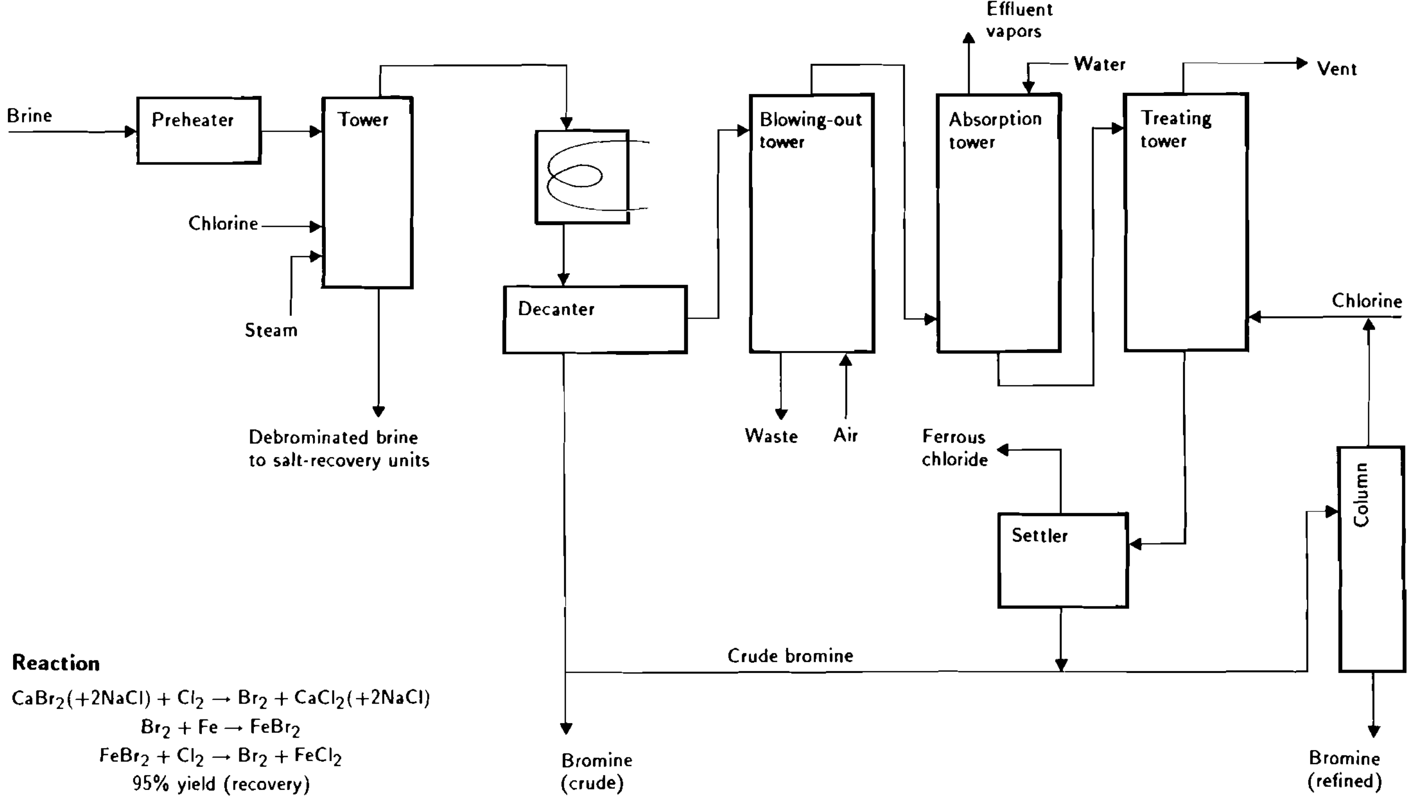
(1) Treatment with chlorine to oxidize the bromide to bromine.
(2) Separation of the bromine vapor from solution using air or steam.
(3) Condensation of bromine vapor (or reaction to form a salt or acid).
(4) Purification of the bromine.

In the blowing-out process, bromine is freed from seawater in a chlorine oxidation reaction: $2NaBr + Cl_2 \rightarrow Br_2 + 2NaCl$. The debrominated seawater, with traces of bromine remaining, is returned to the ocean. Air is then used to vaporize the bromine. Next, sulfur dioxide and water are added to absorb the bromine from the incoming air stream in a counter-current stripping process: $Br_2 + SO_2 + 2H_2O \rightarrow 2HBr + H_2SO_4$. The stripped air is then vented to the atmosphere. Finally, chlorine and steam are used to separate and purify the liquor: $2HBr + Cl_2 \rightarrow Br_2 + 2HCl$ (see *Figure 2.1*). The ratio of chlorine to bromine used in this process is roughly 2:1. Bromine recovery in the blowing-out process is 90–95 percent. The remaining 5–10 percent bromine is either returned to the ocean with the debrominated seawater, emitted to the atmosphere during the air stripping step with the stripped air, or recycled at the process end with the by-product hydrochloric acid (used to neutralize the incoming seawater)(Anzion and Feenstra, 1980).

The steaming-out process follows a similar principle. The oxidation reaction used on brines is: $CaBr_2 + 2NaCl + Cl_2 \rightarrow Br_2 + CaCl_2 + 2NaCl$. Theoretically, one kilogram (kg) of chlorine will release 2.25 kg of bromine, but in reality more than 2.25 kg chlorine is needed. In this process, the bromine is separated from the bromine and salt solution by steam instead of air. Next, iron filings are used to absorb the bromine, producing the salt: $FeBr_2{:}Br_2 + Fe \rightarrow FeBr_2$. The bromine is further oxidized by chlorine, then the vapors are condensed and purified: $FeBr_2 + Cl_2 \rightarrow Br_2 + FeCl_2$. After the brines have been debrominated, the waste liquor is sent to salt recovery units to be used as the incoming raw material (see *Figure 2.2*). A modified process uses sodium carbonate (Na_2CO_3) and sulfuric acid (H_2SO_4) to absorb and recover the bromine respectively.

The efficiency of bromine recovery in the steaming-out process is 95 percent. Traces of bromine remain in the waste brine, which is sent to salt recovery units for production of alkali metal salts. Other bromine losses during production may occur during the absorption step when the stripped air is vented to the atmosphere (Faith *et al.*, 1975).

From Natural Brines and Bitterns



Reaction

$CaBr_2(+2NaCl) + Cl_2 \rightarrow Br_2 + CaCl_2(+2NaCl)$

$Br_2 + Fe \rightarrow FeBr_2$

$FeBr_2 + Cl_2 \rightarrow Br_2 + FeCl_2$

95% yield (recovery)

Figure 2.1. Bromine blowing out process. (Source: Faith *et al.*, 1965.)

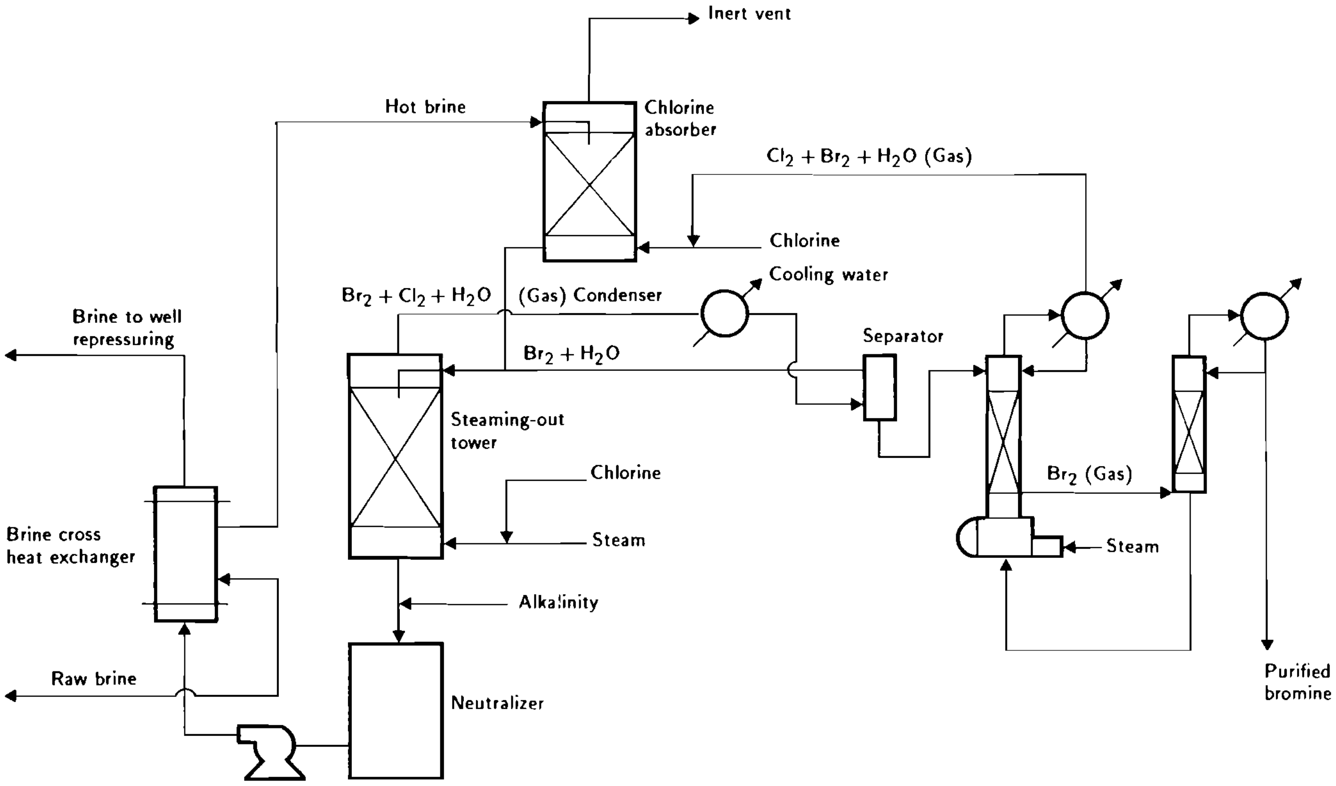


Figure 2.2. Bromine steaming-out process. (Source: Kirk and Othmer, 1978.)

2.3. Major Uses

Bromine is used primarily in the manufacture of organic and inorganic bromides and bromates. Only 17 percent of bromine produced is used in its elemental form (Faith *et al.*, 1975) as a bleaching agent and as a sanitizing or disinfecting agent, specifically in industrial water treatment and swimming pools (Lefond *et al.*, 1975). Historically, the major use of bromine has been in the synthesis of ethylene dibromide (EDB), a compound used in conjunction with tetraethyl lead as an antiknock agent in gasoline. Other organic bromine compounds are used in fumigants, insecticides, flame retardant agents, fire extinguishers, pharmaceuticals, solvents, gauge fluids, catalysts, and dyes. Inorganic bromine compounds are used in the photographic industry, in pharmaceuticals, hair-wave treatments, desiccants, and as catalysts. Hydrobromic acid is the most important intermediate of bromine and is used extensively in the synthesis of organic and inorganic bromine compounds. A list of the major bromine compounds is presented in *Table 2.2* with a brief description of the specific uses. A more extensive list of organo-bromine compounds may be found in Kirk and Othmer (1978) which lists information on the use of 55 chemicals.

2.3.1. Process-product diagrams

As indicated in the introduction, the first step in a materials-balance approach is to re-create the flow of bromine in the economy and environment using information on production, intermediate uses, and end uses. The flow charts in *Figures 2.3*, *2.4*, and *2.5* are intended to track, in detail, the flow of bromine in the industrial economy. *Figure 2.3* is an overview showing bromine extraction, production, intermediates, and end uses. *Figures 2.4* and *2.5* extend the flow chart and show the uses of hydrobromic acid (HBr) and bromine organics, respectively.

The flow charts presented in *Figures 2.3* to *2.5* qualitatively address the question *where does bromine end up in the economy*? Now we examine each of the major end-use categories (which may consist of only one compound as in the case of ethylene dibromide and gasoline consumption) and also examine the question of *where does the bromine end up in the environment*? Two important pieces of information are the bromine content of these compounds and the potential for release into the environment during consumption.

2.3.2. Ethylene dibromide

Traditionally, the primary end-use of bromine has been ethylylene dibromide (EDB) and, until recently, EDB represented approximately 70 percen of the total demand for bromine. About 95 percent of EDB is used as a gasoline additive, while the remaining five percent is used in pesticides and fumigants. Less than one percent is used for solvents in chemical synthesis (Anzion and Feenstra, 1980).

Table 2.2. Major bromine compounds.

Hydrobromic Acid (HBr):	A major intermediate used in the synthesis of organic and inorganic compounds. HBr is used directly as a catalyst.
Hypobromous Acid ($HOBr$):	Primarily used as a germicide in water treatment; also used in insecticides and herbicides.
Organic Compounds	
Ethylene Dibromide ($BrCH_2CH_2Br$):	Used as a gasoline antiknock ingredient. Other uses include fumigants, solvents, pharmaceuticals (sedatives, anesthetics), fire retardants, and dyes.
Methyl Bromide (CH_3Br):	Used as an agricultural fumigant. Minor use as a food preservative in grains, meal, fruits and vegetables, and as a chemical intermediate.
Ethyl Bromide (CH_3CH_2Br):	Used as a fumigant, flame retardant, and in pharmaceuticals.
Styrene Bromide: ($C_6H_5CHBrCH_2Br$):	Used as a catalyst and fumigant.
Ethylene Chlorobromide: (CH_2ClCH_2Br):	Used as a fumigant and solvent.
Dibromochloropropane: ($CH_2BrCHBrCH_2Cl$):	Used as a fumigant.
Bromocyanide ($BrCN$):	Used as a fumigant.
3-Bromopropane ($CH_3CH_2CH_2Br$):	Used as a fumigant.
Propylene Bromide ($CH_3CHBrCH_2Br$):	Used as a solvent.
Acetylene Tetrabromide ($CHBr_2CHBr_2$):	Used as a catalyst, gauge fluid, and separation liquid.
Allyl Bromide (CH_2CHCH_2Br):	Used as a fire retarding agent, primarily n plastics and synthetic fibers.
Vinyl Bromide (CH_2CHBr):	Used as a fire retardant in plastics, synthetic fibers, and also as an intermediate in the synthesis of steroids.

Table 2.2. Continued.

Other Fire Retardants/Fire Extinguishing Agents

Bromochlorodifluoromethane ($CBrClF_2$)
Bromotrifluromethane ($CBrF_3$)
Tetrabromobisphenol ($(C_6H_2Br_2OH)_2C(CH_3)_2$)
Tris(2,3 - dibromopropyl)phosphate ($(BrCH_2CHBrCH_2O)_3PO$)
Methylene Chlorobromide (CH_2ClBr)
Bromodichloromethane ($CHCl_2Br$)
Bromochloromethane (CH_2ClBr)
Bromobenzene (C_6H_5Br)
Hexabromobenzene (C_6Br_6)
Pentabromochlorocyclohexane ($C_6H_6Br_5Cl$)
PBT, Pentabromotoulene ($C_6Br_5CH_3$)
PBB, Polybrominated Biphenyl ($C_6Br_5C_6Br_5$)

Inorganic Compounds

Sodium Bromide ($NaBr$):	Used in photographic films and papers, in pharmaceuticals, as a desiccant for air conditioning, as a catalyst and occasionally in bleaching with hypochlorites.
Silver Bromide ($AgBr$):	Used extensively in the photographic industry.
Potassium Bromide (KBr):	Also used in the photographic industry as a defogging agent during developing.
Heavy Metal Bromides (XBr):	e.g., $PbBr_3$ and $FeBr_3$ are primarily used as catalysts while $MgBr_2$, $SrBr_2$, $PbBr_2$, $CuBr$, and $HgBr_2$ are used in the pharmaceutical industry as sedatives and anesthetics.
Lithium Bromide ($LiBr$):	Becoming increasingly used as a desiccant in air conditioners and industrial drying of air.
Zinc Bromide ($ZnBr_2$):	Used as a catalyst, in radiation shielding, desiccant, and as a gauge and drilling fluid.
Calcium Bromide ($CaBr_2$):	Used in pharmaceuticals, as a catalyst, and in gauge or drilling fluids.
Aluminum Bromide ($AlBr_3$):	Used as a catalyst (with applications similar to $AlCl_3$).
Ammonium Bromide (NH_4Br):	Used in pharmaceuticals (sedatives and anesthetics), in flame retardants, and as a fire extinguishing agent.
Sodium Bromate ($NaBrO_3$):	Used in hair-wave treatments.
Potassium Bromate ($KBrO_3$):	Used as a flour treating agent, in hair-wave preparations, and for shrinkproofing wool.

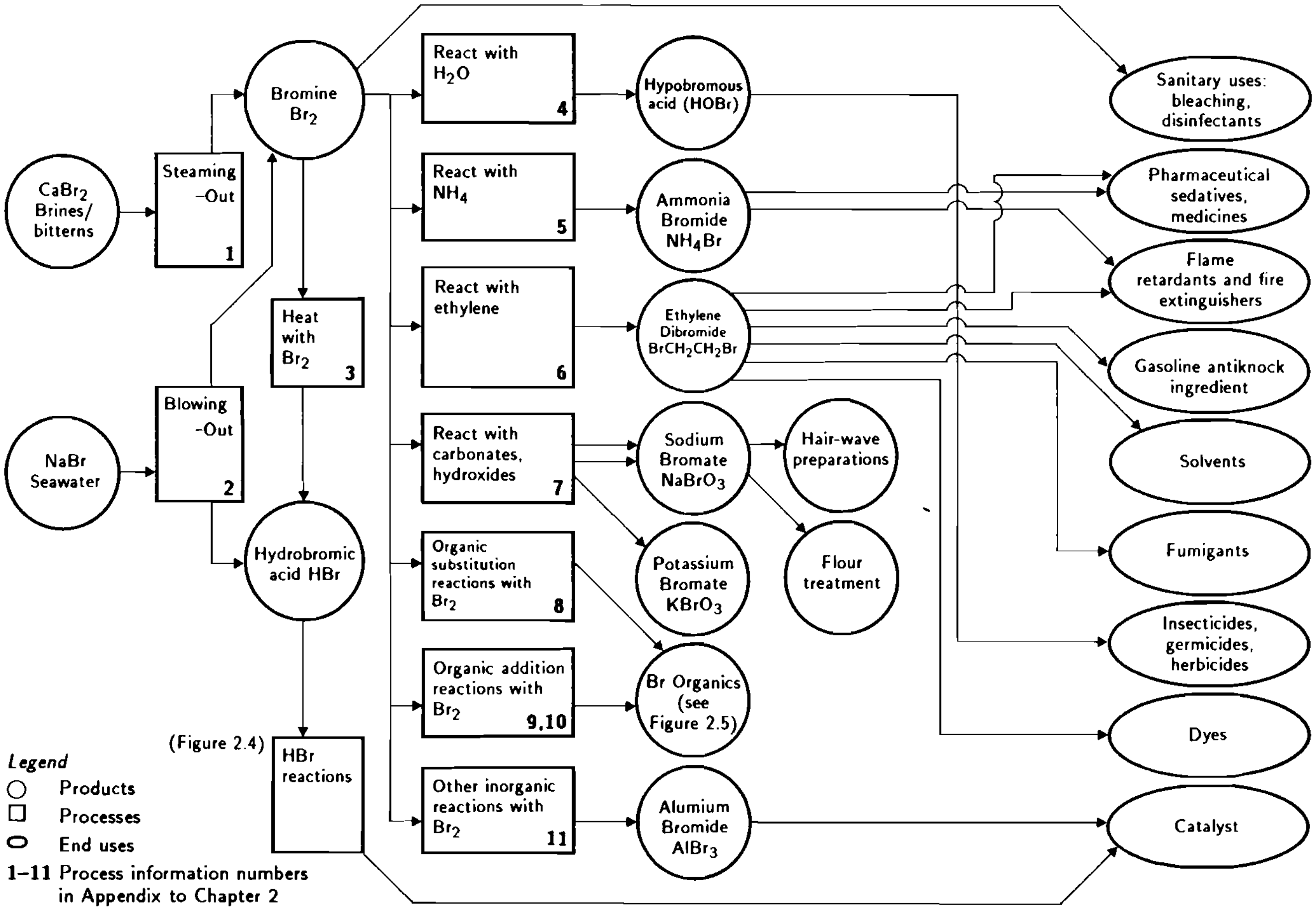


Figure 2.3. **Bromine compounds.**

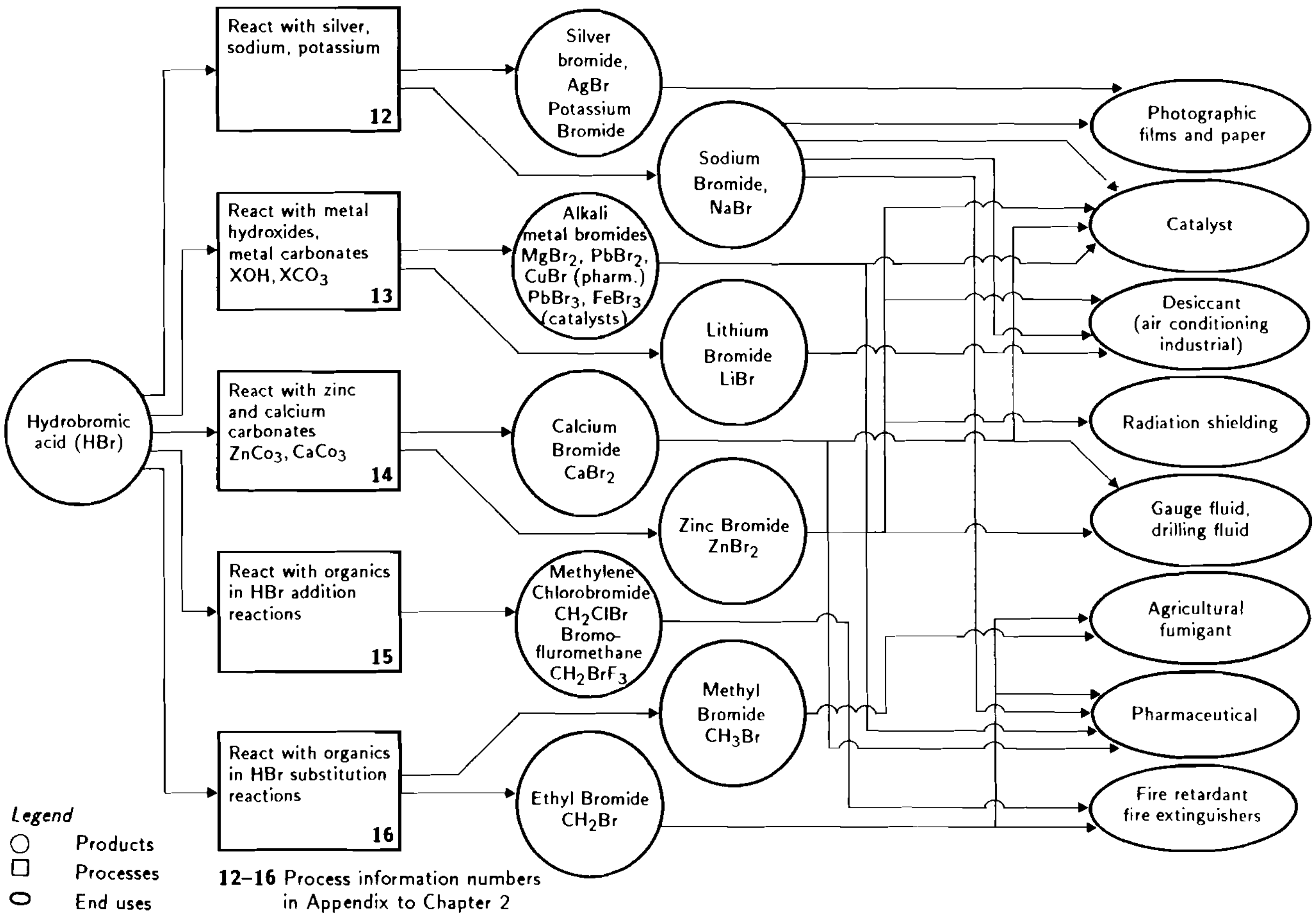


Figure 2.4. Hydrobromic acid compounds.

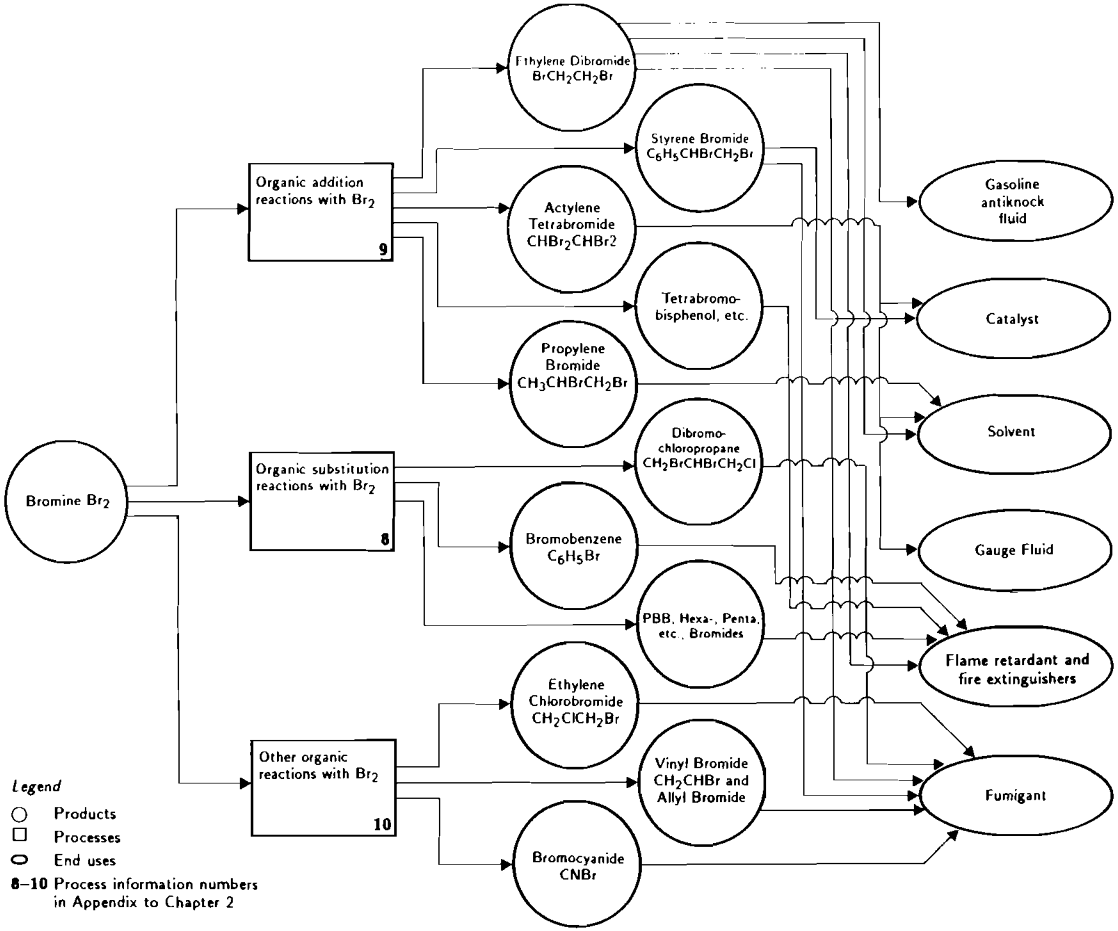


Figure 2.5. **Bromine organics.**

EDB acts as a lead scavenger in antiknock fluids and prevents lead buildup in engines. During combustion, lead oxide (PbO_2) from tetraethyl lead and tetramethyl lead is deposited on the engine; EDB reacts with the PbO_2 to form lead bromide ($PbBr_2$), and other lead-bromine-chlorine compounds which are then vented to the atmosphere. Approximately 75 percent of the total lead and bromine in gasoline leaves the engine system in this manner. The other 25 percent of the lead, bromine, and chlorine (if used) remains in oil filters or in the exhaust system and is eventually discarded with waste oil (Ayres *et al.*, 1985). The amount of bromine emitted to the air or in waste oil can theoretically be estimated from trade data on gasoline consumption and information on the use and composition of antiknock fluids containing EDB, as shown in the following information and simple calculations below.

(1) Composition of antiknock fluid, 1975 (Antiknock fluids for aviation gasoline use pure EDB instead of a 1:1 ethylenedibromide:ethylenedichloride mixture):

tetraethyl lead	61.50%
or tetramethyl lead	50.80%
ethylenedibromide (EDB)	17.85%
ethylenedichloride	18.85%

(2) EDB composition: 86% elemental bromine.
(3) Bromine per gram (g) of antiknock fluid: (0.1785 g EDB/g fluid)(0.86 g Br/g EDB) = 0.1535 g Br/g fluid
(4) Bromine per liter (L) gasoline consumed: (0.1535 g Br/g fluid)(X g fluid/L gas) = Y g Br/L gas (where Y = 0.1535X)
(5) Air Emissions: (0.75)(Y g Br/L gas)
(6) Bromine in waste oil: (0.25)(Y g Br/L gas)

Assuming 75 percent of the bromine reacts with lead to form $PbBr_2$, etc., which is then emitted to the air, bromine air emissions per liter gasoline consumed can be easily calculated from data on the amount of antiknock fluid added per liter of gasoline (X in step 4 above). Unfortunately, there is a paucity of good data available and the amount of antiknock fluid per liter of gasoline varies according to year, gasoline grade, and country. In the Netherlands, where we have more information, an average of 0.76 g/L has been reported (Anzion and Feenstra, 1980).

An alternative approach is to assume that 95 percent of all EDB produced is consumed in gasoline and calculate air emissions based on production data. For instance, the UK produces an average of 26,000 tons per year of EDB, and exports 24,000 tons, the UK being the major supplier of EDB to Europe (Anzion and Feenstra, 1980). The following calculation gives a rough estimate of bromine air emissions in the UK, assuming 2,000 tons per year is the amount of EDB consumed: (2,000 tons EDB/yr)(0.86 ton Br/ton EDB)(0.95 gasoline use) = (1,634 tons of Br consumed in gasoline)(0.75)(1,634 tons Br/yr) = 1,226 tons Br/year emitted to the air.

Table 2.3. Maximum permitted lead content in gasoline, 1984.

Country	*Lead Content (g/L)*
Austria	0.40 premium 0.15 regular
Belgium	0.40
Denmark	0.40
Finland	0.40
France	0.40
Germany, F.R.	0.15
Greece	0.15
Ireland	0.40
Italy	0.40
Luxembourg	0.40
Netherlands	0.40
Norway	0.40 premium 0.15 regular
Portugal	0.84
Spain	0.48–0.65
Sweden	0.15
Switzerland	0.15
UK	0.40

(Source: Roskill Information Services Ltd., 1986.)

A third approach uses data on gasoline consumption and lead content. Based on the composition of antiknock fluid given above, the ratio of lead to bromine in motor gasoline is roughly 2.59:1 (Lyday, 1985). A calculation of bromine in gasoline can be made based on the amount of allowable lead in gasoline. The Rotterdam market in Western Europe reports a range of lead concentration from 0.15–0.40 grams of lead per litre (g Pb/L) in gasoline (National Energy Administration, 1984). *Table 2.3* lists the maximum permitted levels of lead for Western European countries. For present purposes, the assumption is made that the lead content varies from 0.15–0.40 g/L in gasoline in Europe. Therefore, the consumption of bromine per liter of gasoline is 0.0579–0.1544 g Br/L (calculated by dividing the lead content by 2.59).

This latter approach is easiest to use as data on lead consumption in gasoline is more readily available; however, it is becoming more problematic as western countries are shifting toward unleaded gasoline at different rates. Scandinavia, Switzerland, and the Federal Republic of Germany are the forerunners in Europe and are pushing for the majority of cars to use lead-free gasoline by 1990. In 1980, only 25 percent of the gas market used low-lead gasoline in Western Europe. By 1985, projections were for 32 percent of the market, still low when compared to 77 percent of the market use in the US. The EEC's objectives for the phase-out of leaded gasoline are as follows (Roskill Information Service Ltd., 1986):

- Freely available unleaded gasoline in West Europe by October, 1989.
- By 1989, all new vehicles must run on unleaded gasoline.
- From October 1990, all new registration cars will run on unleaded gasoline,

unless the manufacturer can prove that major reengineering would be required.

The Netherlands decreased its maximum from 0.4 g Pb/L to 0.15 g Pb/L effective as of October, 1986. However, Shell reports that regular gasoline currently contains 0.3 g Pb/L and premium contains 0.38 g Pb/L (De Zoeten, 1987).

The impact of lead phase-out on bromine consumption is best illustrated by the US example. Unleaded gasoline was first available in 1974 and regulations in 1983 decreased allowable levels to 0.66 g Pb/L for small refineries and 0.29 g Pb/L for large refineries. By 1986, levels had to be down to 0.0264 g Pb/L (0.1 g Pb/gallon) (Lyday, 1985). As a result, EDB consumed only 55 percent of the total bromine produced in the US in 1983 as compared to 77 percent in 1973; in 1987, EDB demand represented only 20 percent of the total bromine demand in the US. Extrapolations of this market shift suggest that by the year 2000 little, if any, EDB will be consumed in the West as a gasoline additive (Roskill Information Services Ltd., 1986).

2.3.3. Agricultural uses

In agriculture, organo-bromide compounds are used as soil fumigants against wireworms and as grain fumigants to control insects, bacteria, and rodents in the stored grain. Fumigants are also used in packaged goods. The three most important fumigants are methyl bromide (CH_3Br), EDB, and dibromochloropropane (DBCP). Methyl bromide contains 83 percent bromine while dibromochloropropane contains roughly 68 percent bromine. However, toxicological concerns regarding EDB and DBCP have resulted in the decline of agricultural use of these chemicals. In 1984, the US suspended the use of EDB as a soil fumigant and subsequently banned DBCP. The UK banned use of EDB in 1985. Use in Western Europe is now primarily in Italy and Spain.

The consumption of methyl bromide has also dropped, but it continues to be an important bromine fumigant and one of the key bromide compounds produced commercially. For instance, in 1978, the Netherlands consumed 1,870 tons of bromine in fumigants (20 percent of the total bromine demand), mostly in the form of methyl bromide (Anzion and Feenstra, 1980). But, a reduction in allowable dosages in soil from 75–100 g/square meters (m^2) to 40 g/m^2 has significantly lowered the annual consumption of methyl bromide in the Netherlands. On the other hand, use in the Mediterranean countries has increased in the past few years.

Bromine fumigants are very volatile and are easily released into the air during application or within several days thereafter. In the Netherlands it is estimated that 85 percent of the methyl bromide applied to soil prior to 1985 was lost to the air (De Zoeten, 1987). The volatility of bromide fumigants makes them potentially harmful to workers applying the compounds, but long-term environmental impacts are of lesser concern than the air emissions during application (McEwen and Stephenson, 1979). Methyl bromide is also used as a grain fumigant. Here, extensive washing is necessary so that residues left on foodstuffs are small. Therefore, much of the bromine used in grain fumigants is released into surface and ground waters.

Methyl bromide and EDB are occasionally used as nematicides for control of nematodes; heavy applications are required to penetrate the soil and usage can drastically alter the soils. Another minor agricultural compound is 1,2-dibromo-2, 2-dichloroethyldimethyl PO (Dibrom), an organophosphate insecticide.

2.3.4. Flame retardants

Since the 1960s, flame retardants have been the largest growing use of bromine compounds. During 1986, 30 percent of all fire retardants used in the US were bromide compounds, with 85 percent of those retardants being applied to plastics as compared to 14 percent in 1971 (McGraw-Hill Encyclopedia of Science and Technology, 1971; Roskill Information Services Ltd., 1986). The two primary bromides used in plastics are vinyl bromide ($CH_2 = CH_2Br$) and allyl bromide ($CH_2BrCH = CH_2$). Bromide fire retardants are also used in textiles, clothing, paint, construction material, and furnishings. The Western European market is dominated by tris(2,3-dibromopropyl)phosphate, tetrabromobisphenol, vinyl bromide, and polybrominatedbiphenyl compounds (PBBs). Other fire retardants are listed in *Table 2.2.* There are two general categories of fire retardants: additive types with an average of 75 percent bromine and reactive types with an average of 66 percent bromine. Consumption of fire retardants is split roughly in half between the two types (Roskill Information Services, Ltd., 1986). Although fire retardants are not dissipated in the short term, eventually most of the bromine ends up in landfills or in incinerators with discarded plastics, clothing, etc. Organic bromides are also used in fire extinguisher fluids. Here, the primary compounds are bromochloromethane (CH_2BrCl), bromochlorodifluoromethane ($CBrClF_2$), and bromotrifluoromethane ($CBrF_3$), containing 62 percent, 48 percent, and 54 percent bromine, respectively. These compounds may end up in semi-permanent storage, but there are no available data on the lifetime of fire extinguishers. With the growing use of brominated flame extinguishers, the product lifetimes and potential releases of these compounds should be examined.

2.3.5. Sanitary uses

Sanitary uses account for most of the elemental bromine consumed and include industrial wastewater treatment, drinking water disinfection, and swimming pool sanitation. Bromine-chlorine is less toxic than pure chlorine as an industrial disinfectant. In addition, bromine is often preferred to chlorine in swimming pools as it is less irritating. Most of the bromine used in households or industry is eventually discarded into surface waters.

2.3.6. Pharmaceuticals

Bromides have been traditionally used in pharmaceuticals, particularly heavy metal bromides ($MgBr_2$, $SrBr_2$, $PbBr_2$, CuBr, and $HgBr_2$), sodium bromide (NaBr), calcium bromide ($CaBr_2$), and ammonium bromide (NH_4Br). Sedatives, anesthetics, and anti-spasmodic agents are the primary end-uses. However, the popularity of bromine compounds as sedatives has decreased and bromine is more often used in intermediates. Bromine is also used in cosmetics, but in negligible amounts (Kirk and Othmer, 1978).

2.3.7. Photography

Owing to their light-sensitive properties, silver bromide (AgBr), small amounts of potassium bromide (KBr), and sodium bromide (NaBr) are used in the photographic and graphics industries, and in x-ray films. Silver bromide contains roughly 75 percent bromine by weight. Five main categories of use with their respective bromine contents are listed below (Anzion and Feenstra, 1980):

Medical x-ray films	7.5-19 g Br/m^2
Industrial films	7.5-19 g Br/m^2
Graphics films	3.0-7 g Br/m^2
Photographic films	1.9-6 g Br/m^2
Light sensitive paper	0.4-2.3 g Br/m^2

Industrial and medical films consume about 50 percent of the silver bromide while consumer end-uses consume 35 percent and graphic films 15 percent (Roskill Information Services Ltd., 1986). It is estimated that 100 percent of the bromides used in these categories is emitted to the environment in wastewater.

2.3.8. Drilling fluids

Next to flame retardants, drilling fluids have been the fastest growing use of bromine. Calcium bromide and, to a lesser extent, zinc bromide and sodium bromide, are good stabilizers for use in deep well drilling. Clearly, the consumption pattern here is a function of drilling activity. New drilling in Western Europe represented only 1.3 percent of all oil and gas wells from 1977 to 1985. In Europe, drilling decreased by six percent in 1986 (Roskill Information Services Ltd., 1986). The UK is the largest consumer of calcium bromide in Europe because of its North Sea oil activities.

2.3.9. Other uses: flour treatment, dyes, and catalysts

Potassium bromate ($KBrO_3$) is used in the treatment of flour to improve the leavening. However, France, Belgium, Luxembourg, the Netherlands, the Federal Republic of Germany, Italy, and Spain do not allow bromate additives in traded wheat. The US and the UK still allow $KBrO_3$ addition. Sodium bromate ($NaBrO_3$) and potassium bromate are used in hair-wave preparations.

One of the earliest bromine compounds used was the naturally occurring *Tyrian Purple* or 6,6′-dibromo-indigo dye. More recently, bromine has been used in the synthesis of blue indigo dyes which are used for blue jeans. The intermediate compound is bromoamine acid (Kirk and Othmer, 1978). Further information on the use of bromine in dyes is not available.

2.4. Quantitative Analysis

It is necessary to have data on production and/or consumption of either compounds (e.g., EDB, CH_3Br, AgBr, bromates, organics, etc.) or products (e.g., antiknock fluid, fumigants, photographic chemicals, flamestuffs, and pharmaceuticals). Depending on the available information, the material balance can be used to fill data gaps and make assumptions about the fate of bromine.

The available trade data in the summer of 1986 provide information on a more aggregate level than the flow-charts in *Figures 2.3* to *2.5* (see Appendix to this chapter). Therefore, the flow-charts used in this section have eliminated much of the detail of the earlier charts and only focus on major compounds. Due to data restrictions, this section analyzes bromine consumption only for the Netherlands and the US for the years 1978 and 1985. Consumption data are particularly difficult to find for European countries. The quantitative material balance for the Netherlands for 1978 is an adaptation of work done by Anzion and Feenstra (1980). The US Bureau of Mines is the primary source for US production and consumption data. Although the US is not part of the *Future Environments for Europe* case study (Stigliani *et al.*, 1989), it provides a comparison to the Netherlands; in addition, the US is more representative of Western European bromine consumption patterns than the Netherlands.

Information on the general consumption patterns for bromine is a useful introduction to the quantitative section. *Table 2.4* is a compilation of available consumption statistics for bromine compounds and illustrates the variations in use patterns. Worldwide consumption of bromine in 1976 was estimated as follows: EDB 55 percent; agricultural chemicals 17 percent; flame retardants nine percent; dyes seven percent; photographic applications 3.5 percent; pharmaceuticals 3.5 percent; and, others five percent (Kirk and Othmer, 1978). However, in the US and most of the western world, EDB use was much higher, accounting for roughly 70 percent of the bromine demand. By 1985, the consumption pattern in the western world had shifted to: EDB 24 percent; agricultural chemicals 13 percent; flame retardants 20 percent; drilling fluids 18 percent; and, others 25 percent (Roskill Information Service Ltd., 1986).

Table 2.4. Bromine consumption patterns (in percent).

Year *Country*	*1965–75* *UK*[a]	*1965* *USA*[b]	*1970* *USA*[a]	*1973* *USA*[a]	*1976* *World*[c]	*1978* *Netherlands*[a]	*1983* *USA*[d]
EDB	78.8	75	71	75	55	19.6	27
Pesticides	9.1	6	>14	5	>17	56.9	
Sanitary		10		6		10.7	11
Fire Retardants	4.6		5	4	9	3.6	31
Other	7.6	9	10	10	19[e]	9.2	31[f]

Sources:

[a] Anzion and Feenstra, 1980.

[b] Faith, *et al.*, 1975.

[c] Kirk and Othmer, 1978.

[d] Lyday, 1985.

[e] Others: Dyes, 7; Photographic uses, 3.5; Pharmaceuticals, 3.5; Miscellaneous, 5 for 1976.

[f] Others: Drilling fluids, 27; Miscellaneous, 4.

Overall bromine production and consumption have remained about the same, but the end uses have shifted from EDB toward newer uses in flame retardants and drilling fluids. The phase-out of leaded gasoline has had an enormous impact on the bromine market, and it is important to compare the historical and current trends in bromine consumption in order to predict future uses.

Figures 2.6 and *2.7* are material balances for bromine consumption in the Netherlands and the US in 1978. *Tables 2.5* and *2.6* summarize the salient information provided by the material balances: the amount of bromine used in each category and, the potential environmental releases of bromine to the air, water, permanent uses, or unclear endpoints during consumption. The statistics in these Tables demonstrate the usefulness of the materials-balance approach.

The second set of material balances focuses on the 1985 consumption of bromine for the same two countries. Again, *Figures 2.8* and *2.9* are the quantitative material balances with estimates cited in parentheses. *Tables 2.7* and *2.8* summarize the key information provided by the material balance on percentages of bromine compounds consumed and percentages of estimated environmental releases. Finally, *Figure 2.10* and *Table 2.9* present data on the overall consumption of bromine in Western Europe. However, this information should be used with caution as the data gaps were greatest here. One final note regarding the quantitative flow charts: the tonnages reported are tons of bromine consumed, not tons of a particular compound.

2.5. Conclusions

Clearly, during the 1950s, 1960s, and 1970s, the majority of bromine was used as a gasoline additive. As shown in *Table 2.6*, the US consumed 60 percent of its bromine in the manufacturing of EDB during 1978, while sanitary and bleaching uses consumed 9.7 percent, fire retardants used 19 percent, and agricultural uses six percent.

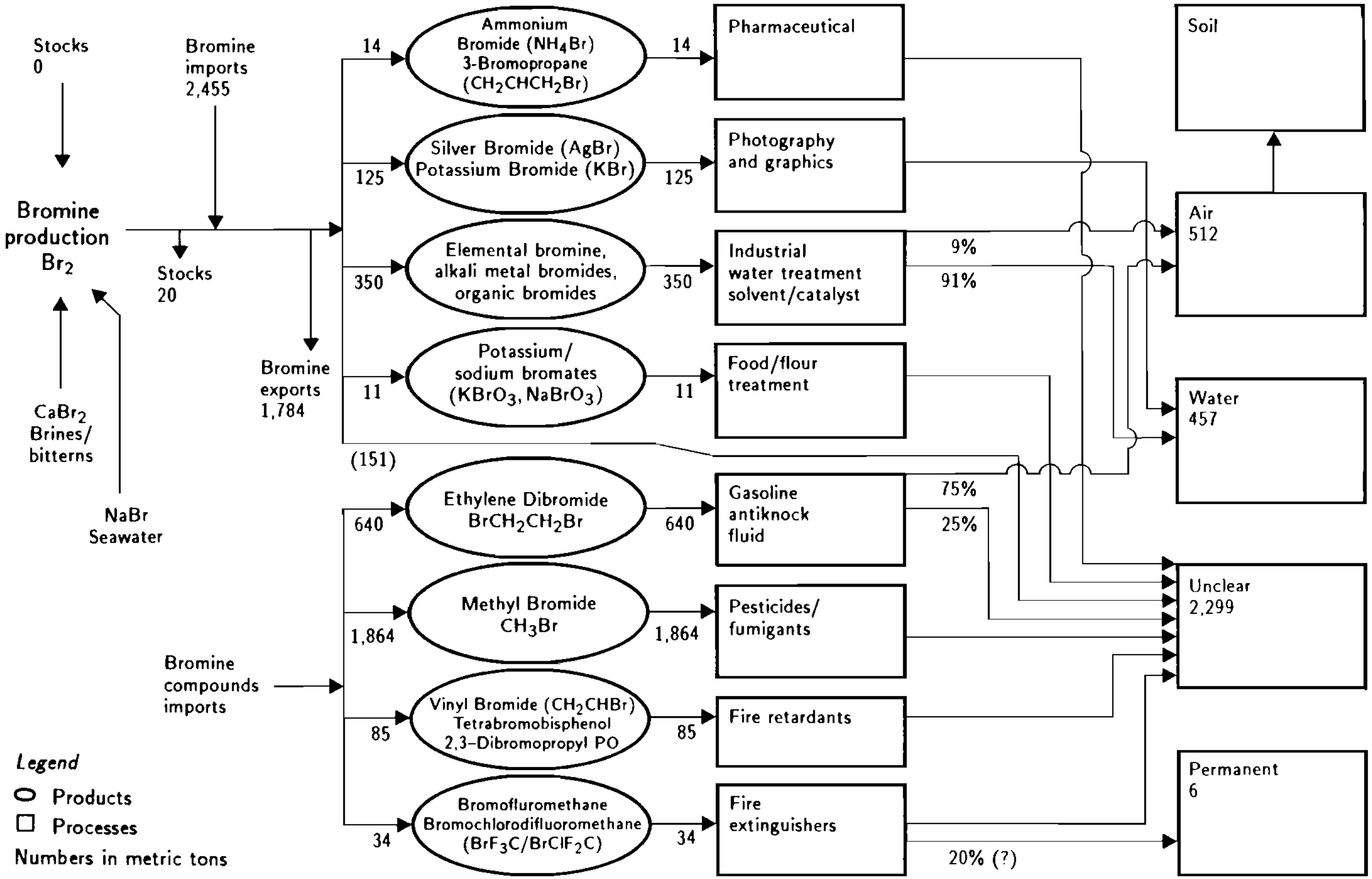


Figure 2.6. Bromine consumption in the Netherlands in 1978 (tons).

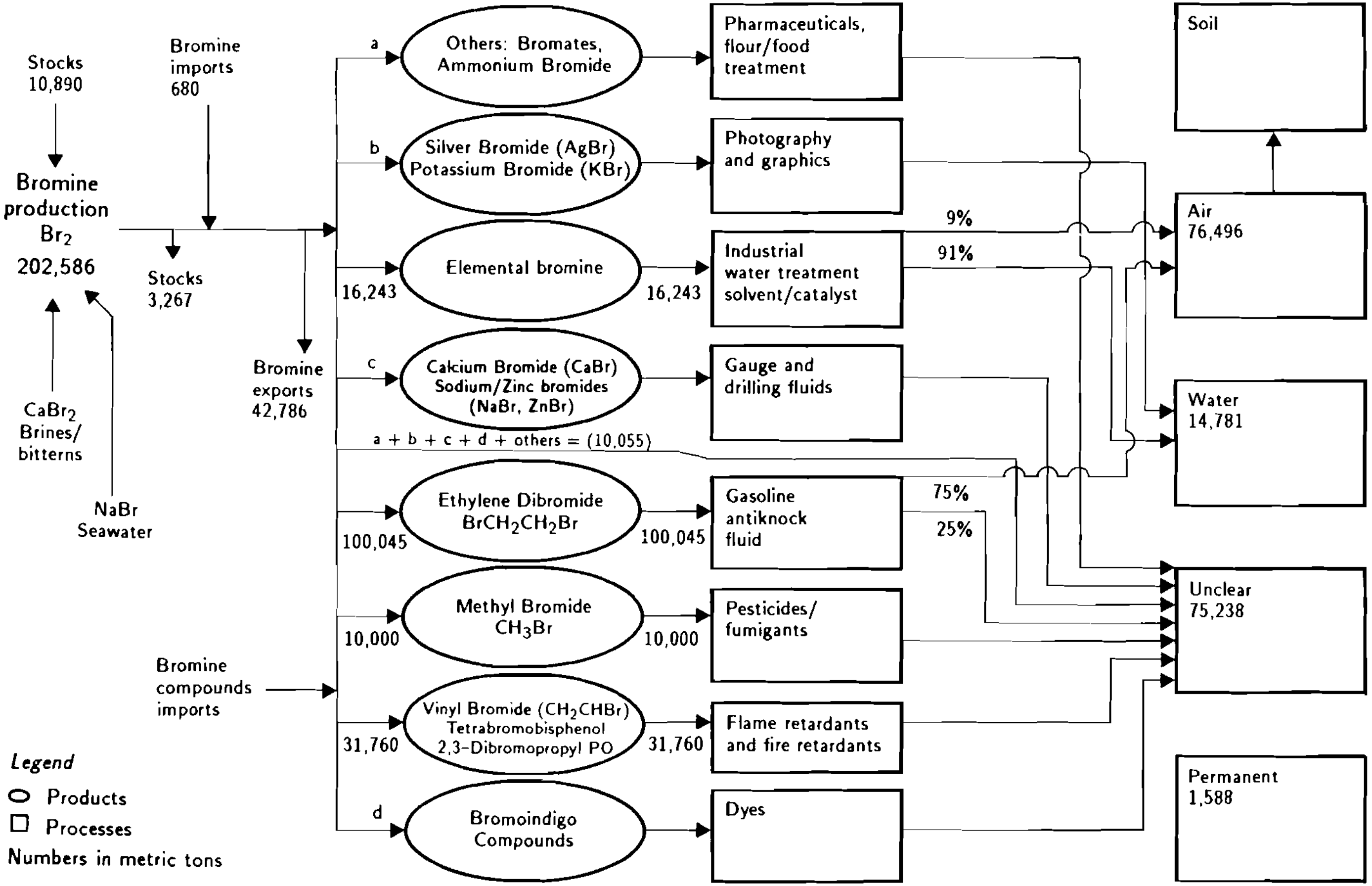


Figure 2.7. Bromine consumption in the USA in 1978 (tons).

Table 2.5. Releases of bromine in the Netherlands in 1978 (metric tons).

	Air	*Water*	*Permanent*	*Unclear*	*Total*
Gas (EDB)	480			160	640
Firestuffs			6	113	119
Pesticides/fumigants				1,864	1,864
Photography (AgBr)		125			125
Industry/sanitary	32	318			350
Pharmaceuticals		14		14	
Drilling fluids					
Other				162	162
Total	512	457	6	2,299	3,274
Percentage of total	15.64	13.96	0.18	70.22	100.00

Table 2.6. Releases of bromine in the USA in 1978 (metric tons).

	Air	*Water*	*Permanent*	*Unclear*	*Total*
Gas (EDB)	75,034			25,011	100,045
Firestuffs			1,588	30,172	31,760
Pesticides/fumigants				10,000	10,000
Photography (AgBr)					
Industry/sanitary	1,462	14,781			16,243
Pharmaceuticals					
Drilling fluids					
Other				10,055	10,055
Total	76,496	14,781	1,588	75,238	168,103
Percentage of total	45.51	8.79	0.94	44.76	100.00

The consumption patterns today are quite different, as shown in *Tables 2.7* and *2.8*. In the Netherlands, EDB continued to consume roughly 22.6 percent of the demand (550 tons in 1985 and 649 tons in 1978). But, use of methylbromide (CH_3Br) decreased from 1,864 tons to 1,044 tons (from 60 percent of the demand in 1978 to 43 percent in 1985). Use of bromine in firestuffs increased slightly from 119 to 235 tons representing 9.67 percent of the consumption while use in photography decreased to 1.5 percent of demand (36 tons down from 125 tons). Data was not available for the other categories.

European consumption of bromine in 1985 was similar to the US consumption pattern, but Western Europe consumed fewer firestuffs and more bromine fumigants. Use of EDB was also higher in Europe as the phase-out of leaded gasoline in Western Europe is lagging behind the US Fire regulations in Europe are expected to change and bromine use in firestuffs should reflect these new safety regulations. At the same time, the use of EDB and bromine fumigants is dropping. It appears that a shift in bromine consumption will occur in the next decade, paralleling the US market shift which took place in the late 1970s and early 1980s. The one exception is the consumption of drilling fluids. Demand will be limited due to the low level of new drilling activity in Western Europe.

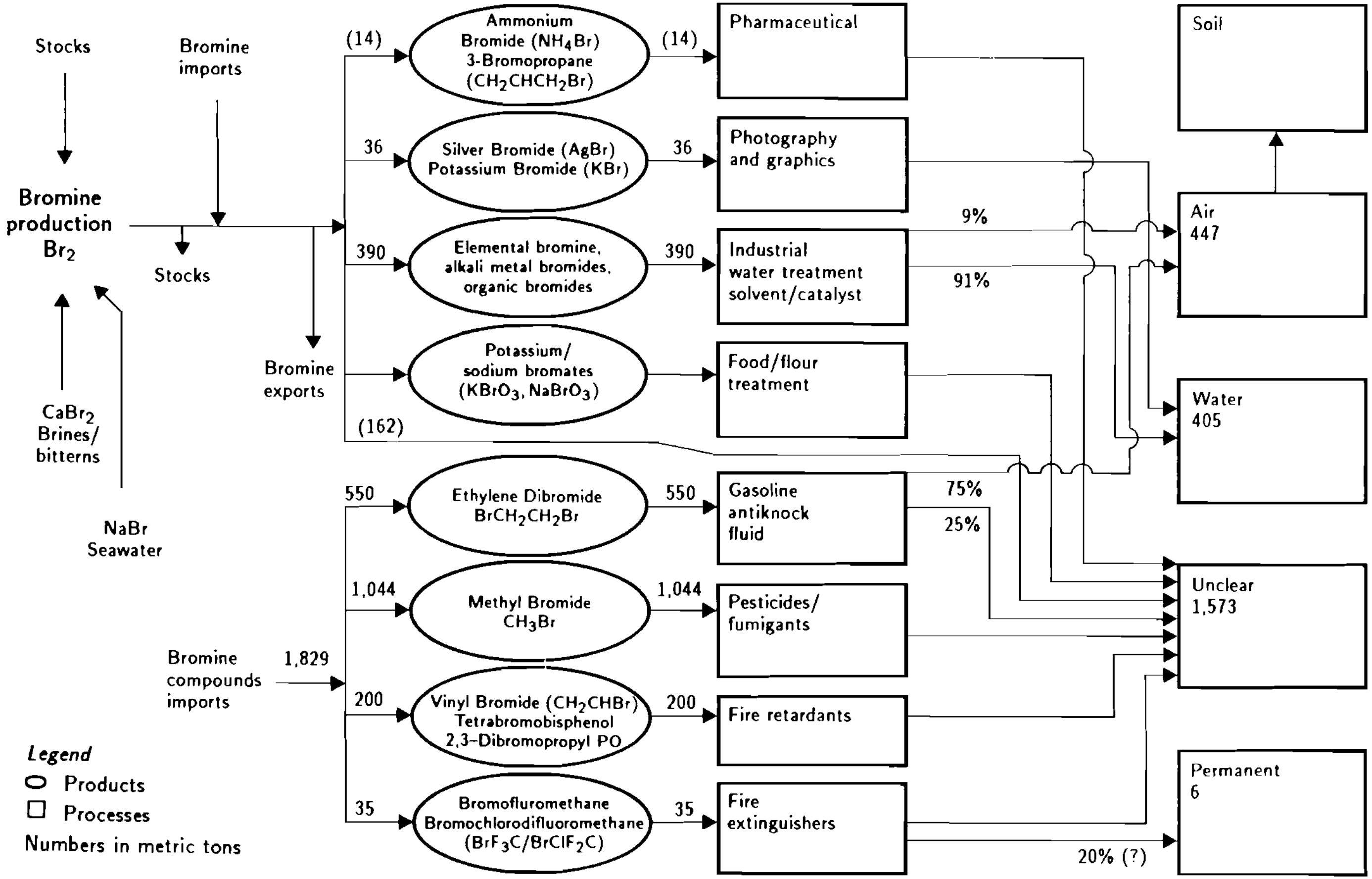


Figure 2.8. Bromine consumption in the Netherlands in 1984/85 (tons).

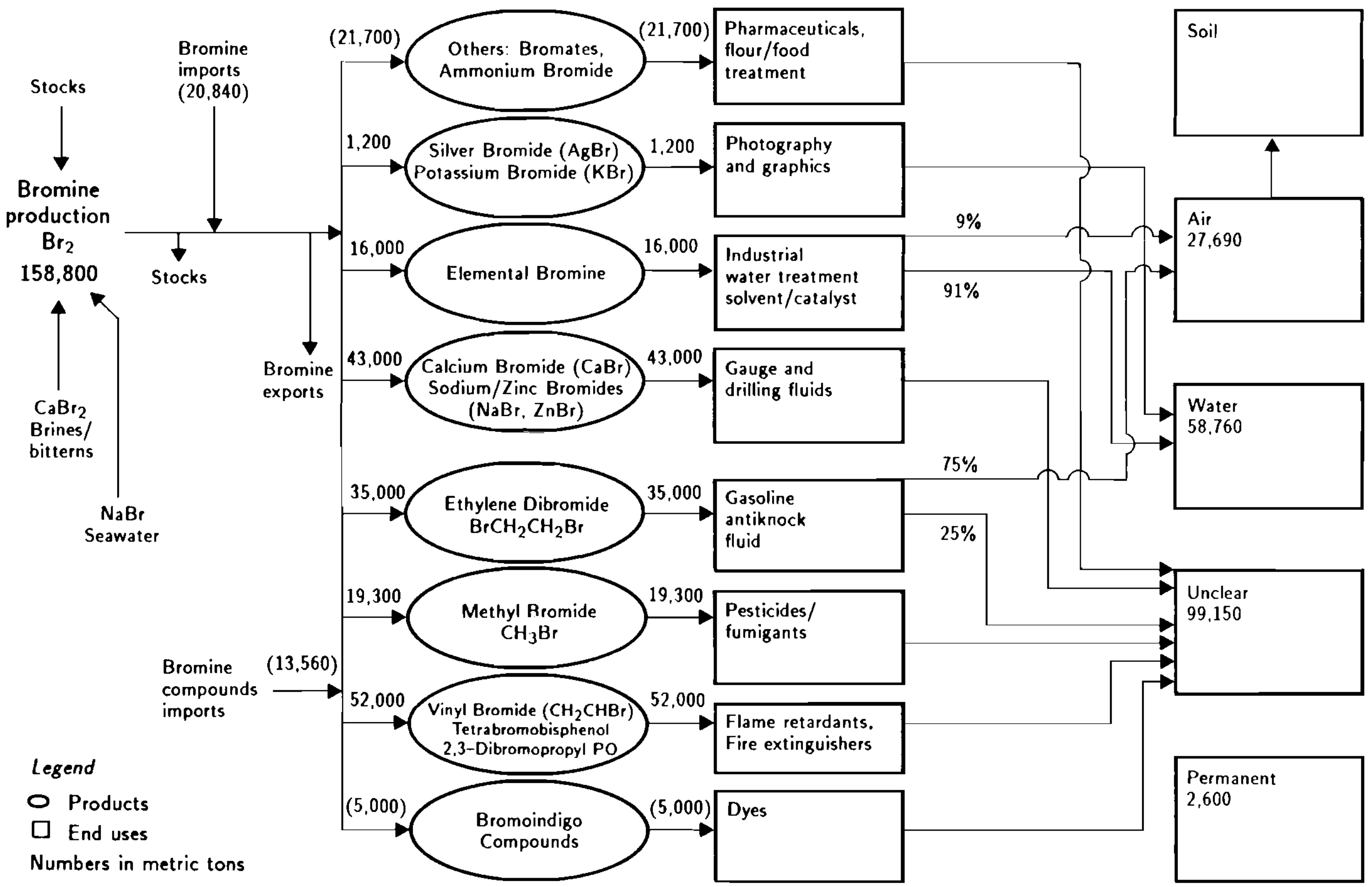


Figure 2.9. Bromine consumption in the USA in 1985 (tons).

Table 2.7. Releases of bromine compounds in the Netherlands in 1984–5 (metric tons).

	Air	*Water*	*Permanent*	*Unclear*	*Total*	*Percentage of total*
Gas (EDB)	412			138	550	22.62
Firestuffs			6	229	235	9.67
Pesticides/fumigants				1,044	1,044	42.95
Photography (AgBr)		36			36	1.48
Industry/sanitary	35	355			390	16.04
Pharmaceuticals		14			14	0.58
Drilling fluids					0	0.00
Other				162	162	6.66
Total	447	405	6	1,573	2,431	100.00
Percentage of total	18.39	16.66	0.25	64.71	100	–

Table 2.8. Releases of bromine compounds in the USA in 1985 (metric tons).

	Air	*Water*	*Permanent*	*Unclear*	*Total*	*Percentage of total*
Gas (EDB)	26,250			8,750	35,000	18.12
Firestuffs			2,600	49,400	52,000	26.92
Pesticides/fumigants				19,300	19,300	9.99
Photography (AgBr)		1,200			1,200	0.62
Industry/sanitary	1,440	14,550			16,000	8.28
Dyes					5,000	2.59
Drilling fluids		43,000			43,000	22.26
Other				21,700	21,700	11.23
Total	27,690	58,760	2,600	99,150	193,200	100.00
Percentage of total	14.33	30.41	1.35	51.32	100	

What impact will the shift in consumption patterns have on the environment? The link between consumption and environmental releases is the most difficult area to quantify. For instance, it is known that for EDB consumed in gasoline, 75 percent of the bromine is emitted to the air in the form of $PbBr_2$ or other Pb-Cl-Br compounds, and 25 percent goes into sewers, landfills, or incinerators with waste oil. Application of soil fumigants in agriculture releases bromine into the air within the first few days, but the exact amount is unknown. Use of grain fumigants releases bromine to surface and ground waters due to the extensive washing required. Bromine used for sanitary, industrial, or photographic purposes ends up in surface waters. Flame retardants are the most difficult to trace as the product lifetimes are unknown, but the assumption here is that most retardants are disposed of in landfills or incinerated with waste plastics, clothing, etc. Fire extinguishers also depend on the product lifetime, but the assumption here is that ten percent of the bromine is in permanent storage with unused extinguishers. The use of calcium bromide, sodium bromide, and zinc bromide in drilling fluids appears relatively harmless as these salts are inert

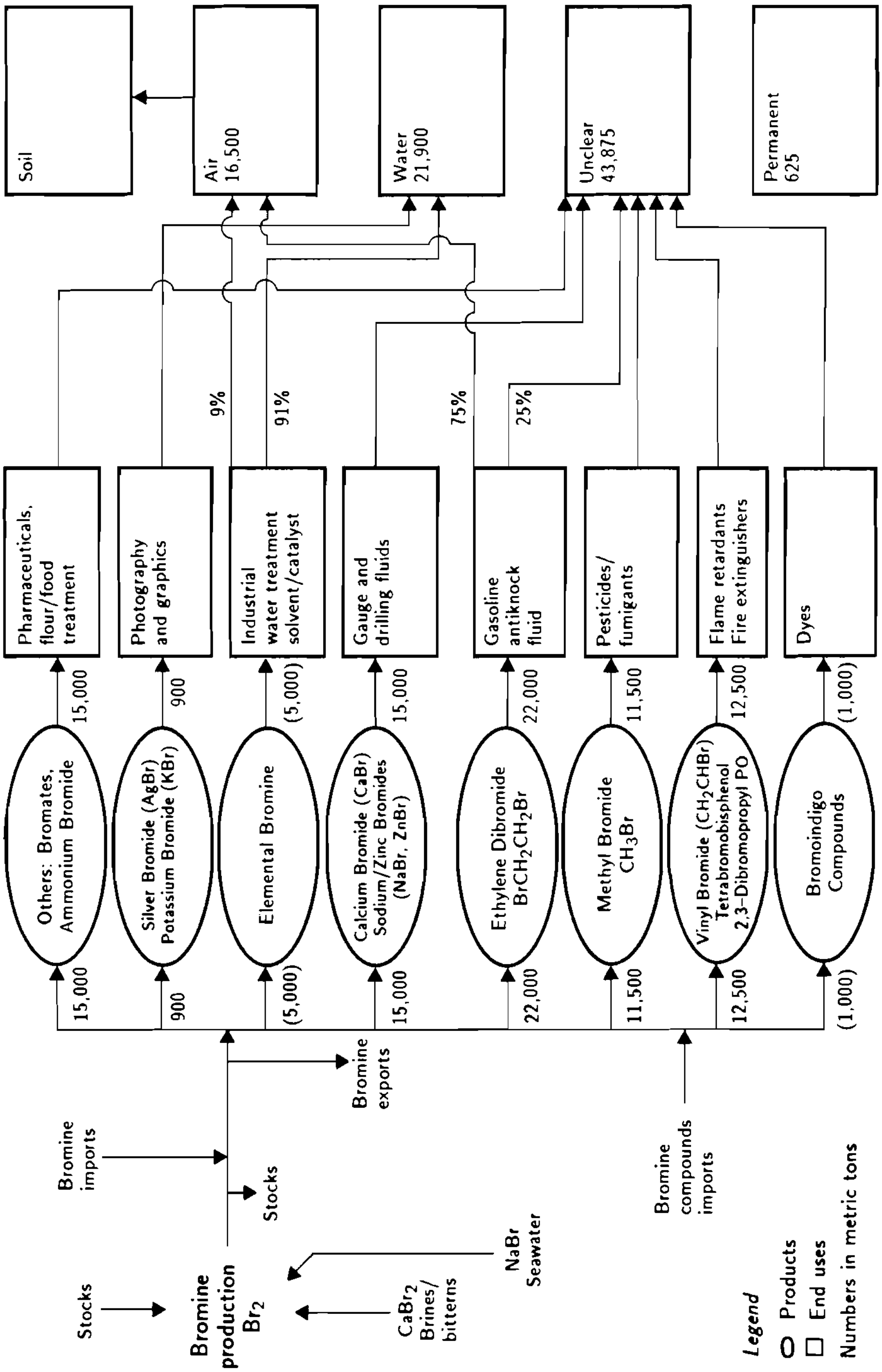


Figure 2.10. Bromine consumption in Western Europe in 1985 (tons).

Table 2.9. Consumption of bromine in Western Europe in 1985 (metric tons).

	Air	*Water*	*Permanent*	*Unclear*	*Total*	*Percentage of total*
Gas (EDB)	16,500			5,500	22,000	26.54
Firestuffs			625	11,875	12,500	15.08
Pesticides/fumigants				11,500	11,500	13.87
Photography (AgBr)[a]		900			900	1.09
Industry/sanitary[b]		5,000			5,000	6.03
Pharmaceuticals[c]		1,000			1,000	1.21
Drilling fluids		15,000			15,000	18.09
Other[d]				15,000	15,000	18.09
Total	16,500	21,900	625	43,875	82,900	100.00
Percentage of total	19.90	26.42	0.75	52.93	100	–

[a] Varies from 605 to 1,200 tons.

[b] Industry estimate based on very little data and also unreliable.

[c] Estimate based on worldwide use of 4,000–8,000 tons.

[d] Estimate of *other* is based on very little data; includes dyes with a usage of 30,000 tons worldwide .

and are the same constituents found in the raw material brines and seawater. It is possible that bromine will be released into groundwater aquifers near drilling sites in the form of salt bromides; the only potential problem here is contamination of freshwater aquifers by salt water.

The information and assumptions on environmental releases can be incorporated into the material balance to evaluate the potential releases of bromine into the air, water, and soil either directly or indirectly. Even so, the unclear category accounts for roughly 50 percent of all bromine consumed in the US and Western Europe, and 65–70 percent of the bromine consumed in the Netherlands. The use of bromines in firestuffs, fumigants, and pesticides is largely responsible for these unknown environmental releases and further research into these areas is necessary.

Nonetheless, the available information supports several important conclusions. Traditionally, air emissions during consumption of EDB have been the largest environmental release of bromine (industrial uses are a minor secondary source of air pollution). In the US during the 1970s and earlier, at least 46 percent of all bromine consumed went into the air in the form of $PbBr_2$ or $PbClBr$ compounds (or elemental bromine from industrial usage). This number may be higher as it does not include air emissions from the unclear category. In the Netherlands, historical air releases were lower as less EDB was consumed – only 16 percent of bromine consumed was released into the air. But, the extensive use of methyl bromide in fumigants probably releases significant amounts of bromine to the air which is not accounted for (it is in the unclear category) Accountable releases into water bodies were less than 15 percent in both countries during the 1970s. Therefore, the two historical problems have been air emissions and the question of environmental releases from bromine used in agriculture.

During the 1980s, the phase-out of leaded gasoline has significantly reduced bromine air emissions. The US decreased its bromine air emissions by two-thirds between the years 1978 and 1980, and it is likely that similar results will be seen in Europe in the next decade. In the Netherlands, air emissions have not changed yet, but are expected to decrease as leaded gasoline is phased out. On the other hand, the Netherlands has reduced its consumption of methyl bromide, which may reduce air releases as much as the phase-out of leaded gasoline. Releases to soils are not quantified, but are generally a result of fallout on roadsides from automobile air emissions. Thus, these should also decrease.

However, this good news is not the entire story as bromine production and consumption worldwide is still growing. The shift in consumption patterns during the last decade shows that other products are replacing EDB in the bromine market. Clearly, flamestuffs and drilling fluids are growing uses of bromine and will account for much of the dissipative releases in the future. Drilling fluids may not be a problem (aside from the issue of contaminating freshwater aquifers). However, there are still many questions surrounding the use of flamestuffs. What is the lifetime of these products? Are these compounds more toxic than the bromine compounds used historically? Where does the bromine end up? Possibly it may appear in the air due to incineration of plastics and other products treated with fire retardants; alternatively, the bromine may end up in landfills. In addition, the environmental implications of continued use of bromine in agriculture are unknown. Deciphering the unclear category can provide invaluable information on future releases of bromine.

Therefore, despite the virtual elimination of EDB, bromine levels in the air may not decrease and this result should not come as a surprise. Rather, the material balance shows that other end uses may emit the same net amount of bromine into the air, water, or soil. The fundamental questions become: which compounds are most toxic? And are the shifting consumption patterns beneficial for the environment? Finally, the material balance approach shows that focusing on industrial emissions for bromine is a narrow approach which does not begin to account for the air and water releases generated by the consumption of numerous bromine products.

Appendix: Bromine Chemistry

This appendix corresponds to the process-product flow charts for bromine shown in *Figures 2.3*, *2.4*, and *2.5*. Each reaction is referenced by a number on the flow charts.

Extraction:

Bromine is commercially produced by either a blowing-out process for dilute bromine concentrations as in seawater or a steaming-out process for more concentrated brines (generally over 1000 ppm). Both processes involve the following basic steps:

(a) Treatment with chlorine to oxidize the bromide to bromine.
(b) Separation of bromine vapor from solution.

(c) Condensation of bromine vapor (or reaction to form a salt or acid).
(d) Purification of bromine.

The reactions for the steaming-out process for brine and the blowing-out process for seawater are:

(1) Brines:

$CaBr_2 + 2NaCl + Cl_2 \rightarrow Br_2 + CaCl_2 + 2NaCl$
$Br_2 + FE \rightarrow FeBr_2$
$Br_2 + Fe \rightarrow FeBr_2$

Basis: 1 metric ton bromine
Brine 1,000 tons (1000 ppm bromine)
Chlorine 0.55 tons
Air variable

(2) Seawater:

$2NaBr + Cl_2 \rightarrow Br_2 + 2NaCl$
$Br_2 + SO_2 + 2H_2O \rightarrow 2HBr + H_2SO_4$
$2HBr + Cl_2 \rightarrow Br_2 + 2HCl$

A modified process for steps (b) and (c) (bromine separation from the air and acidification to condense the vapor) is sometimes used in the blowing-out process:

$$3Na_2CO_3 + 2Br_2 + BrCl \rightarrow NaBrO_3 + 4NaBr + NaCl + 3CO_2$$

$$NaBrO_3 + 5NaBr + 3H_2SO_4 \rightarrow 3Br_2 + 3Na_2SO_4 + 3H_2O$$

Basis: 1 metric ton bromine
Seawater 17,000 tons
Chlorine 0.405 tons
H_2SO_4 (96%) 2.25 tons
SO_2 0.45 tons
Air variable

(3) HBr may be formed using one of several reactions, with the first two reactions predominantly used:

$$H_2 + Br_2 \rightarrow 2HBr$$

$$H_2S + 4Br_2 + 4H_2O \rightarrow 8HBr + H_2SO_4$$

$$SO_2 + Br_2 + 2H_2O \rightarrow 2HBr + H_2SO_4$$

$$H_2SO_4 + 2NaBr \rightarrow 2HBr + Na_2SO_4$$

HBr is also formed as a by-product of organic bromine substitution reactions as in reaction (8) below.

(4) Hypobromous Acid (HOBr):

$$5Br_2 + 5H_2O \rightarrow 2HOBr + HBrO_3 + 7HBr$$

(5) Ammonium Bromide (NH_4Br):

$$NH_3 + H_2O + Br_2 \rightarrow NH_4Br + HOBr$$

(6) Ethylene Dibromide (EDB) formation reaction:

$H_2C = CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$

A new formation reaction has been recently developed in the US using a gamma ray reaction with ethyl bromide:

$HBr + C_2H_4 \rightarrow C_2H_5Br$

(7) Bromate Reactions for $KBrO_3$ and $NaBrO_3$:

$Br_2 + 4H_2O + 2NaOH \rightarrow 2NaBrO_3 + 5H_2$ (hydroxide rx.)

$3Br_2 + 3Na_2CO_3 \rightarrow 5NaBr + NaBrO_3 + 3CO_2$ (carbonate rx.)

(8) Bromine Substitution Reactions for Organic Compounds: This class of reactions involves direct substitution of hydrogen with bromine. Various catalysts are used such as iron, iron bromide, aluminum bromide, phosphorous tribromide, and iodine. Hydrogen bromide is a by-product of this reaction. An example shown here is the formation reaction of bromobenzene (C_6H_5Br):

$C_6H_5 + Br_2 \rightarrow C_6H_4Br + HBr$

(9) Bromine Addition Reactions for Organic Compounds: This class of reactions involves the direct combination of bromine (Br_2) and the parent unsaturated organic compound, e.g., ethylene ($CH_2 = CH_2$). EDB is formed using this process, as is styrene bromide (1,2 dibromoethylbenzene), the example shown here:

$C_6H_5CHCH_2 + Br_2 \rightarrow C_6H_5CHBrCH_2Br$

(10) Other Organic Bromine Reactions:

(a) Ethyl Chlorobromide (CH_2ClCH_2Br):

$2CH_2 = CH_2 + Br_2 + Cl_2 \rightarrow 2CH_2ClCH_2Br$

(b) Bromocyanide (CNBr)

$Br_2 + KCN \rightarrow CNBr + KBr$

(c) Vinyl Bromide (CH_2=CHBr)

$CHCH + HBr \xrightarrow{H_2O_2} CH_2CHBr$

(11) Bromine Inorganic Reactions: The inorganic reactions involve the direct addition of bromine to aluminium or an alkali metal. The primary inorganic compounds formed with bromine are LiBr and $AlBr_3$ in the following reaction:

$2Li + Br_2 \rightarrow 2LiBr$

$2Al + 3Br_2 \rightarrow 2AlBr_3$

(12) Sodium, Silver and Potassium Bromides (NaBr, AgBr, KBr): Addition reactions with HBr and sodium/silver/potasium carbonates or hydroxides, e.g.,

$NaOH + HBr \rightarrow NaBr + H_2O$

$Na_2CO_3 + 2HBr \rightarrow 2NaBr + CO_2 + H_2O$

(13) Other Bromide Inorganics ($LiBr, PbBr_3, FeBr_3$): Similar addition reactions with HBr and alkali metal carbonates or hydroxides, e.g.,

$LiOH + HBr \rightarrow LiBr + H_2O$

$Li_2CO_3 + 2HBr \rightarrow 2LiBr + CO_2 + H_2O$

(14) Zinc and Calcium Bromides ($ZnBr_2, CaBr_2$): Addition reactions with HBr and zinc/calcium carbonates, e.g.,

$ZnCO_3 + 2HBr \rightarrow ZnBr_2 + H_2CO_3$

$CaCO_3 + 2HBr \rightarrow CaBr_2 + H_2CO_3$

(15) HBr Addition Reactions for Formation of Organic Compounds: This class of reactions involves the addition of HBr to organic unsaturated parent compounds, as in the formation of (1,3) chlorobronopropane:

$CH_2 = CHCH_2Cl + HBr \rightarrow CH_2BrCH_2CH_2Cl$

(16) HBr Replacement Reactions for Formation of Organic Compounds: These reactions involve the replacement of the -OH group or a halogen group by bromine in the presence of an aluminum bromide or other catalyst, as in the formation of methyl bromide:

$$CH_3OH + HBr \xrightarrow{AlBr_3} CH_3Br + H_2O$$

CHAPTER 3

Chlorine: Anthropogenic Sources and Flows

Janet Yanowitz

3.1. Introduction

Chlorine exists as a greenish-yellow gas at ordinary temperatures and pressures. It is highly reactive and thus is never found free in nature except in high temperature volcanic gases. Chlorine combines with metals, nonmetals, and organic materials to form hundreds of chlorine compounds and is estimated to account for 0.15 percent of the earth's crust. It occurs most abundantly in soluble chlorides such as sodium chloride in sea water and rock salt, calcium chloride, and metallic chlorides.

3.2. Production

Chlorine was first produced as a pure material in 1774 by Carl Scheele who reacted manganese dioxide (MnO_2) with hydrogen chloride (HCl) to produce a pungent gas which he named ***dephlogisticated murine acid*** (later muriatic acid). It was not until 1810 that Sir Humphry Davy established that the new material was a new chemical element. The first electrolytic process for the manufacture of chlorine was patented by Charles Watt in Great Britain in 1851; in 1868 Henry Deacon produced chlorine from hydrochloric acid and oxygen.

Currently, millions of tons of chlorine are produced each year. The major commercial source of chlorine is electrolysis of alkali solutions of naturally occurring chlorides using diaphragm or mercury cells. Both types of cells make caustic ($NaOH$ or KOH), chlorine, and hydrogen.

Table 3.1. Chlorine compounds and their major uses.

Important chlorine compounds	*Major uses*
Molecular Chlorine (Cl_2)	Disinfection of water, chlorination of hydrocarbons, bleaching of pulp and textiles
Sodium Chloride ($NaCl$)	Food additive, source of chlorine
Hydrogen Chloride (HCl)	Chlorination of hydrocarbons, pickling of steel, oil-well acidizing, food processing
Potassium Chloride (KCl)	Source of chlorine
Chlorine Dioxide (ClO_2)	Disinfection of water
Sodium Chlorite [$Na(ClO_2)$] Calcium Chlorite [$Ca(ClO_2)_2$] Potassium Chlorite [$K(ClO_2)$]	Bleaching of textiles, wood and paper pulp
Sodium Hypochlorite [$Na(OCl)$] Calcium Hypochlorite [$Ca(OCl)_2$]	Bleaching and disinfection
Potassium Chlorate ($KClO_3$)	Fireworks, matches, explosives
Sodium Chlorate ($NaClO_3$)	Weed killer
Potassium Perchlorate ($KClO_4$)	Fuels for rockets and jet
Ammonium Perchlorate (NH_4ClO_4)	Propulsion
Aluminum Chloride ($AlCl_3$)	Catalyst in petroleum, drug and cosmetics industries
Titanium Chloride ($TiCl_4$)	Smoke screen agent, sky writing
Methyl Chloride (CH_3Cl)	Solvent, intermediate in the production of silicone rubbers, tetramethyl lead and quaternary ammonium compounds, refrigerant

Table 3.1. Continued.

Important chlorine compounds	*Major uses*
Methylene Chloride (CH_2Cl)	Solvent, intermediate in the production of fluorocarbons
Chloroform $(CHCl_3)$	Solvent, intermediate in the production of fluorocarbons
Carbon Tetrachloride (CCl_4)	Solvent for dry cleaning and in industry
Ethyl Chloride (C_2H_5Cl)	Intermediate in the production of silicone rubbers, ethyl cellulose and tetraethyl lead
Ethylene Dichloride $(C_2H_4Cl_2)$	Intermediate in the production of vinyl chloride, polysulfide rubbers and ethylene diamine
Epichlorohydrin $(ClCH_2CHOCH_2)$	Intermediate in the production of epoxy resins, polymerized to form epichlorohydrin rubbers
Sulfur Chloride (S_2Cl_2)	Vulcanization of rubber
Trichloroethylene (CCl_2CHCl)	Solvent for drycleaning and industrial degreasing and cleaning
Perchloroethylene (CCl_2CCl_2)	Solvent for drycleaning and industry, intermediate in fluorocarbon production
Phosgene $(COCl_2)$	Intermediate in the production of isocyanates for urethanes, fumigant, intermediate in the production of urea
Chloroprene $(CH_2CHCHClCH_2)$	Polymerized to neoprene rubber
Neoprene $(^{--}CH_2CHCHClCH_2{}^{--})$	Adhesives, coatings, wire and cable insulations, automobile fittings and protective clothing
Hypalon $(^{--}C_3H_6CHClCH_2CHSO_2ClC_2H_4{}^{--})$	Elastomer with high ozone and oxidation resistance, used in gaskets, wire and cable insulation, roof coatings, white sidewall tires and coated fabrics
Vinyl Chloride (CH_2CHCl)	Polymerized in various ways and with various monomers to make a variety of resins
$C_2Cl_2F_4$ = CFC − 114	Aerosol propellant
$CHClF_2$ − CFC − 22	Refrigerant, plastics
CCl_2F_2 − CFC − 12	Refrigerant, aerosol propellant, foam blowing
CCl_3F − CFC − 11	Aerosol propellant, refrigerant, foam blowing

3.3. Major Uses

Originally the only large scale use of chlorine was in bleaching powder (calcium hypochlorite) used in the paper and textile industries. Early in the twentieth century it became possible to ship liquid chlorine, which could be used directly for bleaching. The paper and pulp industry is still a major consumer of chlorine-containing bleaching agents.

Chlorine is an effective germicide and chlorination of drinking water supplies has become common in many parts of the developed and developing world. Chlorination has played a major part in almost eliminating waterborne diseases from those areas in which it is found. Biological growth in industrial water supplies is commonly controlled using chlorine as an antifouling reagent.

Although the amount of chlorine employed for bleaching and disinfecting has increased since it was first used, the fraction of the total chlorine production used in these areas has declined, because of the tremendous increase in the amount of chlorine consumed by the chemical industry. Chlorine is widely used in the production of organic and inorganic chemicals.

Industrially, chlorination is carried out by four general methods. The first uses molecular chlorine (Cl_2) for substitution of hydrogens. These are chain reactions, initiated by ultraviolet (UV) light, catalysts or thermal scission of the Cl_2 molecule. The second method is Cl_2 addition across an unsaturated bond. A third process utilizes HCl which also adds across an unsaturated bond or substitutes on an alcohol. The fourth method, known as oxychlorination, requires HCl, oxygen (O_2), and a catalyst. Chlorine is produced *in situ* and then can either substitute for hydrogen or add across an unsaturated bond.

Scores of chlorine-containing hydrogen compounds are of commercial and industrial importance. Generally, the presence of chlorine in an organic molecule increases the density, viscosity, and chemical reactivity of the compound while decreasing its specific heat, solubility in water, and flammability.

By far the greatest volume demand for chlorinated organics is in the plastics market. Polyvinyl chloride is the most significant example. Several elastomers, or rubbers are made which incorporate chlorine in the product, e.g., neoprene and hypalon.

The use of chlorinated materials as chemical intermediates is also important. For example, most of the ethylene dichloride produced is consumed in the production of vinyl chloride monomer. Methyl chloride is an intermediate for many materials including silicones, tetramethyl lead and higher chlorinated methanes. Benzyl chloride is a reagent in the pharmaceutical industry for the production of amphetamines, phenobarbital and many other medicinal compounds. Phosgene is reacted with diamines in the preparation of diisocyanates, these are then reacted with glycol to form polyurethanes.

Many important agricultural chemicals are chlorinated organics. Aldrin, dieldrin, chlordane and heptachlor are all chlorinated aromatic compounds. Many chloroorganics are excellent solvents for hydrophobic substances such as fats, oils and greases. Carbon tetrachloride, trichloroethylene and tetrachloroethylene are important drycleaning solvents and they also have many industrial solvent applications.

A summary of the most important chlorine containing compounds and their major uses is provided in *Table 3.1.*

3.4. Applicability of Materials-Balance to Chlorine

The structure of a materials-balance of the major flows of chlorine from manufacturing through to dissipative, consumptive end uses is shown in three process-product diagrams in *Figures 3.1*, *3.2*, and *3.3.* No quantitative data have been gathered. The reader may also refer to two material-balances, for chlorobenzenes by Johnston, *et al.* (1979) and fluorocarbons by Ayres (1978). The chemical equations for the processes described in the figures are given in the Appendix to this chapter.

Ideally, this analysis should be extended, to include all anthropogenic sources of chlorine, in particular the many uses of sodium chloride, including road de-icing and the incineration of refuse containing sodium chloride. Kaiser and Carroti (1970), have shown that burning normal refuse without the presence of plastics generates hydrogen chloride and they believe that this is due to the presence of sodium chloride in foodstuffs, leather, etc.

Many of the uses of chlorine are dissipative. Chlorinated solvents are frequently used until they evaporate. Chlorine-containing plastics are disposed of in municipal garbage heaps where they remain until they are burned or landfilled. The use of pesticides, fumigants, and fertilizers distribute chlorine containing compounds directly into the environment. The addition of chlorine to water supplies results in the formation of a variety of chlorinated organics. In general, chlorinated hydrocarbons are not found naturally and are not readily biodegradable. Moreover, they are chemically stable, and in many cases toxic to animals and plants and mutagenic or carcinogenic. Because of these characteristics, it is important to account for the chlorine and chlorine-containing compounds that we are currently producing and distributing. To rid our environment of these chemicals in the future will be an expensive and intractable problem.

Perhaps the most obvious use of the material balance on chlorine will be in the area of atmospheric chemistry. Significant amounts of chloride have been found in rainwater samples. Generally, chloride content decreases the further away the samples are taken from the sea coast except in cases of anomalously high concentrations in urban areas. The systematic surplus of chloride in rainwater in cities points to the influence of anthropogenic sources [National Resource Council (NRC), 1976].

Chlorine containing compounds in the atmosphere (for example those released during solvent use) can react chemically to be transformed into several chemically active classes of materials. Photochemical reactions that produce atomic chlorine are of great interest because they play a role in the behavior of atmospheric ozone.

Heath (1985) has found that averaged over the entire globe, about 12 percent of the ozone at an altitude of 40 kilometers (km) disappeared between 1978 and 1984. To explain the ozone decrease most hypotheses assume large

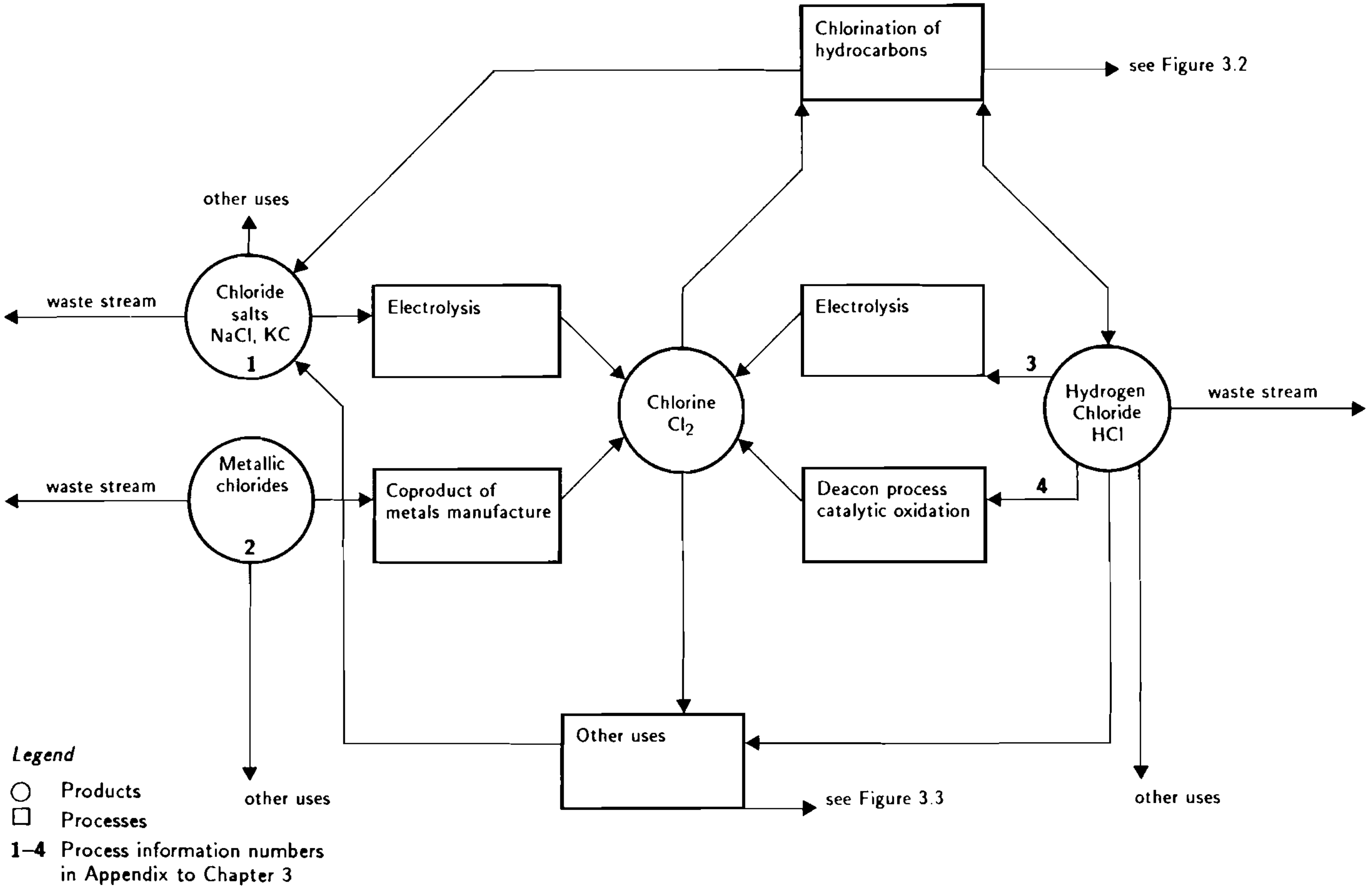
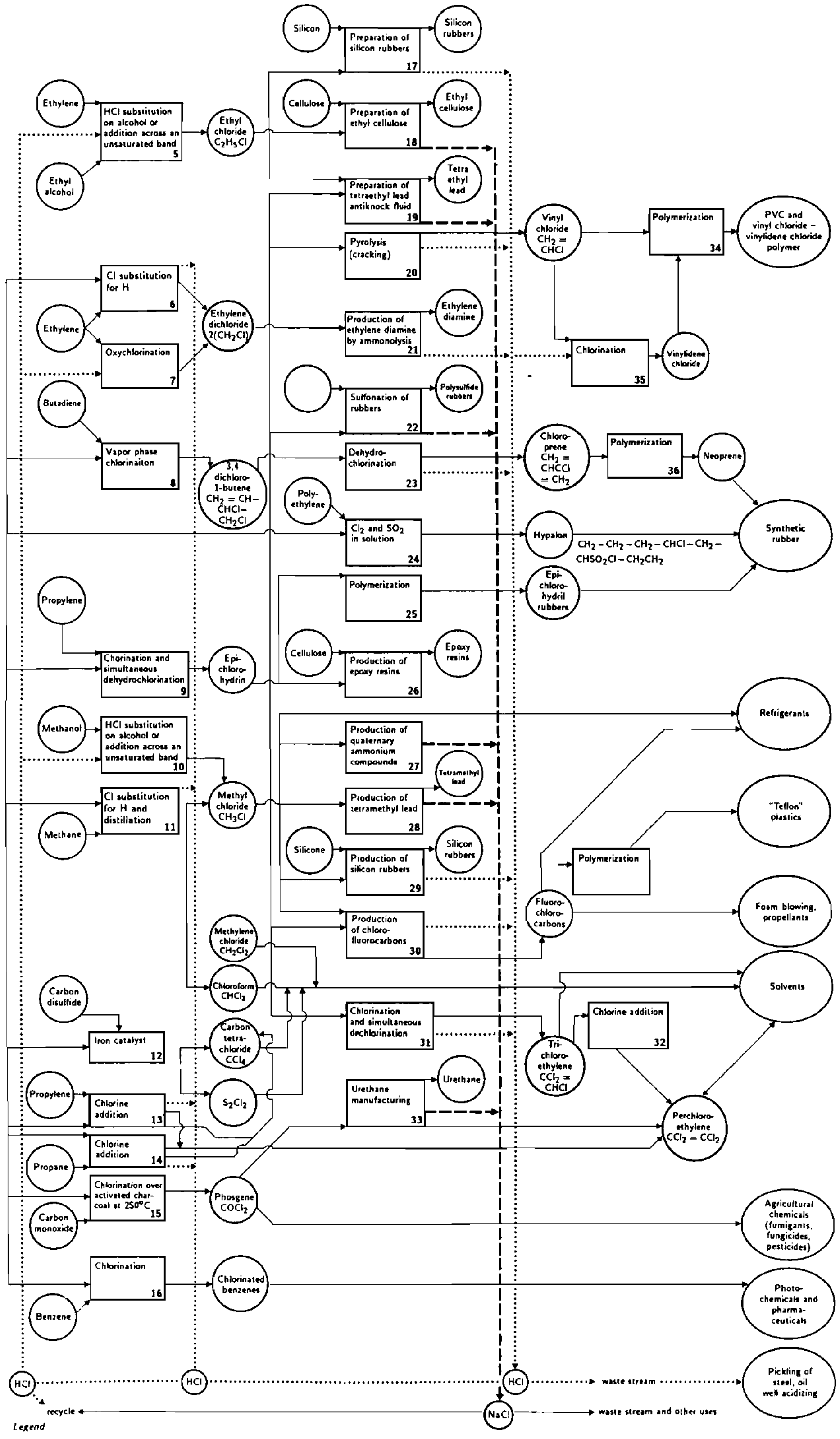


Figure 3.1. **Materials balance for chlorine.**


Silicon
Preparation of silicon rubbers 17
Silicon rubbers
Ethylene
HCl substitution on alcohol or addition across an unsaturated band 5
Ethyl alcohol
Ethyl chloride C_2H_5Cl
Cellulose
Preparation of ethyl cellulose 18
Ethyl cellulose
Preparation of tetraethyl lead antiknock fluid 19
Tetra ethyl lead
Pyrolysis (cracking) 20
Vinyl chloride $CH_2 = CHCl$
Polymerization 34
PVC and vinyl chloride - vinylidene chloride polymer
Cl substitution for H 6
Ethylene
Oxychlorination 7
Ethylene dichloride $2(CH_2Cl)$
Production of ethylene diamine by ammonolysis 21
Ethylene diamine
Chlorination 35
Vinylidene chloride
Butadiene
Sulfonation of rubbers 22
Polysulfide rubbers
Vapor phase chlorinaiton 8
3,4 dichloro-1-butene $CH_2 = CH-CHCl-CH_2Cl$
Dehydro-chlorination 23
Chloro-prene $CH_2 = CHCCl = CH_2$
Polymerization 36
Neoprene
Poly-ethylene
Cl_2 and SO_2 in solution 24
Hypalon
$CH_2-CH_2-CH_2-CHCl-CH_2-CHSO_2Cl-CH_2CH_2$
Synthetic rubber
Propylene
Polymerization 25
Epi-chloro-hydril rubbers
Chorination and simultaneous dehydrochlorination 9
Epi-chloro-hydrin
Cellulose
Production of epoxy resins 26
Epoxy resins
Methanol
HCl substitution on alcohol or addition across an unsaturated band 10
Production of quaternary ammonium compounds 27
Refrigerants
Cl substitution for H and distillation 11
Methane
Methyl chloride CH_3Cl
Production of tetramethyl lead 28
Tetramethyl lead
"Teflon" plastics
Silicone
Production of silicon rubbers 29
Silicon rubbers
Polymerization
Fluoro-chloro-carbons
Foam blowing, propellants
Methylene chloride CH_2Cl_2
Production of chloro-fluorocarbons 30
Carbon disulfide
Chloroform $CHCl_3$
Solvents
Iron catalyst 12
Carbon tetra-chloride CCl_4
Chlorination and simultaneous dechlorination 31
Tri-chloro-ethylene $CCl_2 = CHCl$
Chlorine addition 32
Propylene
Chlorine addition 13
S_2Cl_2
Urethane manufacturing 33
Urethane
Perchloro-ethylene $CCl_2 = CCl_2$
Chlorine addition 14
Propane
Chlorination over activated char-coal at 250°C 15
Carbon monoxide
Phosgene $COCl_2$
Agricultural chemicals (fumigants, fungicides, pesticides)
Chlorination 16
Benzene
Chlorinated benzenes
Photo-chemicals and pharma-ceuticals
HCl
HCl
HCl
waste stream
Pickling of steel, oil well acidizing
recycle
NaCl
waste stream and other uses
Legend

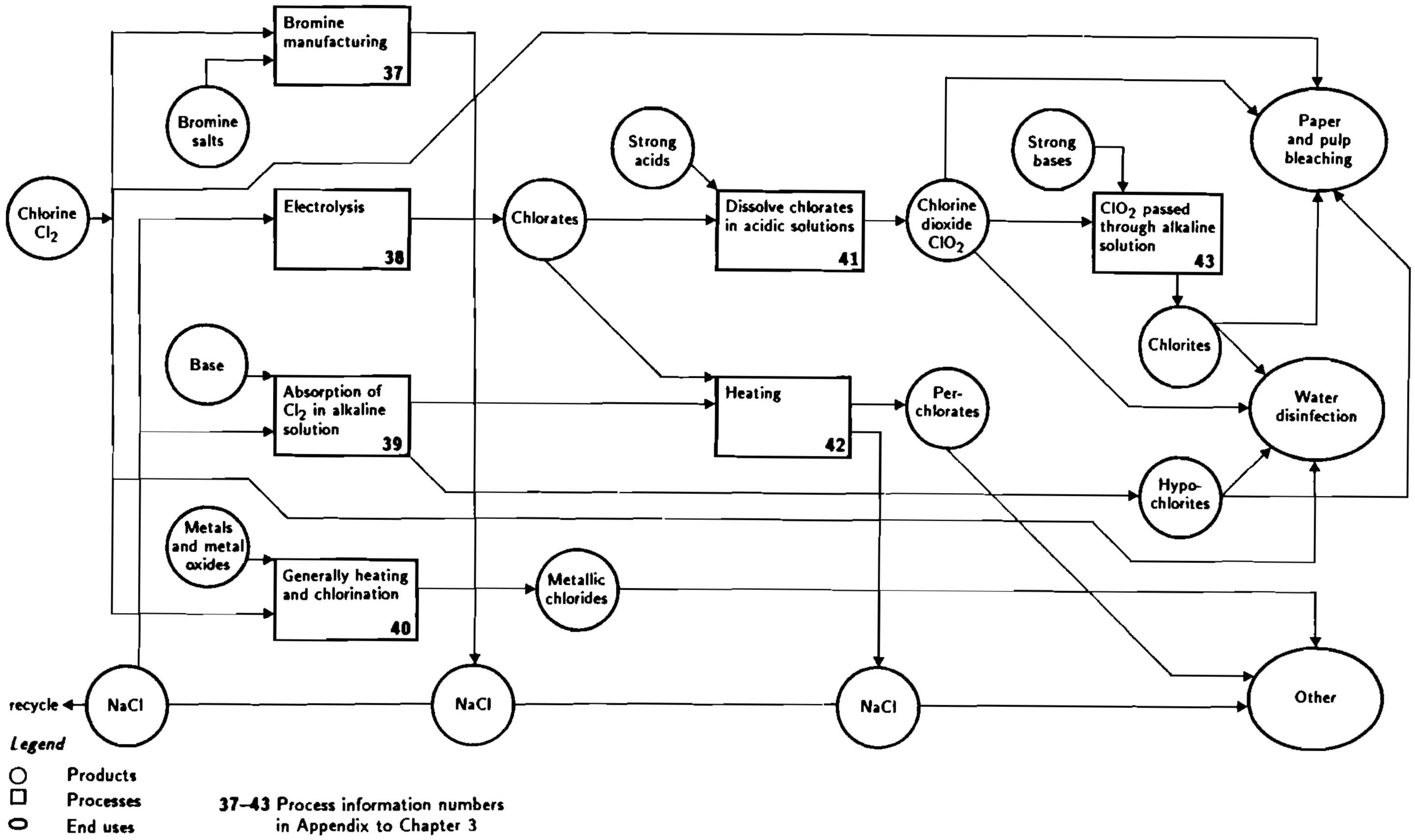


Figure 3.3. **Materials balance for inorganic chemicals from chlorine.**

concentrations of chlorine atoms in active forms that can catalyze the destruction of ozone. The loss of ozone around 40 km is particularly significant because that is the altitude where chlorine is thought to be the most potent destroyer of ozone. In the lower stratosphere, much of the chlorine is tied up in relatively inert compounds like hydrogen chloride or chlorine nitrate; above 35 km, however, solar radiation tends to break down complex molecules into simpler species. Among those simpler forms are chlorine atoms and chlorine monoxide that can catalyze the destruction of ozone (C&EN, 1986).

The atmospheric concentration of trace chlorinated gases is growing steadily. Concentrations of chlorofluorocarbon-11 (CFC-11) and CFC-12 are increasing at an astonishing rate of five percent per year. Studies have also shown that methyl chloroform and carbon tetrachloride are growing at rates of seven percent and one percent per year, respectively. According to Pauline Midgely, technical liason at ICI Americas (a major manufacturer of CFCs), these results mean that essentially all of the CFC-11 and CFC-12 that have been emitted to the troposphere are still there (C&EN, 1986). ICI's scientists have concluded that these gases are destroyed only by the photolysis reactions high in the stratosphere which are believed to be responsible for the destruction of ozone. CFC-11 and CFC-12 have life-spans in the atmosphere of about 75 and 110 years, respectively. Carbon tetrachloride has a lifetime of 50 years. Other CFCs have comparable lifetimes (C&EN, 1986).

Chlorinated hydrocarbons (CHCs) represent some of the most vexing waste disposal problems. [One of the most dramatic and troublesome cases of hazardous wastes in the recent past has been the case of poly-chlorinated biphenyls (PCBs).] The most common method of detoxifying and destroying chloroorganics has been incineration. However, the incineration of chlorinated hydrocarbons is difficult and expensive. Unsaturated chlorides are probably the most difficult organic substances to incinerate. They must be burned at very high temperatures to insure complete combustion to HCl. In practice this means that temperatures in excess of 500°C are required to combust chlorinated hydrocarbons completely (Tsang and Shaub, 1982).

The thermodynamics of CHC combustion are complex. The bulk of the chlorine-bearing species generally forms HCl and Cl_2 in the the combustion products. In practical operation, the formation of Cl_2 is undesirable because it is highly corrosive and relatively difficult to remove from stack gases. Auxiliary fuel with sufficient hydrogen content can suppress Cl_2 formation and create more HCl. However, in fuel-rich systems the presence of carbon monoxide (CO) will be unavoidable and CO can react with chlorine to form phosgene, a highly toxic substance (Tsang and Shaub, 1982).

Depending on the structure and the H/Cl ratio of the combusted materials, and the temperature of combustion, chlorine may end up in many different compounds. In fact, the combustion of chlorinated hydrocarbon compounds can produce intermediate species that are more stable than the parent chlorinated hydrocarbon. At low combustion rates, high sooting [polycyclic aromatic hydrocarbon (PAH)] formation is favored. The propensity for PAH formation increases as the chlorine content of the mixture is increased. In particular, combustion of chlorinated hydrocarbons has been reported to have the potential to produce chlorinated dioxins (Senkan, 1982).

Potential emissions of chlorine-containing gases are most commonly, and inexpensively controlled by scrubbing the main exit-gas stream and any tail-gas stream with water. However, this merely changes the problem from an airborne one to that of water pollution. Even if all of the chlorine is present as recoverable HCl, the disposal of the HCl poses problems. Fully 90 percent of the HCl produced in the US in 1972 was the by-product of chlorinations (Current Industrial Reports, 1973). According to an NRC study (1976), by-product hydrogen chloride is considerably in excess of what is recovered and reported. The fate of the excess is unknown, but it is most likely disposed of in effluent water streams.

When hydrogen chloride dissolves in water, it forms hydrochloric acid. Its action in water is similar to that of chlorine in bleaching and disinfecting operations. Both are highly corrosive. Chlorine is a strong oxidizing agent that can oxidize metals and other materials. It forms a strong acid that can dissolve the protective oxide film so that a fresh metallic surface is exposed to additional corrosion. The chloride ion is an electrolyte which accelerates electrochemical corrosion and enhances corrosion of some metals by the formation of chloride complexes. These foster solubilization and dispersion of corrosion products that might otherwise remain to form a passive barrier (NRC, 1976).

Claeys *et al.* (1980) have shown that the use of chlorine as a bleaching agent in the food and paper industries results in the formation of chlorinated organics that eventually reach aquatic ecosystems. Chlorine added to water containing nitrogenous material rapidly forms chloramines, which are known to be carcinogenic (Jolley *et al.*, 1980). Chlororganics are also formed in simulated biofouling conditions (Bean *et al.*, 1980). These products may be deposited in sediments, and may be reintroduced into water systems through microbial action (Jolley *et al.*, 1980).

Several chlorinated compounds have been identified in bleach-plant streams at concentrations that are toxic to fish (Claeys *et al.*, 1980). Many other chlorinated materials were detected at concentrations that are below lethal levels. However, all of the compounds identified in this study account for less than two percent of the total organically bound chlorine in those effluents (Claeys *et al.*, 1980). Many of the compounds found in waste streams of paper plants are mutagenic (Rannug, 1980).

Thus, ultimate disposal and detoxification of dispersed chlorine and chlorine products is not easily accomplished. Current production levels of these materials will therefore have a significant impact on the future concentrations of chlorinated materials in the environment. The materials-balance approach highlights the fact that most of the chlorine ends up in consumer products. In the absence of recycling, most of this chlorine accumulates in the environment, embodied in these products. Much of the chlorine is eventually released to the environment in forms that are harmful to the atmosphere, water systems and biota.

Appendix: Chlorine Chemistry

This appendix corresponds to the process-product flow charts for chlorine shown in *Figures 3.1*, *3.2*, and *3.3*. Each reaction is referenced by a number on the flow charts.

Chemical Equations for *Figure 3.1*

(1) $2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH$

$2KCl + 2H_2O \rightarrow Cl_2 + 2KOH$

(Encyclopedia Brittanica, 1973)

(2) $2FeCl_3 \rightarrow 2Fe + 3Cl_2$

$TiCl_4 \rightarrow Ti + 2Cl_2$

etc.

(McGraw-Hill, 1971)

(3) $2HCl \rightarrow H_2 + Cl_2$

(McGraw-Hill, 1971)

(4) $4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$

(McGraw-Hill, 1971)

Chemical Equations for *Figure 3.2*

(5) $C_2H_4 + HCl \xrightarrow{AlCl_3} C_2H_5Cl$

or

$CHCHOH + HCl \rightarrow C_2H_5Cl$

(McGraw-Hill, 1971)

(6) $C_2H_4 + Cl_2 \rightarrow ClCH_2 - CH_2Cl$

(McGraw-Hill, 1971)

(7) $2C_2H_4 + 4HCl + O_2 \rightarrow 2ClCH_2 - CH_2Cl + 2H_2O$

(McGraw-Hill, 1971)

(8) The chlorination of butadiene in the vapor phase leads to two products, 3,4 dichloro-1-butene ($CH_2 = CH-CHCl-CH_2Cl$) and 1,4 dichloro-2-butene ($ClCH_2 - CH = CH - CH_2Cl$). The latter is isomerized to the former in the presence of cuprous chloride.

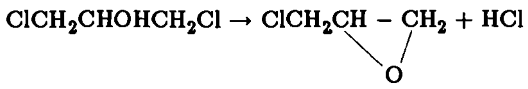
$2C_4H_6 + 2Cl_2 \rightarrow CH_2 = CHCl - CH_2Cl + ClCH_2CH = CHCH_2Cl$

$ClCH_2CH = CHCH_2Cl \xrightarrow{CuCl} CH_2 = CH - CHCl - CH_2Cl$

(Witcoff and Reuben, 1980)

(9) $CH_3 - CH = CH_2 + Cl_2 \rightarrow ClCH_2CH = CH_2 + HCl$

$ClCH_2CH = CH_2 + Cl_2 + H_2O \rightarrow ClCH_2CHOHCH_2Cl + HCl$



$ClCH_2CHOHCH_2Cl \rightarrow ClCH_2CH - CH_2 + HCl$ (with O bridging CH and CH_2)

(Witcoff and Reuben, 1980)

(10,11) The chlorination of methane results in four products; methyl chloride (CH_3Cl), methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4). If only methyl chloride is desired the preferred synthesis route is via the addition of HCl to methanol.

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$

$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$

$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$

$CH_3OH + HCl \rightarrow CH_3Cl + H_2O$

(Witcoff and Reuben, 1980)

(12) $CS_2 + 3Cl_2 \xrightarrow{Fe} CCl_4 + S_2Cl_2$

$2S_2Cl_2 + CS_2 \rightarrow CCl_4 + 6S$

(Witcoff and Reuben, 1980)

(13) $2C_3H_6 + 16Cl_2 \rightarrow Cl_2C = CCl_2 + 4CCl_4 + 12HCl$

(Witcoff and Reuben, 1980)

(14) $C_3H_8 + 8Cl_2 \rightarrow Cl_2C = CCl_2 + CCl_4 + 8HCl$

(Witcoff and Reuben, 1980)

(15) $CO + Cl_2 \rightarrow COCl_2$

(Witcoff and Reuben, 1980)

(16) Chlorination of benzene to form chlorinated benzenes. [See Johnston *et al.* (1979) for detailed materials-balance.]

(Witcoff and Reuben, 1980)

(17) $Si + nC_2H_5Cl \rightarrow (C_2H_5)_n SiCl_{(4-n)} + (n-2)Cl_2$, $(n = 1 - 4)$

$(C_2H_5)_n SiCl_{(4-n)} + (4-n)H_2O \rightarrow (C_2H_5)_n Si(OH)_{(4-n)} + (4-n)HCl$

(Witcoff and Reuben, 1980)

(18) CH_2ClCH_3 + cellulosepolymer + NaOH → cellulose$-0-C_2H_5$ + NaCl

(Considine, 1974)

(19) $4C_2H_5Cl + 4PbNa \rightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl$

(Herrick *et al.*, 1979)

Ethylene dichloride (EDC) is added to tetraethyl lead anti-knock fluids to scavenge lead in leaded gasolines. These mixtures normally contain about 30 percent EDC by weight (Considine, 1974.)

(20) $ClCH_2 - CH_2Cl \rightarrow CH_2 = CHCl + HCl$

(Witcoff and Reuben, 1980)

(21) $ClCH_2 - CH_2Cl + 2NH_3 \rightarrow H_2N - CH_2 - CH_2 - NH_2 + 2HCl$

(Herrick *et al.*, 1979)

(22) $nClCH_2 - CH_2Cl + nNa_2S_4 \rightarrow (CH_2CH_2S_4)_n + 2nNaCl$

(Considine, 1974)

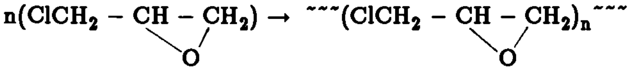
(23) $CH_2 = CH{-}CHCl{-}CH_2Cl \rightarrow CH_2 = CH{-}CCl{-}CH_2 + HCl$

(Witcoff and Reuben, 1980)

(24) $\sim\sim\sim(CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2)_n + \sim\sim\sim nCl_2 + nSO_2 \rightarrow$

$\sim\sim\sim(CH_2 - CH_2 - CH_2 - CHCl - CH_2 - CSO_2Cl - CH_2 - CH_2)_n\sim\sim\sim\sim$

(Witcoff and Reuben, 1980)

(25) 

$n(ClCH_2 - CH - CH_2) \rightarrow \sim\sim\sim(ClCH_2 - CH - CH_2)_n\sim\sim\sim$

(26) Epoxy resins are typically condensed from bisphenol A with epichlorohydrin. The chlorine in the epichlorohydrin is released during the reaction and taken up in the form of sodium chloride (Witcoff and Reuben, 1980.)

(27) $R - N - (CH_3)_2 + CH_3Cl + NaOH \rightarrow R - N^+ - (CH_3)_3 + NaCl + OH^-$

(Herrick *et al.*, 1979)

(28) $3CH_3Cl + 3PbNa \rightarrow Pb(CH_3)_3 + 2Pb + 3NaCl$

(Considine, 1974)

(29) $Si + nCH_3Cl \rightarrow (CH_3)_nSiCi_{(4-n)} + (n-2)Cl_2 \quad , \quad (n = 1 - 4)$

$(CH_3)_nSiCl_{(4-n)} + (4 - n)H_20 \rightarrow (CH_3)_nSi(OH)_{(4-n)} + (4 - n)HCl$

(Witcoff and Reuben, 1980)

(30) Production of chlorofluorocarbons. See Ayres (1978) for a detailed materials balance.

(31) $ClCH_2 - CH_2Cl + 2Cl_2 \rightarrow CHCl = CCl_2 + 3HCl$

$ClCH_2 - CH_2Cl + 3Cl_2 \rightarrow CCl_2 = CCl_2 + 4HCl$

The two products, perchloroethylene and trichloroethylene are formed simultaneously. The proportion can be controlled by reaction conditions.
(Witcoff and Reuben, 1980)

(32) $CHCl = CCl_2 + Cl_2 \rightarrow Cl_2C = CCl_2 + HCl$
(Witcoff and Reuben, 1980)

(33) $R(NH_2)_2 + 2COCl_2 \rightarrow R(NCO)_2 + 4HCl$
(Herrick *et al.*, 1979)

(34) $nCH_2 = CHCl \rightarrow$ ~~~ $(CH_2CHCl)_n$ ~~~
(Witcoff and Reuben, 1980)

(35) $CH_2 = CHCl + HCl \rightarrow CH_2 = CCl_2 + H_2$
(Witcoff and Reuben, 1980)

(36) $nCH_2 = CH - CCl = CH_2 \rightarrow$ ~~~ $(CH_2 = CH - CCl = CH_2)_n$ ~~~
(Witcoff and Reuben, 1980)

Chemical Equations for *Figure 3.3*

(37) $2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$
(McGraw-Hill, 1971)

(38) $NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2$
$KCl + 3H_2O \rightarrow KClO_3 + 3H_2$
(McGraw-Hill, 1971)

(39) $Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O$
(McGraw-Hill, 1971)

(40) $2Cl_2 + TiO_2 \rightarrow TiCl_4 + O_2$
$3Cl_2 + 2Al \rightarrow 2AlCl_3$
$3Cl_2 + Al_2O_3 + 3C \rightarrow 2AlCl_3 + 3CO$
$3Cl_2 + 2Fe \rightarrow 2FeCl_3$
etc.
(McGraw-Hill, 1971; Encyclopedia Brittanica, 1973)

(41) $2KClO_3 + 3H_2C_2O_4 \rightarrow 2ClO_2 + 2H_2O + 2CO_2 + 2KHC_2O_4$
$Ca(ClO_3)_2 + 4HCl \rightarrow CaCl_2 + 2ClO_2 + Cl_2 + 2H_2O$
(Encyclopedia Brittanica, 1973)

(42) $4KClO_3 \rightarrow 3KClO_4 + KCl$

$4NaClO_3 \rightarrow 3NaClO_4 + NaCl$

(McGraw-Hill, 1971)

(43) $2ClO_2 + 2NaOH + H_2O_2 \rightarrow 2NaClO_2 + O_2 + 2H_2O$

(McGraw-Hill, 1971)

CHAPTER 4

Sulfur: Anthropogenic Sources and Flows

Vicky Norberg-Bohm

4.1. Introduction

Sulfur is an abundant and inexpensive chemical which is used in numerous and varied compounds of commercial importance. The majority of sulfur is used to create sulfuric acid. Based on worldwide production tonnage, sulfuric acid is the largest chemical commodity. It is often called the barometer of industrial activity because of its wide use in a variety of industries and the rapid response of production to changes in consumption.

4.2. Sources and Production of Sulfur and Sulfuric Acid

Worldwide, there are currently three major sources for the production of elemental sulfur and sulfuric acid:

- Native sulfur found in the limestone caprock of salt domes, volcanic deposits, or bedded anhydrites.
- Hydrogen sulfide present in "sour" natural gas, refinery gas, and other fuel gases.
- Ferrous and nonferrous metallic sulfides.

In addition, there are two sources which currently make minor contributions and which represent potential future sources; gypsum and anhydrite, and coal.

The sources of sulfur most important in Western Europe are metallic sulfides from ores and hydrogen sulfides from various gas streams. As of the mid-1970s, about 70 percent of the sulfur production (in the form of sulfuric acid) in Western Europe was from pyrites (ferrous sulfides) and smelter waste gases (metallic sulfides). Most of the elemental sulfur produced came from the Lacq "sour gas" fields in France. A minor source of sulfur is the evaporitic anhydrite deposits in Sicily (Nriagu, 1978). Production from pyrites is declining due to the large capital investments needed for new mines. Production from secondary sources such as hydrocarbons is increasing because of stricter environmental regulations on atmospheric emissions.

Gypsum was formerly used in Europe as a source of sulfur. The method was developed by Germany during World War I to solve the problem of sulfur shortages. The process was refined and was a significant source of sulfur at least up until 1959 (Duecker and West, 1959). The process is apparently no longer commercially viable, and this is in part, due to the large energy requirements. However, because gypsum is plentiful and cheap, and also a waste product of many processes that use sulfuric acid, it may represent a future source of sulfur.

Due to stricter environmental regulations, and particularly limitations imposed on atmospheric sulfur emissions, sulfur recovered by the removal of sulfur from fossil fuels before, during or after combustion may become an important source of sulfur and sulfuric acid. Currently, an insignificant amount of the sulfur that is recovered from emissions control technologies is used for by-product sulfur production; it is considered a waste product.

Several industrial processes recover the sulfur from spent sulfuric acid and sludges. These include petroleum refining, sulfonations, pulp and paper, and explosives. This is generally accomplished by heating to decompose the sulfuric acid to sulfur dioxide, oxygen, and water. The sulfur dioxide then becomes the raw material for the manufacture of sulfuric acid. This recycling is generally done on site and is unlikely to appear in economic trade data.

Sulfuric acid is rarely used for its sulfur content, but rather for its properties as an acid, catalyst, or drying agent. There are two major processes for making sulfuric acid: the chamber process, and the contact process. The chamber process was the earlier process developed for the manufacture of sulfuric acid. Since the advent of the contact process, it has declined in importance. By 1973, only 0.5 percent of the acid produced in the US was by the chamber process. No new chamber plants have been built in the US since 1956.

Details on the industrial processes for extraction and production of sulfur and sulfuric acid are given in the Appendix to this chapter. For a more detailed history of sulfur and sulfuric acid production and use see Nriagu (1978), Duecker and West (1959), and Meyer (1977).

4.3. Major Uses

As mentioned above, sulfur and sulfuric acid are used in an extremely large number of industrial processes. This is demonstrated in *Table 4.1* from Nriagu (1978) which shows the major uses of sulfuric acid and the percentage of acid used in each category. It is notable that only one use, superphosphate and phosphatic type fertilizers, accounted for more than five percent of the total. A similar pattern is seen in the breakdown of end uses in *Table 4.2* from the US Mineral Yearbook (1984). This use pattern shows phosphatic fertilizers

Table 4.1. Distribution of sulfuric acid by end use in the United States between 1950 and 1970[a].

Use	*Percent of total*		
	1951	*1965*	*1968*
Industrial water treatment	–	0.7	0.7
Aluminum sulfate, commercial and iron-free	2.8	2.3	2.2
Chlorine dioxide	–	0.5	0.8
Tall oil	0.3	0.5	0.3
Cellophane (includes cellulose film, sheets, or products)	–	0.8	0.6
Rayon	4.9	2.7	2.1
Synthetic detergents and sodium phosphates	1.5	2.0	1.5
Superphosphate and phosphatic-type fertilizers	26.2	36.1	44.0
Ammonium sulfate, synthetic and chemical by-product	8.3	5.6	4.1
Ammonium sulfate, coke oven	–	2.1	2.2
Benzol (coke oven, light-oil refining only)	0.5	0.2	0.1
Iron and steel pickling	6.6	4.2	2.8
Nonferrous metallurgical purposes, including pickling	1.4	1.1	1.1
Copper leaching	–	1.3	1.2
Uranium leaching and processing	–	0.9	2.0
Chromium chemicals, including bichromates and chromic acid	0.6	0.3	0.3
Titanium dioxide	8.7	7.4	4.3
Other inorganic pigments	–	0.2	
Explosives, industrial and military (mixed acid included below in other chemicals)	0.8	0.4	3.1
Chlorine drying	–	0.4	0.4
Storage batteries	0.6	0.5	0.4
Petroleum catalyst, including clay treatment	1.0	1.2	1.2
Aviation and high-test gasoline, petroleum alkylate	6.5	5.4	4.6
Petroleum sulfonates (lube-oil additives)	1.0	10	1.3
Other petroleum products, excluding sulfonated hydrocarbons and detergents	4.6	2.7	[b]
Rubber, including synthetic	0.9	0.2	0.1
Alcohols	–	2.6	2.4
Dyes and intermediates	2.1	1.3	1.4
Pesticides	0.9	0.7	0.3
Hydrochloric acid	1.2	0.4	0.6
Hydrofluoric acid	0.9	2.7	2.3
Boric acids and borates	0.3	0.3	0.2
Medicinals	0.2	0.3	0.1[b]
Other chemicals	13.7	8.0	3.9
Other uses	3.5	3.0	7.3
Exports			0.1
Total	100.0	100.0	100.0

[a] The total amounts of sulfuric acid consumed in 1951, 1965 and 1968 were 14.7, 25.7, and 28.8 million tons, respectively.

[b] Part of consumption included in other uses.

(Source: Nriagu, 1978.)

Table 4.2. Sulfur and sulfuric acid sold or used in the United States, by end use (thousand metric tons, sulfur content).

Specific inductive capacity (SIC)	*End use*	*Elemental sulfur*[a]		*Sulfuric acid (sulfur equivalent)*		*Total*	
		1983	*1984*	*1983*	*1984*	*1983*	*1984*
102	Copper ores	–	–	175	341	175	341
1094	Uranium and vanadium ores	–	–	82	53	82	53
10	Other ores	–	–	45	63	45	63
20	Food and kindred products	d	d			d	d
26,261	Pulpmills and paper products	14	29	248	266	262	295
28,285, 286,2816	Inorganic pigments, paints & allied products, individual organic chemicals, other chemical products	115	127	125	109	240	236
281	Other inorganic chemicals	250	285	316	379	566	664
282,2822	Synthetic rubber; other plastic materials & synthetics	34[b]	65[b]	315	314	349[b]	379[b]
2823	Cellulosic fibers, including rayon	c	c	96	51	96	51
283	Drugs	–	–	28	24	28	24
284	Soaps and detergents	23	14	104	83	127	97
286	Industrial organic chemicals	–	–	367	307	367	307
2873	Nitrogenous fertilisers	–	–	52	85	52	85
2874	Phosphatic fertilisers	–	–	7,113	8,621	7,113	8,621
2879	Pesticides	–	–	28	23	28	23
287	Other agricultural chemicals	563	480	60	15	623	495
2892	Explosives	–	–	20	39	30	39
2899	Water-treating compounds	–	–	130	70	130	70
28	Other chemical products	–	–	67	132	67	132
29,291	Petroleum refining; other petroleum/coal products	142	278	677	676	819	954
30	Rubber and miscellaneous plastic products	d	d	31	d	31	d
331	Steel pickling	–	–	94	88	94	88
333	Nonferrous metals	–	–	11	16	11	16
33	Other primary metals	–	–	6	37	6	37
3691	Storage batteries (acid)	–	–	58	58	58	58
	Exported sulfuric acid	–	–	55	20	55	20
	Total identified	1,141	1,278	10,303	11,870	11,444	13,148
	Unidentified	801	734	427	518	1,228	1,252
	Grand total	**1,942**	**2,012**	**10,730**	**12,388**	**12,672**	**14,400**

[a] Does not include elemental sulfur used for production of sulfuric acid. [b] Includes elemental sulfur used in cellulosic fibers. [c] Included with synthetic rubber and other plastic materials and synthetics. [d] Withheld to avoid disclosing company propriety data; included with unidentified. (Source: US Bureau of Mines, 1984.)

accounting for 66 percent of the total sulfur use, petroleum refining products accounting for seven percent, and all other uses accounting for five percent or less. Although the exact percentages vary, one can assume similarly diverse uses for Europe. As will be discussed later, this makes the use of a materials-balance method quite complex.

Table 4.3 lists important end uses embodying sulfur compounds (Nriagu, 1978). More detailed tables are given in Fulton (1975). There is some overlap between these tables and also some differences. In addition, there are a few important sulfur compounds discussed by Lowenheim and Moran (1975) that do not appear in the other literature and are listed below.

- Sodium thiosulfate: used in the photographic industry, tanning leather, chemical manufacture.
- Copper sulfate: used in fungicides, algaecides, feed supplement, soil nutrient, flotation agents, electroplating, chemical intermediates.
- Calcium sulfate: used in plaster, soil neutralizer, filler and bulking agent in paints, paper and insecticides.

4.4. Process-Product Diagrams

The first step in using the materials-balance approach on a given element is to create a flow chart showing the pathways of that element through the industrial economy. The chart will indicate mineral deposits, extraction processes, intermediary processes and chemicals, and final end uses. The process product diagram for sulfur is presented in three charts *Figures 4.1*, *4.2*, and *4.3* (see Appendix to this chapter). *Figure 4.1* shows sulfur extraction and sulfuric acid production. *Figure 4.2* shows processes, intermediary chemicals and end uses for sulfur. *Figure 4.3* shows the same for sulfuric acid.

In some cases there is incomplete process data and in other cases there is no information about a given process. Nevertheless, we can examine the applicability of the materials-balance method to sulfur, and determine what data are available. From this point onward, the available data can dictate the utility of, and need for, more details on any given process.

Note that the end uses in Appendix C are more aggregated than those given in *Table 4.3*. They basically indicate the end use categories as shown in the Minerals Yearbook, 1984. This is the level of detail at which trade data can be found in the US, and is an indication of what might be hoped for in Europe. The information may be useful for the future development of the sulfur process-product diagram.*

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* Two useful references were found just as this report was being completed, Lefond (1975) and Meyer (1977). Both of these contain some process information which has not been incorporated into this report.

Table 4.3. Major uses of sulfur compounds.

Compound	*Uses*
Native sulfur	Fungicides and insecticides; soil conditioners; compounding and vulcanizing rubber; fertilizer; manufacture of matches and gun powder.
Molten sulfur	Solvent; sulfur-sodium battery; cement in construction panels; improving the quality of asphalt; highway marking paint; rigid foamed sulfur for various applications; manufacture of dyes and pigments; manufacture of free-machining steel; polymerization inhibitors.
Hydrogen sulfide	Manufacture of sulfuric acid or elemental sulfur; preparation of other metal sulfides; syntheses of sulfolane, thiophenes, thiols, mercaptans, and other thioorganc compounds; laboratory reagent in qualitative analysis.
Sulfur chlorides	Chlorinating and sulfurizing agents; in additives to extreme pressure lubricants; production of Artgum erasers; drying agent for coatings of ink, paint, or varnish; cold-vulcanize articles made of rubber sheets; synthesis of acid anhydrides; catalysts in chlorination of organic compounds.
Thionyl chloride	Preparation of fatty acid chlorides; preparation of pharmaceuticals and dyes (e.g., antihistamines, vitamin A palmitate, pyrethrum); dehydrating agent; chlorosulfurating agent; production of disinfectants and surfactants.
Sulfur dioxide	Manufacture of sulfuric acid; production of sulfite pulp; bleaching and antichlorinating agent; food preservative; fumigant for animal and vegetable products; extractant and precipitant in manufacture of commercial and food proteins; treatment of water supplies and boiler waters;

4.5. Applicability of Materials-Balance to Sulfur

The process-product diagrams presented above show only some of the anthropogenic sulfur emissions. They concentrate on the industrial processes which use sulfur or sulfuric acid as intentional and desired inputs into the process. On a global basis, these are not the largest anthropogenic contributions of sulfur. They come instead from fossil fuel combustion and from ore smelting. The anthropogenic sulfur cycle is shown schematically in *Figure 4.4*. Ivanov and Freney (1983) estimate that globally 113 teragrams (Tg) (tera = 10^{12} = T) of sulfur is emitted to the atmosphere in the combustion of fossil fuels and the smelting of ores; 28 Tg are used for fertilizer production, and 28 Tg are used by other chemical industries. Thus, 33 percent of the sulfur extracted from the lithosphere is used in industrial processes, half of this being used in the manufacture of fertilizer. While industrial sources do not represent the majority of the

Table 4.3. Continued.

Compound	*Uses*
	cleaning filter beds and wells; inert atmosphere in magnesium metallurgy; decolorize beet sugar juice; production of starch from corn; surface alkali neutralizer in glass manufacture; preparation of chrome liquor for leather tanning; refrigerant in mechanical refrigerators; antichlor in textile processing, ore flotation, etc.; low-cost reagent for manufacture of many chemicals.
Liquid SO_2	Reaction medium; extractant (e.g., in Edeleanu petroleum refining process); solvent in batteries.
Sulfuric acid	
Dithionites	Textile operations, including dyeing, printing, and stripping; bleaching of wood pulp, soap, sugar, molasses, and glue.
Sulfonates	Catalysts; emulsifying agents in detergents; lubricating oil additives; insecticides; manufacture of phenolic compounds, pharmaceuticals, tanning agents, and pesticides;
Sulfoxides	Polmerization and spinning solvent; reaction medium; cleaning solvent for industrial plants.
Sulfonamides	Synthesis of diuretics and other sulfa drugs; production of the sweetening agent saccharin.
Chloromethanethiols	Agricultural fungicides.
Sulfur dyes	Dyestuffs, and in manufacture of pigments, particularly for garment industry.
Sulfuric acid esters	Excellent solvents; pesticides; alkylation reactions; intermediates in preparation of alcohols.
Carbon disulfide	Rayon and nylon manufacture; processing chemicals; rubber industry; production of cellophane.

(Source: Nriagu, 1978).

anthropogenically mobilized sulfur, they contribute a significant fraction and thus raise concern over the final environmental destination of this sulfur.

Sulfur emissions are of more importance on a regional than on a global scale. There are significant differences among European countries in the contribution to anthropogenic sulfur emissions from non-combustion industrial sources. When looking at Western Europe, the countries with large pulp and paper industries and relatively low coal use for electricity generation show a much different picture than the global average. *Tables 4.4* and *4.5* show the trend of emissions in Finland and Sweden. The emissions from industrial non-combustion sources in 1983 represent 52 percent and 32 percent of the total sulfur emissions for Finland and Sweden, respectively. Also, the percentage of total emissions from non-combustion sources have been increasing and are expected to continue to increase. It is important to note that the above data for Finland and Sweden are for atmospheric emissions only, while the global estimate included all

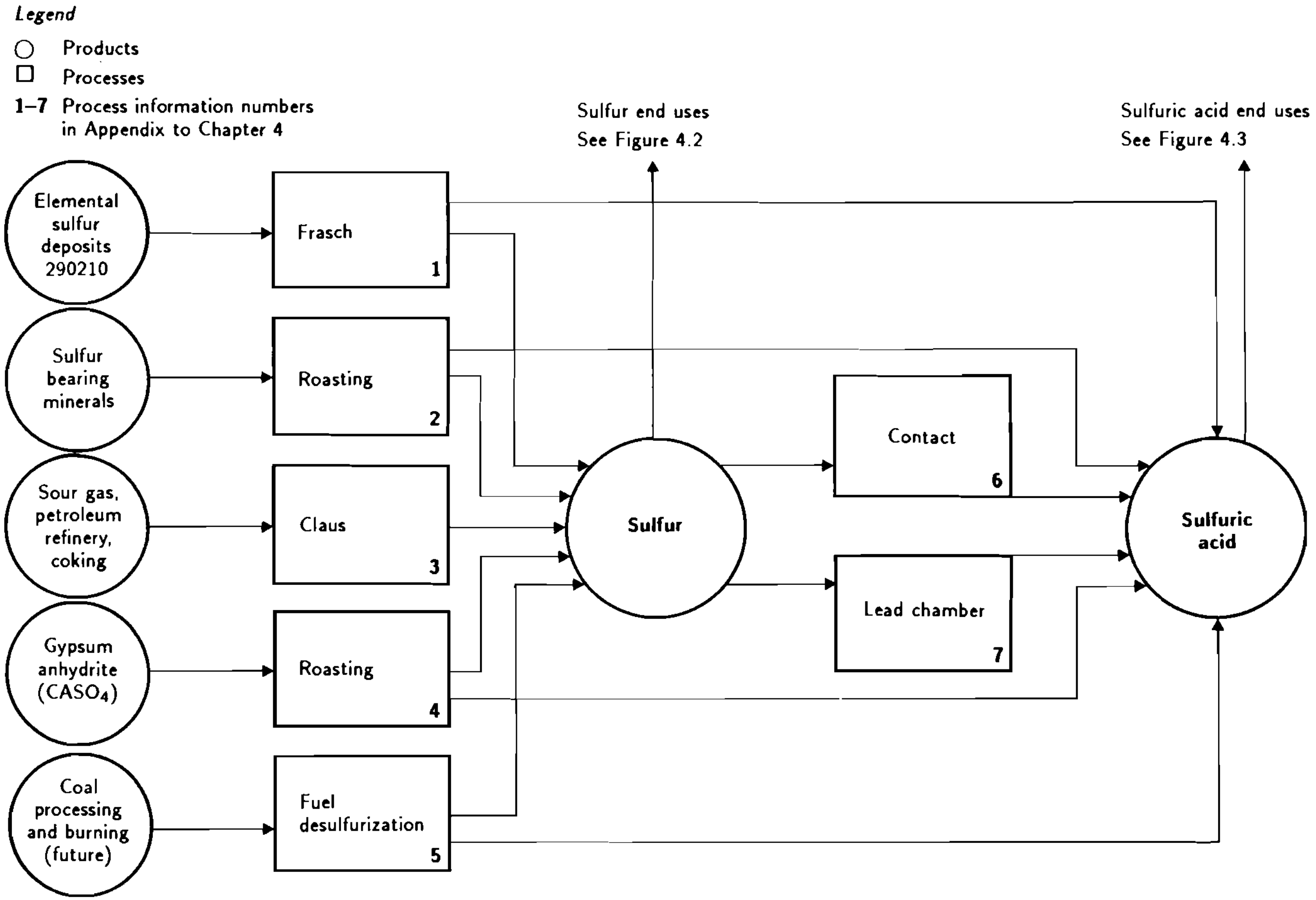

Figure 4.1. Extraction of sulfur and production of sulfuric acid.

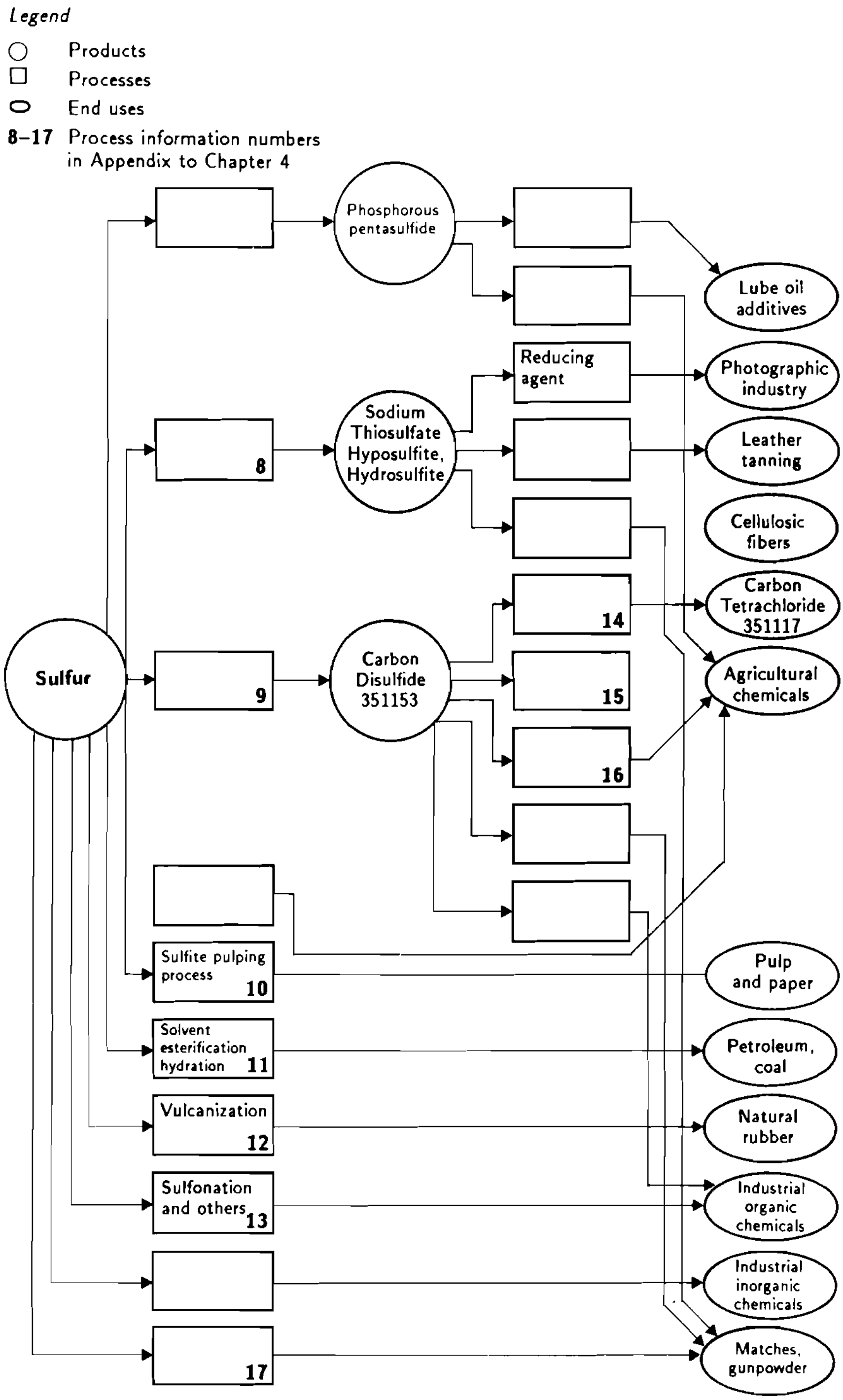

Figure 4.2. **End uses of sulfur (excluding sulfuric acid).**

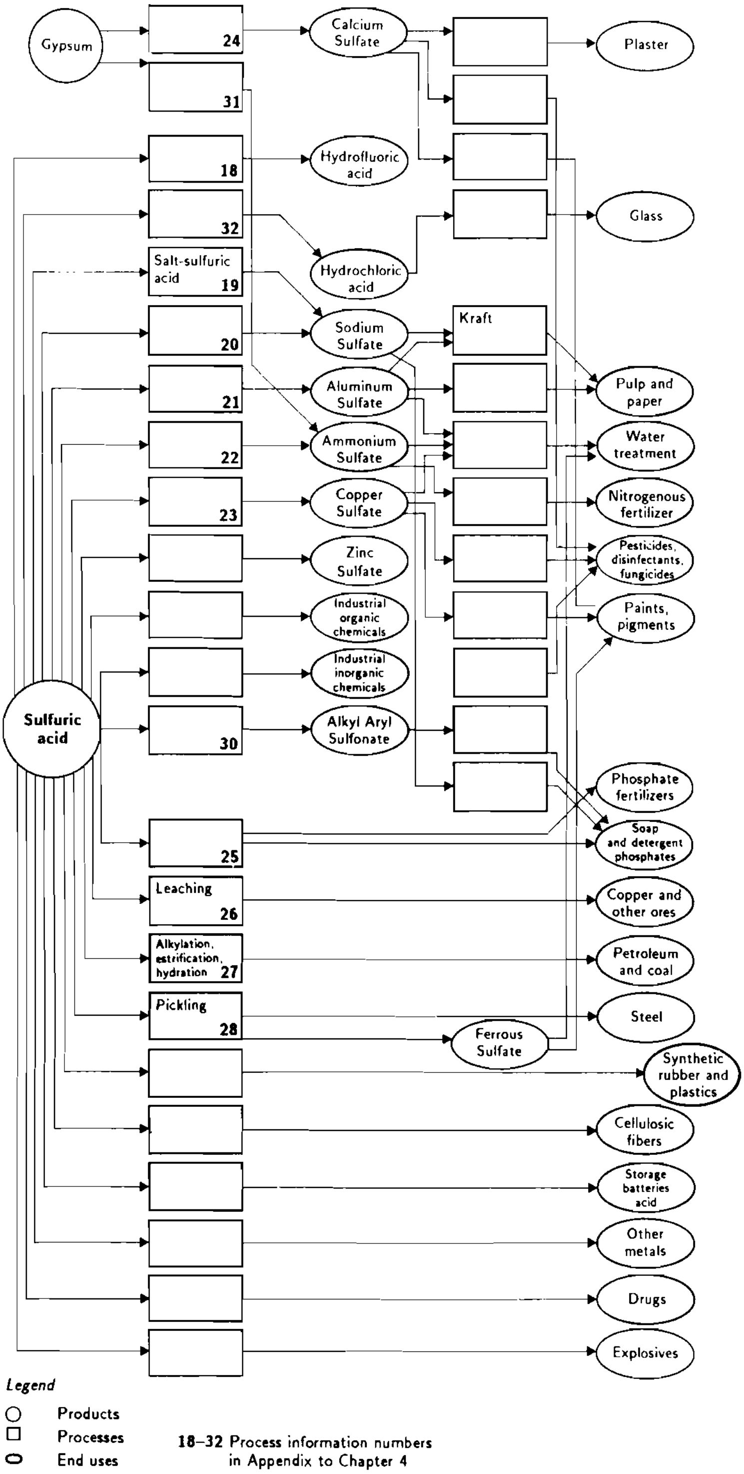

Figure 4.3. **End uses of sulfuric acid.**

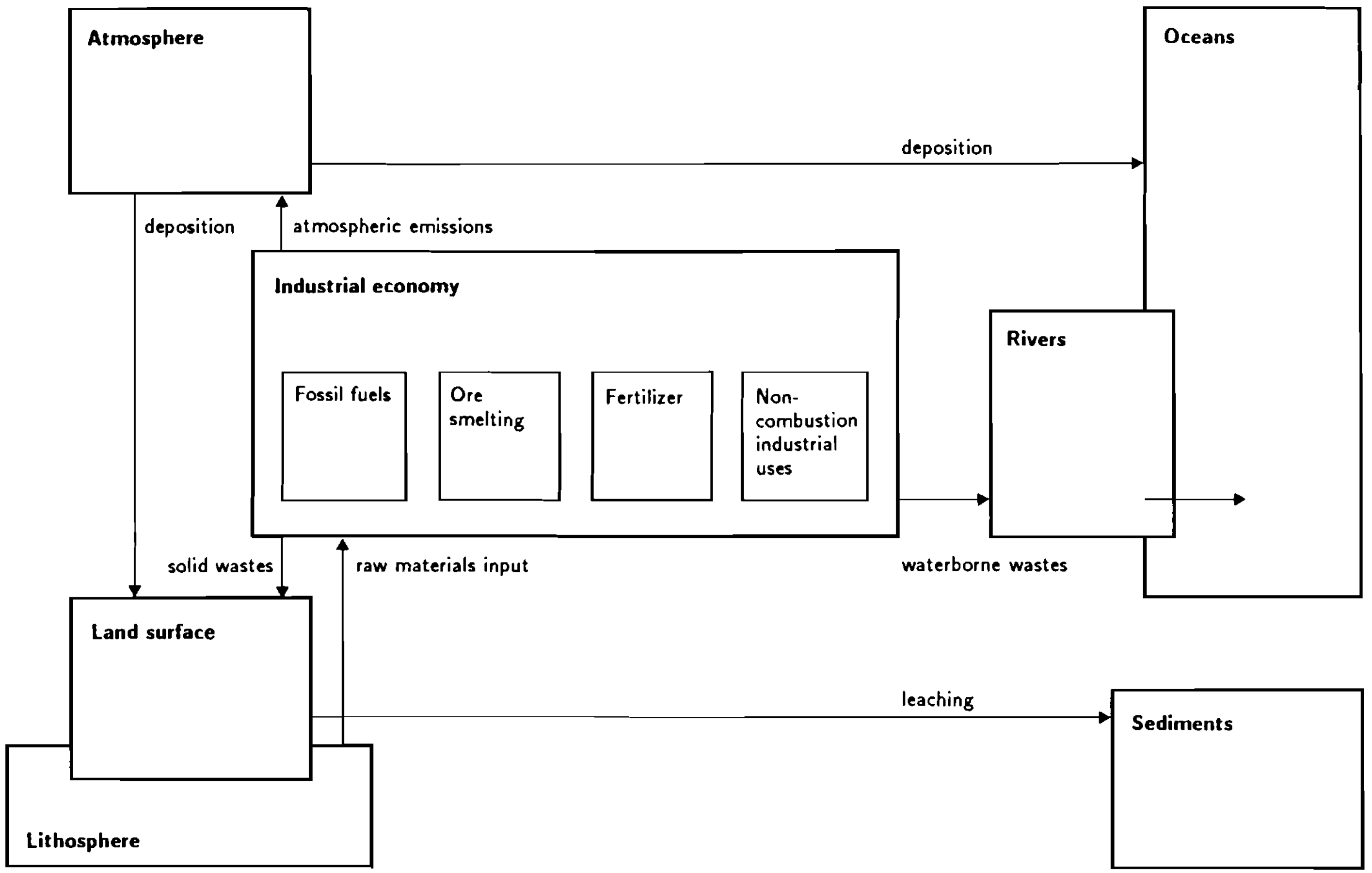

Figure 4.4. Anthropogenic sulfur cycle.

Table 4.4. Summary of sulfur emissions in Finland for 1980, 1983 and 1985 and estimated emissions for 1993 and 2000.

	Emission of SO_2 *in thousand tons*				
Source of emission	*1980*	*1983*	*1985*	*1993*[a]	*2000*[a]
Fuels	329	171	213	186	150
Oils	246	119	122	87	70
Coal	80	46	84	85	65
Peat	3	6	7	14	15
Manufacture of chemical pulp	104	75	70	52	42
Sulphate pulp	43	41	45	35	25
Sulphite pulp	52	24	15	7	7
Semichemical pulp	8	10	10	10	10
Other processing industry	151	111	92	55	48
Oil refining	60	34	30	20	18
Basic chemical and metal industry	87	73	62	35	30
Other industry	4	4	–	–	–
Total	584	357	375	293	240
Reduction compared to 1980 (in percent)		39	36	50	59

[a] Estimated

(Source: Ministry of the Environment, Finland, 1986)

Table 4.5. Sulphur dioxide emissions in Sweden in 1,000 tonnes.

Emission source	*1950*	*1955*	*1960*	*1965*	*1970*	*1975*	*1980*	*1983*
Industrial processes	230	240	220	290	235	230	155	98
Combustion of oils	80	180	320	480	680	453	338	187
Combustion of coal and coke and other solid fuels	170	120	100	40	10	2	3	17
Total	480	540	640	810	925	685	496	302

(Source: National Swedish Environmental Protection Board.)

sulfur mobilized by the industrial economy. The percentages of airborne emissions from industrial sources in Finland and Sweden thus represent only part of the total sulfur which is cycled through the environment by industrial processes.

Table 4.6 compares the sulfur mobilized by the industrial economy in Western Europe for non-combustive uses, the atmospheric sulfur emissions from combustion, and the total anthropogenic sulfur budget. The percentage of sulfur utilized by the industrial economy (non-combustion uses) is much higher than the global average given by Ivanov and Freney. For Western Europe as a whole, industrial uses account for just over half of the total sulfur budget.

Table 4.6. Sources of anthropogenic sulfur in 1980 [kilotonnes of sulfur (Kt S)].

	Atmospheric emissions[a]					
Country	*Combustion*	*Industrial*	*Industrial/ Total*	*Sulfuric acid consumption*[b]	*Industrial sulfur consumption*[c]	*Industrial sulfur/ Total sulfur*[d]
Austria	147	30	17%	101	119	45%
Belgium/Luxemburg	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, FRG	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 (TAP) 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 and coke production). It was not possible to divide this data from the TAP Project into combustion and non-combustion emissions for this sector.

[b] Data from UNIDO Trade Data

[c] Assumes 85% of industrial sulfur is sulfuric acid.

[d] Total sulfur is the industrial sulfur plus combustion emissions.

The above analysis indicates that the details of the industrial economy and a materials-balance approach for sulfur may be quite interesting. If one looks at atmospheric emissions only, it can be argued, with the exceptions noted above, that sulfur wastes from industrial sources are on an order of magnitude lower than those from fuel combustion sources, and therefore do not warrant further study. However, when looking at the total anthropogenic sulfur budget for Europe, the industrial non-combustive uses are approximately half of the total budget and are significant for almost all of the Western European countries.

Having concluded that the industrial use of sulfur is a significant portion of the Western European anthropogenic sulfur budget, we now ask if it is an environmental hazard? 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 and what is not recycled becomes a waste.

Currently, sulfur does not appear to be a problem pollutant in large international rivers. Direct releases of sulfur-bearing effluents have been almost eliminated through environmental regulation. However, humans have had an impact on the sulfur concentration in rivers. It is estimated that in Europe man-induced sulfur runoff is between two and eight times the natural flow (Husar and Husar, 1985). This raises the questions of the long-term environmental impacts of this increased level of sulfur in rivers and how much of this increased concentration is due to non-combustion industrial sources.

Much of the sulfuric acid used in industry which is not recycled (and not discharged to the atmosphere) is reduced to the solid forms of calcium sulfate and calcium sulfite. There is little in the literature on the land-based disposal of sulfur wastes from industriae processes. The lack of information in texts about sulfur and the environment (Ivanov and Freney, 1983; Nriagu, 1978; Meyer, 1977) suggests that these wastes are not a major hazard. The common opinion about non-atmospheric sulfur wastes from industry is described in a passage from Meyer (1977, pp. 161–162):

> Agricultural sulfur is applied and spread for the purpose of manipulating the sulfur soil cycle and the entire soil cycle, including that of nitrogen and phosphorus. The goal is to increase productivity of the soil. Ideally, a large fraction of this sulfur enters the biological sulfur cycle, and a fraction of it enters protein. The rest remains in the soil and eventually reenters the sediment. 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.

This common opinion leaves several questions unanswered. What will be the long term (100 years) impact of anthropogenic sulfur on the sediments? How will increased sulfur sediments interact with other natural and anthropogenioc chemicals in the hydrosphere? At what rate does this sulfur become part of the sediment? Most importantly, does this simple explanation adequately account for the flow of sulfur from industrial uses?

Clues about the potential problems caused by the disposal of calcium sulphate and calcium sulphite 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 and Luckevich, 1984; Morrison, 1982). These solid sulfur wastes pose three potential problems. One is purely waste disposal. The wastes are often in a sludge form which is difficult to dewater. The shear magnitude of wastes over the long term, say 100 years, will create disposal problems. In addition, the disposal of these wastes on land creates land which is then unusable for other purposes in the foreseeable future. The second is the possibility of environmental mobilization and 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 ground 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 problem is the possibility of sulfur gas emissions forming as hydrogen sulfide.

Concern over the disposal of solid sulfur wastes is of particular importance due to the trend toward reduced atmospheric emissions of sulfur. This trend, combined with the regulation of sulfur effluents, means that much more of the anthropogenic sulfur wastes are being disposed of on land and that we can expect this trend to continue and possibly to increase. The possibility of countering this trend in the near future is for more sulfur to be recycled and less to be mined. Research and development into possible uses for the sulfur-bearing wastes from flue gas desulfurizatioe continues. One promising use is in the cement industry (Ellison and Luckevich, 1984; Chemical Marketing Reporter, 1985).

This brief look into the hazards of solid sulfur wastes has indicated that there may be reason for concern about their final environmental destination. On the other hand, gypsum is an abundant, naturally occurring substance that many people believe is environmentally benign. Greater understanding of the environmental impact of industrial sulfur wastes will help determine whether continuing with a materials-balance analysis of sulfur should be a priority.

The materials-balance approach for sulfur has been useful by raising concern over the environmental destination of industrial sulfur. It indicates that perhaps not enough is known about the potential hazards of sulfur wastes, and that moving them from water and air to land is only a short-term solution that may cause problems in the future.

If it is determined that tracing the path of sulfur through the industrial economy would be useful, the feasibility of such a study must be examined. The numerous and diverse uses of sulfur and sulfuric acid means that the number of processes to be understood is vast. This and the fact that the sulfur is not generally embodied in end products complicate the use of the materials-balance approach. For example, only one use, fertilizers, has more than a five percent share of the sulfur end use in the US. The fact that sulfur is used for processing rather than being embodied in a product (i.e., it is a potential point source pollutant rather than a non-point source) complicates the materials-balance approach because not only is it necessary to know the manufacturing process, but it is also necessary to know how the waste streams are treated. What percentages of the sulfur are discharged into the air, water or land? What is their chemical form? Thus, the degree of quantification is seriously limited by the availability of data referring to the numerous pathways of sulfur in the industrial economy.

Two arguments can be made in favor of a materials-balance approach for sulfur. The first is that atmospheric emissions data for sulfur from industrial processing are considered unreliable and unverifiable for most of the European countries (Hordijk, 1987). If better estimates could be made using the materials balance approach, this would be very useful. Secondly, the materials-balance approach has identified one extremely large sector of sulfur use, fertilizer manufacturing. In this way, it has identified one area where the materials-balance approach is feasible.

4.6. Conclusion

Analysis of production data compared with emissions data indicates that in Western Europe the industrial economy contributes a major portion of the anthropogenically mobilized sulfur. Whether this sulfur will become an environmental hazard is uncertain. In addition, the difficulties of applying this approach to sulfur and the potential usefulness of this approach have been identified.

Appendix: Sulfur Processes

This appendix corresponds to the process-product flow charts for sulfur shown in *Figures 4.1*, *4.2*, and *4.3*. Each reaction is referenced by a number on the flow charts.

Processes for *Figure 4.1*

(1) Frasch Process – Sulfur from Sulfur Deposits

This process is used to retrieve sulfur from deposits in the limestone caprock of salt domes. It is used extensively in the US. It may not be significant for Western Europe, although there is a Frasch mine in Poland at Osiek, 13 miles south of Tarnolbrzeg. A modified Frasch process is used in Sicily, Poland, and the USSR to extract sulfur from evaporitic anhydrite deposits.

A well is drilled into the sulfur formation. Three concentric pipes are inserted. Superheated treated water is sent down the outer pipe where it melts the sulfur. Compressed air is sent down the middle pipe and it forces the molten sulfur-air mixture to the surface where it is pumped to heated pans which cause the air to escape.

The resulting sulfur is 99.0–99.9% pure. It may contain ash, moisture, H_2SO_4 and oil or carbonaceous materials.

Waste Streams: The superheated water is recovered from bleeder wells and is used to preheat more treated water. It is too contaminated to be re-used in the boilers. Gases emitted from melting sulfur may include sulfur dioxide and hydrogen sulfide. No details on the composition of the waste stream are available (Lowenheim and Moran, 1975; Duecker and West, 1959).

(2) Sulfur from Sulfide Ores of Iron, Copper, Zinc, and Lead

Sulfide ores are burned in an oxidizing atmosphere to produce both sulfur dioxide (SO_2) gas and a calcine which may be further treated for the recovery of the metal. Sometimes the SO_2 is the main product, sometimes a by-product.

Iron Sulfide: Pyrite and pyrrhotite are the major sulfur bearing materials used to produce SO_2. The largest pyrite deposits in Europe are in the Alentejo region of Portugal and the Huelva Province of Spain. Other major deposits include Cyprus, France, the Federal Republic of Germany, Italy, and Norway.

Basic Chemical Reactions

$7FeS_2 + 6O_2 \rightarrow Fe_7S_8 + 6SO_2$

$Fe_7S_8 + O_2 \rightarrow 7FeS + SO_2$

$3FeS + 5O_2 \rightarrow Fe_3O_4 + 3SO_2$

$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3$

The amount of sulfur recovered depends on the amount of oxygen available, and the roasting process. It is especially dependent on temperature.

The ore may contain other metallic sulfides. Secondary reactions include:

$Cu_2S + O_2 \rightarrow 2Cu + SO_2$

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

In addition, the following gaseous reaction will occur and should be kept to a minimum because SO_3 formation represents a sulfur loss.

$2SO_2 + O_2 \rightarrow 2SO_3$

Also, SO_3 will react with other metallic oxides to form metallic sulfates. This creates the undesirable results of sulfur loss to a calcine (a sulfur rich calcine is also generally undesirable).

Copper Roasting: The conditions for copper roasting are generally determined by the desired qualities of the calcine for further recovery of copper. There are three types of roasting; partial, dead, and sulfating.

Basic Chemical Reaction for Partial & Dead Roasting

$7FeS_2 + 6O_2 \rightarrow Fe_7S_8 + 6SO_2$

$Fe_7S_8 + O_2 \rightarrow 7FeS + SO_2$

$3FeS + 5O_2 > Fe_3O_4 + 3SO_2$

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

$2Cu_2O + O_2 \rightarrow 4CuO$

$4Fe_3O4 + O_2 \rightarrow 6Fe_2O_3$

For a partial roast, the gas strength will average 12–14% SO_2; for a dead roast, the gas strength will average 11–13% SO_2.

Zinc Roasting: Roasting is generally limited to zinc flotation concentrates.

Basic Chemical Reactions

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

$7FeS_2 + 6O_2 \rightarrow Fe_7S_8 + 6SO_2$

$Fe_7S_8 + O_2 \rightarrow 7FeS + SO_2$

$3FeS + 5O_2 \rightarrow Fe_3O_4 + 3SO_2$

$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3$

$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$

As with copper, the desired calcine generally determines the roasting procedure, and the resulting sulfuric acid concentrate. Significant gas purification is required to remove solid, liquid, gaseous impurities, and excess water vapor.

The SO_2 created by the roasting of these ores may be converted to sulfur by either of the following reactions:

$SO_2 + C \rightarrow CO_2 + S$

$2H_2S + SO_2 \rightarrow 2H_2O + 3S$

(Duecker and West, 1959).

(3) Claus Process – Sulfur from Sour Natural Gas, Petroleum Refining, and Coking Plants (Hydrogen Sulfide)

This method is used in France at the Lacq Sour Gas Facilities. The hydrogen sulfide is produced from these products using standard saponification methods.

Basic Chemical Reactions

$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$

$2H_2S + SO_2 \rightarrow 3S + 2H_2O$

The overall reaction is: $2H_2S + O_2 \rightarrow 2S + 2H_2O$ 90% yield (Morse, 1985; Lowenheim and Moran, 1975).

(4) Sulfur from Gypsum

This method was developed in Germany during World War I to solve the problem of sulfur shortages. It has been refined and used in many European countries at least through the 1950s.

$CaSO_4 + 2C \rightarrow 2CO_2 + CaS$

$CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2$

$3CaS + CaSO_4 \rightarrow 4CaO + 2S_2$

For every ton of acid produced, a ton of Portland cement is also produced. The liberation of sulfur must be practically complete as the Portland cement must contain less than 0.5% calcium sulfide. This is accomplished through the following reactions:

$2CaSO_4 + C \rightarrow 2CaO + CO_2 + 2SO_2$

$8CaO + Al_2SiO_7 \rightarrow 2Ca_3SiO_5 + Ca_2Al_2O_5$

These reactions produce Portland Cement and 9% SO_2 gas. The gas is used for making H_2SO_4 (Duecker and West, 1959).

(5) Sulfur from Desulfurization of Coal

This is currently not a major source of sulfur. For information on processes under development see Morrison (1982) and Meyer (1977).

(6) Contact Process – Sulfur to Sulfuric Acid

Sulfur dioxide is the form of sulfur used in making sulfuric acid. It is not a traded commodity, and it is therefore considered part of the chemical process for making sulfuric acid. SO_2 is manufactured in the following ways:

- From elemental sulfur and sulfur bearing minerals.

  $S + O_2 \rightarrow SO_2$

  $2SO_2 + O_2 \rightarrow 2SO_3$

  The amount of SO_3 produced is minimized by control of the burning process. The sulfur dioxide produced from roasting sulfur-bearing minerals must be purified before being used for sulfuric acid production.

- From gaseous hydrogen sulfide (from sour gas, petroleum refining, and coking plants). This is basically the first half of the Claus process.

  $2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$

- From Gypsum. This is basically the first half of the process used to create elemental sulfur from gypsum.

  $CaSO_4 + 2C \rightarrow 2CO_2 + CaS$

  $CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2$

Basic Chemical Reactions

$2SO_2 + O_2 \rightarrow 2SO_3$

$SO_3 + H_2O \rightarrow H_2SO_4$

96–98% conversion
92–96% yield sulfur

A vanadium or platinum catalyst is required. The addition of an interpass absorption design reduces atmospheric pollution and increases the yield of SO_2 to 99.7–99.9% (Considine, 1974).

Waste Streams: Oleum (pyrosulfuric acid, $H_2S_2O_7$) is used in the process and is also created. It appears that some H_2SO_4 may be discharged to the atmosphere.

Platinum Catalyst: 1.5 to 3.5 ounces per ton of 100% H_2SO_4, 10% loss.

Vanadium catalyst: 225 to 300 lb per ton of 100% H_2SO_4, 6% to 7% loss (Lowenheim and Moran, 1975).

(7) Chamber Process for Converting Sulfur to Sulfuric Acid

No new chamber plants have been built in the US since 1956. Since 1945, all plants have used vanadium catalysts.

For information on the conversion of sulfur to sulfur Dioxide, see notes under process (4).

Basic Chemical Reactions

$$2NO + O_2 \rightarrow 2NO_2$$

$$NO_2 + SO_2 + H_2O \rightarrow H_2SO_4 + NO$$

98–99% conversion
92–96% yield sulfur

Waste Streams: Any remaining gases, including a small amount of SO_2 (Lowenheim and Moran, 1975; more detailed chemical reactions can be found in Duecker and West, 1959).

Processes for *Figure 4.2* (not all processes discussed)

(8) Sodium Thiosulfate

From soda ash and sulfur dioxide:

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$$

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

From sodium sulfite and sulfur:

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

As a by-product of sodium sulfide:

$$2Na_2S + Na_2CO_3 + 4SO_2 \rightarrow$$
$$3Na_2S_2O_3 + CO_2$$

Any excess sodium sulfide reacts with sulfur dioxide to yield sodium sulfite. The sodium sulfite can be converted to sodium thiosulfate as described above.

$$Na_2S + SO_2 + H_2O \rightarrow Na_2SO_3 + H_2S$$

As a by-product of sulfur dye manufacture:

The sodium thiosulfate filtrate from the dying process may be concentrated and crystalized (Lowenheim and Moran, 1975).

(9) Carbon Disulfide (CS_2)

From sulfur and natural gas, gas oil, or fuel oil:

$CH_4 + 4S \rightarrow CS_2 + 2H_2S$

Carbon disulfide is produced by reacting methane with vaporized sulfur at high temperatures and removing carbon disulfide from the reacted gases.

From charcoal carbon and sulfur:

$C + 2S \rightarrow CS_2$

Carbon disulfide is produced by reacting charcoal and sulfur in the presence of heat. Carbon disulfide production using charcoal or coke as the source of carbon has been almost completely replaced by the more modern plants using petrochemicals as a source of carbon. As of 1962, 85% of CS_2 production was based on natural gas (Lowenheim and Moran, 1975).

(10) Sulfite Pulping Processes

Basic Chemical Reactions for Creation of Liquor

$S + O_2 \rightarrow SO_2$

$2SO_2 + H_2O + CaCO_3 \rightarrow Ca(HSO_3)_2 + CO_2$

$2SO_2 + H_2O + MgCO_3 \rightarrow Mg(HSO_3)_2 + CO_2$

$2SO_2 + Mg(OH)_2 \rightarrow Mg(HSO_3)_2$

also → $NaHSO_3$ sodium bisulfite
→ NH_4HSO_3 ammonium bisulfite

Waste Streams: For calcium sulfite ($CaSO_4$), waste liquor cannot be recycled. $CaSO_4$ is formed in the pulping process and is a waste product. The liquor may be incinerated. Sodium and magnesium bases can be recovered, with or without sulfur recovery as an option. Ammonium bases can be burned with or without sulfur recovery as an option (Shreeve, 1967; Considine, 1974).

(11) Petroleum Refining and Petrochemicals

Sulfur dioxide is used as a solvent in the extraction process. The solvent is recirculated with small losses. Liquid sulfur dioxide is added to crude.

(12) Vulcanization of Rubber

Sulfur is added to the rubber and the mixture is heated. The sulfur cross-links with the large rubber molecules and makes it a giant organic molecule.

For one of the many possible reactions, the chemical S_2Cl_2 is used, created from the reaction:

$2S + Cl_2 \rightarrow S_2Cl_2$

(Considine, 1974).

(13) Industrial Organic Chemicals

This chemistry is quite complex. One important reaction is sulfonation.

$RH + (HO)_2SO_2 \rightarrow RSO_2OH + H_2O$

(14) Cellulosic Fibres from Carbon Disulfide

$-CH_2OH + NaOH \rightarrow -CH_2ONa + H_2O$

$CH_2ONa + CS_2 \rightarrow CH_2OCSSNa$

Viscose rayon is manufactured by steeping cotton linters or purified wood pulp with caustic soda and then xanthating the alkali cellulose with carbon disulfide. The resulting cellulose xanthate is treated with sodium hydroxide to form a colloidal viscose solution which is filtered and aged. This is treated in a sulfuric acid and sodium sulfate bath to form regenerated cellulose (as filaments or rayon sheeting), cellophane, sodium sulfate, and carbon disulfide.

Before stricter regulations, 80% to 85% of the carbon disulfide was emitted to the atmosphere, as well as large amounts of hydrogen sulfide. The hydrogen sulfide is now captured using scrubbers and the carbon disulfide is captured by adsorption on active carbon beds where it is then recovered and reused (Bhatia, 1978).

(15) Carbon Tetrachloride

$CS_2 + 3Cl_2 \xrightarrow{\text{Fe catalyst}} S_2Cl_2 + CCl_4$

$CS_2 + 2S_2Cl_2 \rightarrow 6S + CCl_4$

$6S + 3C \rightarrow 3CS_2$

Carbon tetrachloride is also produced from hydrocarbons by chlorination. It is projected that its production from carbon disulfide will decline.

(16) Organic Fungacide from Carbon Disulfide

$H_2NCH_2CH_2NH_2 + 2CS_2 \rightarrow HSCSNH\ (CH_2)_2\ NHCSSH$

$HSCSNH\ (CH_2)_2\ NHCSSH + 2NaOH \rightarrow NaSCSNH\ (CH_2)_2NHCSSNa + 2H_2O$

(17) Phosphorus Pentasulfide (P_4S_{10})

$P_4 + S_{10} \longrightarrow P_4S_{10}$

Phosphorus pentasulfide is produced in a batch operation by direct union of the elements (Lowenheim and Moran, 1975).

Processes for *Figure 4.3* (not all processes discussed)

(18) Hydrofluoric Acid

From fluorospar and sulfuric acid:

$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$

By treating fluorspar with concentrated sulfuric acid in a furnace, hydrogen flouride gas is produced. The by-product is calcium sulfate (Lowenheim and Moran, 1975).

(19) Hydrochloric Acid

From salt:

$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$

$NaCl + NaHSO_4 \rightarrow HCl + Na_2SO_4$

More than 90% of hydrochloric acid production results as a by-product of organic chlorination reactions (Lowenheim and Moran, 1975).

(20) Sodium Sulfate (Salt-Cake)

From natural brines:

$Na_2SO_4 + 10H_2O \rightarrow Na_2SO_4\ 10H_2O$

$Na_2SO_4\ 10H_2O \rightarrow Na_2SO_4 + 10H_2O$

This is the principal source in the US.

From Rayon Spin Bath:

During the spinning process, 0.5 kg of sodium sulfate is produced for each 0.45 kg of rayon spun.

By the Hargreaves-Robinson Process:

$2NaCl + SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$

93–98% yield

This process is important in Europe (Lowenheim and Moran, 1975).

(21) Aluminum Sulfate

$Al_2O_3\ 2H_2O + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 5H_2O$

Bauxite, a naturally occurring hydrated alumina, is used as the raw material. It typically contains 52–57% Al_2O_3 and one to 10% Fe_2O_3. The iron is removed from the product by a reduction reaction mostly using barium sulfide. Other reducing agents include sodium sulfide, hydrogen sulfide, sodium bisulfate or sulfur dioxide (Lowenheim and Moran, 1975).

(22) Ammonium Sulfate

From Coal Gas:

$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

Ammonium sulfate may be produced as a by-product of coking plants. Production is 7.5 to 13 kg per metric ton of coal with 95–97% recovery. The ammonia in the coal gas is made to react with the sulfuric acid. Recovery of the ammonia is by one of three methods. See Lowenheim and Moran (1975) for more details.

From synthetic ammonia and sulfuric acid:

$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

The ammonia is directly neutralized with sulfuric acid and the water is removed by evaporation. The ammonia sulfate is recovered by crystallization. The yield is practically 100%.

Other sources:

Ammonium sulfate is a potential by-product of the production of hydrogen cyanide, the leaching of ores with ammonia, and the production of some organic chemicals. As of 1975, none of these processes produced significant amounts of ammonium sulfate.

From gypsum or anhydrite:

$2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$

$(NH_4)_2CO_3 + CaSO_4\ 2H_2O \rightarrow (NH_4)_2SO_4 + CaCO_3 + 2H_2O$

(Lowenheim and Moran, 1975).

(23) Copper Sulfate:

From copper oxide ores:

$CuO + H_2SO_4 + 4H_2O \rightarrow CuSO_4 + 5H_2O$

99% yield

This is often a by-product of copper refining.

From copper and sulfuric acid:

$2Cu + 2H_2SO_4 + O_2\ (air) + 8H_2O \rightarrow 2CuSO_4\ 5H_2O$

The raw material is scrap or shot copper (Faith *et al.*, 1975; Lowenheim and Moran, 1975).

(24) Ammonium Sulfate from Gypsum

$CaSO_4 + (NH_4)_2\,CO_3 \rightarrow CaCO_3 + (NH_4)_2SO_4$

This process is used by several large producers outside the US (Considine, 1974).

(25) Phosphate Fertilizers from Sulfuric Acid

Single superphosphate:

$$Ca_3(PO_4)_2\,CaF_2 + 3H_2SO_4 \rightarrow Ca(H_2PO_4)_2 + 3CaSO_4 + 2HF$$

Wet process orthophosphoric acid:

$$Ca(H_2PO_4)_2\,CaF_2 + 2H_2SO_4 + 2H_2O$$
$$\rightarrow 2H_3PO_4 + 2CaSO_4H_2O + 2HF$$

There are many other proprietary processes for manufacturing phosphate fertilizers. When sulfuric acid is used, generally calcium sulfate will be the by-product. It is discarded as waste.

(26) Leaching of Copper and Other Ores

$$CuS + H_2SO_4 \rightarrow CuSO_4 + H_2S$$

Mine and copper oxide dumps are leached with weak sulfuric acid. Cement copper is precipitated from the resulting solutions by flowing over iron turnings. The resulting material is sent to the smelter (Considine, 1974).

(27) Petroleum Refining and Petrochemicals

Sulfuric acid is used in the following processes:

- Alkylation and dealkylation.
- Esterification of organic alcohols or acids, for example, ethyl acetate.

  $$CH_3CH_2OH + CH_3COOH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_20$$

- Hydration and hydrolysis.
  An example of this is ethyl alcohol from the ethyl hydrogen sulfate method.

  $$3C_2H_4 + 2H_2SO_4 \rightarrow C_2H_5HSO_4 + (C_2H_5)_2SO_4 + \text{aqua}$$
  $$\rightarrow 3C_2H_5OH + \text{aqueous } 2H_2SO_4$$

(Considine, 1974).

Waste Streams: Organosulfur emissions include carbonyl sulfides, carbon disulfides, mercaptans, alkyl sulfides, and thiophene and its derivatives, Bhatia (1978).

(28) Steel Pickling

Steel pickling is the preferential removal of oxide or mill scale from the surface of metal by immersion in sulfuric acid (or other acids).

Ferrous sulfate as a by-product of steel pickling:

$$FeSO_4 + H_2SO_4 + nH_2O + Fe \rightarrow 2FeSO_4 7H_2O + H_2 + (n - 14) H_2O$$

Most ferrous sulfate is produced from the waste liquor of the steel pickling process. The supply of steel pickling liquor is much greater than demand for ferrous sulfate, and is therefore a waste product. Waste pickle liquor is often neutralized with alkali and sent to slurry pits for drying. The low cost of sulfuric acid and ferrous sulfate has made it uneconomical to recover. Some ferrous sulfate is produced as a by-product from the sulfate process for titanium dioxide (Lowenheim and Moran, 1975).

(29) Kraft Process for Making Pulp

Wood chips are cooked at an elevated temperature and pressure in a white liquor, a solution of sodium sulfide and sodium hydroxide. The spent cooking liquor, known as black liquor, is separated from the cellulose, concentrated and burned to recover the cooking chemicals as sodium carbonate and sodium sulfide. About 95% to 98% of the chemicals in the liquor are recovered in the spent liquor. The chemical losses are most often replaced using salt cake, Na_2SO_4. Sometimes sodium sulfite or sulfur are used. The sodium carbonate is converted to sodium hydroxide by the addition of lime. The recovered chemicals are recycled for use in the cooking liquor.

Waste streams: Waste streams at the various stages of the kraft pulping process include alkyl mercaptans, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, carbonyl sulfide. For more detailed information about the waste streams and treatment of the wastes prior to disposal, see Bhatia (1978). It is likely that there have been significant changes in waste disposal for the paper industry since Bhatia's account in 1978.

(30) Alkyl Aryl Sulfonate

There are numerous chemical varieties. An example is sodium dodecyl benzene sulfonate.

$$C_6H_6 + C_{12}H_{24} \xrightarrow{(AlCl_3)} C_6H_5C_{12}H_{25}$$

$$C_6H_5C_{12}H_{25} + H_2SO_4 \rightarrow C_{12}H_{25}C_6H_4SO_3H + H_2O$$

$$C_{12}H_{25}C_6H_4SO_3H + NaOH \rightarrow C_{12}H_{25}C_6H_4SO_3Na + H_2O$$

85–95% yield.

As of 1975, 50% of all synthetic detergents were of this type. Other sulfur synthetic detergent types are fatty alcohol sulfates, alkyl benzene sulfonates (ABS, hard), and linear alkyl sulfanates (LAS, soft). In 1965, the detergent industry in the US voluntarily switched from ABS to LAS detergents for the domestic market due to water pollution problems. However, LAS is also a potential water pollution threat. Current information on regulation and use in Europe is needed (Lowenheim and Moran, 1975).

(31) Calcium Sulfate

$$CaSO_4\, 2H_2O + \text{heat} \rightarrow CaSO_4\, \frac{1}{2}H_2O + 1\frac{1}{2}H_2O$$

Calcium sulfate is made by calcining gypsum rock to remove three-quarters of the water of crystallization.

By-product calcium sulfate can be washed, dried and reground. It can be used in the manufacture of gypsum wallboard.

(32) Sodium Sulfate (Salt-Cake)

$2NaCl + H_2SO_4 \rightarrow 2HCl + Na_2SO_4$

98% yield.

$Na_2SO_4 + 10H_2O \rightarrow Na_2SO_4\ 10H_2O$

95% yield.

The major source of sodium sulfate is as a by-product of the salt-sulfuric acid process for the manufacture of hydorchloric acid. For other methods of manufacture and for major uses see process (20) (Lowenheim and Moran, 1975).

CHAPTER 5

Nitrogen: Anthropogenic Sources and Flows

Vicky Norberg-Bohm

5.1. Introduction

Nitrogen fixation is the conversion of molecular nitrogen (N_2) from the atmosphere to a form available for plants, animals, humans, and industrial uses. Production of synthetic ammonia (NH_3) is by far the most important industrial nitrogen fixation process. Therefore, nitrogen compounds, both organic and inorganic, can generally be regarded as derivatives of ammonia. It is for this reason that ammonia is considered the parent substance of the nitrogen system of compounds. Ammonia has been commercially important for over 100 years. It is the second largest industrial chemical by tonnage and the first by value of production. It is the most produced chemical by volume in the processing of petrochemicals.

5.2. Sources and Production of Nitrogen (Ammonia)

The first significant commercial source of ammonia, developed in the 1880s, was as a by-product in the making of manufactured gas through the destructive distillation of coal. The next development was by Fritz Haber in 1913, when he synthesized ammonia by the direct combination of nitrogen and hydrogen in the presence of a catalyst of iron oxide, plus small quantities of cerium and chromium at high pressures and temperatures. Karl Bosch adapted this process to industrial production, largely to meet the demand for ammonia for explosives during World War I. The so-called *Haber-Bosch* process is the basis for almost all the ammonia manufactured today. There have been many improvements to the basic process, utilizing various operating conditions and synthesis designs.

Variations of the process are used today with design pressures between 100 and 1000 atmospheres, and design temperatures between 200°C and 700°C.

Before World War II the major source of hydrogen for the synthesis of ammonia was the reaction of coal or coke with steam in the water-gas process. A small number of plants used electrolysis of water or coke-oven by-product hydrogen. Since World War II the major source of hydrogen has been natural gas obtained by steam-hydrocarbon reforming. Other sources in order of importance are oil, coal, lignite, and the electrolysis of water. The partial oxidation process is also used to produce hydrogen from natural gas and other liquid hydrocarbons. As of 1975, 75 to 80 percent of the world supplies of hydrogen for the manufacture of ammonia came from hydrocarbons, 65 percent of these were from natural gas.

Another source of nitrogen has always been air. Originally, nitrogen was obtained either from a liquid-air separation plant or by burning a small amount of hydrogen in the synthesis gas. Modern ammonia plants eliminated these process steps by the use of secondary reforming, a process in which methane is burned in air in an amount required to produce a 3:1 mole ratio of hydrogen to nitrogen synthesis gas.

Other processes which have been used commercially for nitrogen fixation include arc processes and the cyanamide process. An example of an arc process is the Berkeland-Eyde process in which air is passed through an electric arc, often flattened or extended by a magnetic field. One percent nitric oxide (NO) is formed and then converted to nitrates by chemical procedures. Cheap electricity is a prerequisite for the industrial use of this process so it is rarely used today. In the cyanamide process, calcium carbide is reacted with the nitrogen in air to form calcium cyanamide ($CaCN_2$). The calcium cyanamide is dissolved in water to form urea and ammonia. The last cyanamide plant in the Western world closed in June, 1971.

There are several known processes for nitrogen fixation which are not currently exploited commercially. These include ionization and chemonuclear reactions to obtain oxides of nitrogen, fixation of nitrogen as metal nitrides or dinitrogen complexes of transition metals, and reducing nitrogen bound up in certain transition metal complexes to ammonia. In addition, biological fixation by nitrogen-fixing microbes through genetic engineering is being developed for agricultural applications. For more information on the *Haber-Bosch* process, including the history of process improvements and details about the process technology, see Considine (1974) and Lowenheim and Moran (1975).

5.3. Major Uses

It is estimated that ammonia and its derivatives are used in the manufacture of 2,500 industrial products. Ammonia is used in tonnage quantities in the manufacture of agricultural chemicals, explosives, solvents, dyes, resins, pharmaceuticals, and synthetic fibers. Significant amounts are used in the treatment of textiles, metals, water and rubbers, for process acid neutralization, corrosion inhibition, and commercial air conditioning. Smaller quantities are used for crop

Table 5.1. Estimates of total production of ammonia and a breakdown into uses in the United States.

	Ammonia or equivalent (1000 tons)					
Use	*1960*	*1964*	*1968*	*1971*	*1974*	*1975*
Fertilizers	3,430	5,880	9,700	9,780	11,000	12,000
Explosives	130	280	400	550	730	760
Synthetic fibers and plastics	230	530	690	980	1,420	1,550
Chemicals	180	400	630	740	800	830
Pulp and paper	30	40	80	90	90	100
Metallurgy	30	40	60	70	80	90
Animal feeds[a]	60	150	290	440	540	640
Other[b]	330	410	500	560	580	600
Export	140	150	450	590	460	300
Total	4,560	7,880	12,800	13,800	15,700	16,870

[a] Primarily as urea.

[b] Refrigeration, rubber, water treatment, detergents, textiles, dyes, etc.

(Source: Slack and James, 1979.)

Table 5.2. Major areas of ammonia consumption[a].

	Percentage of Consumption			
Consuming areas	*Fertilizer*	*Fibers and plastics Intermediates*	*Nonfertilizer*	*Total*
Ammonia-direct application	26.6	–	–	26.6
Ammonium nitrate (AN)	17.0	–	4.0	21.0
Nitric acid for non-AN uses	1.1	1.6	4.2	6.9
Urea	10.1	0.8	1.6	12.5
Ammonium phosphate	11.2	–	–	11.2
Ammonium sulfate	5.9	–	–	5.9
Nitrogen solution and mixed fertilizers	4.4	–	–	4.4
Acrylonitrile	–	2.2	–	2.2
Hexamethylenediamine	–	0.7	–	0.7
Amides and nitriles	–	–	0.6	0.6
Caprolactam	–	0.2	–	0.2
Losses (transportation, handling, and storage)	–	–	–	3.0
Miscellaneous other uses	–	–	4.8	4.8
Percentage of market	76.3	5.5	15.2	100.0

[a] Based on practice in the United States.

(Source: Considine, 1974.)

defoliation, pipe sealing, algae control, animal feeds, pest control, and bacteria control.

Worldwide, 80 percent of nitrogen is used in fertilizers and 20 percent in industrial chemical products. A breakdown of nitrogen consumption by end use for the United States is given in *Table 5.1* (Slack and James, 1979). A breakdown of nitrogen consumption by major chemicals and three aggregated end use

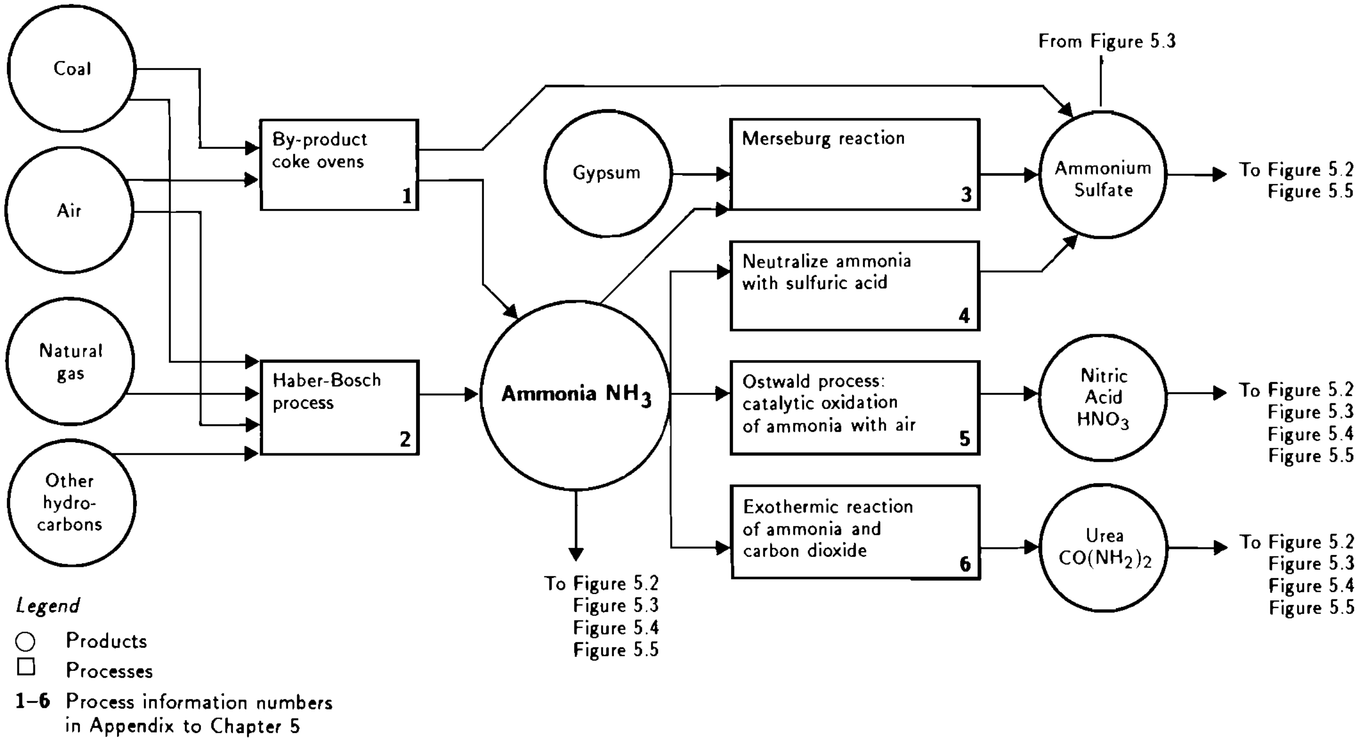

Figure 5.1. Production of ammonia and some key derivatives: nitric acid, urea, and ammonia sulfate.

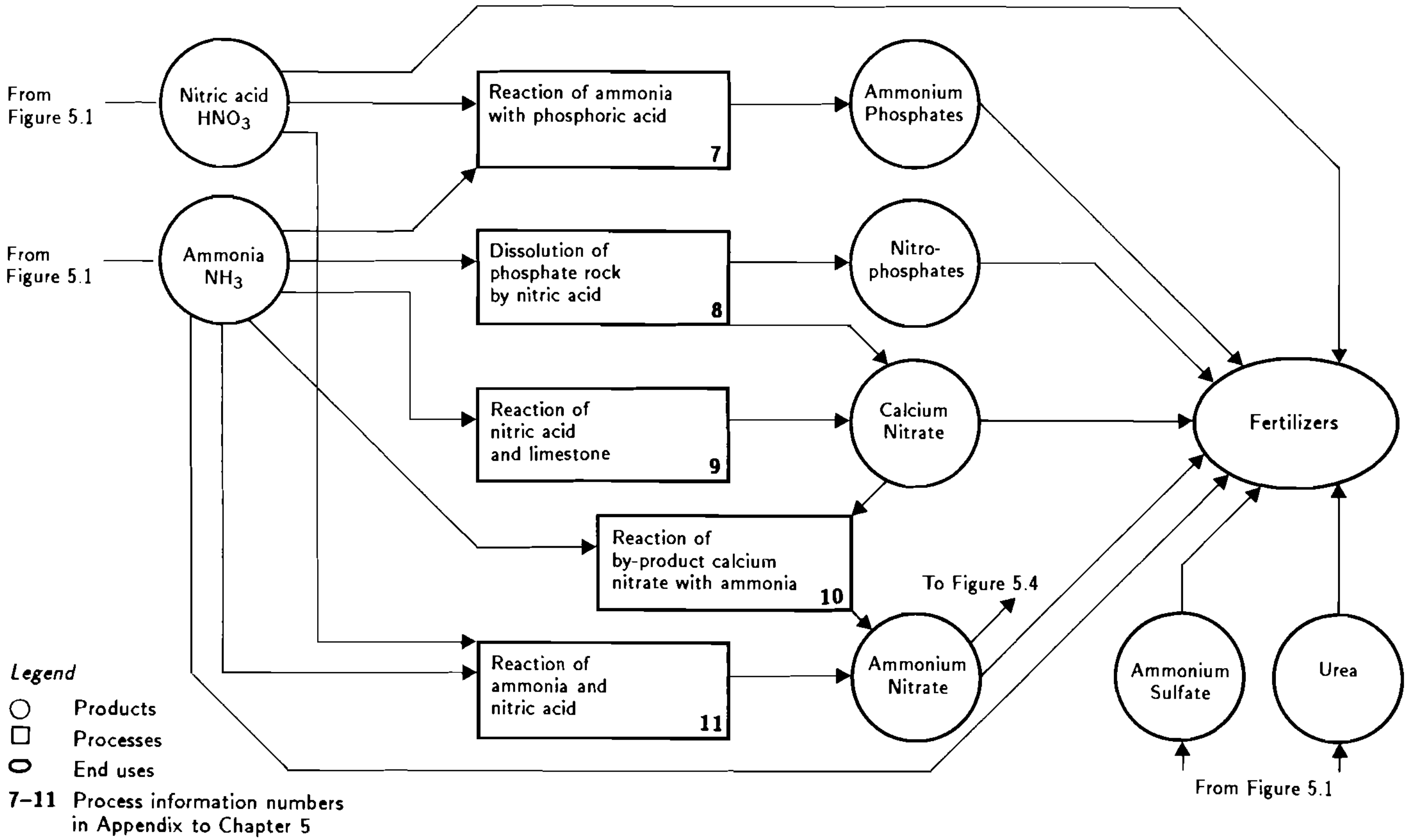

Figure 5.2. Production of nitrogenous fertilizers.

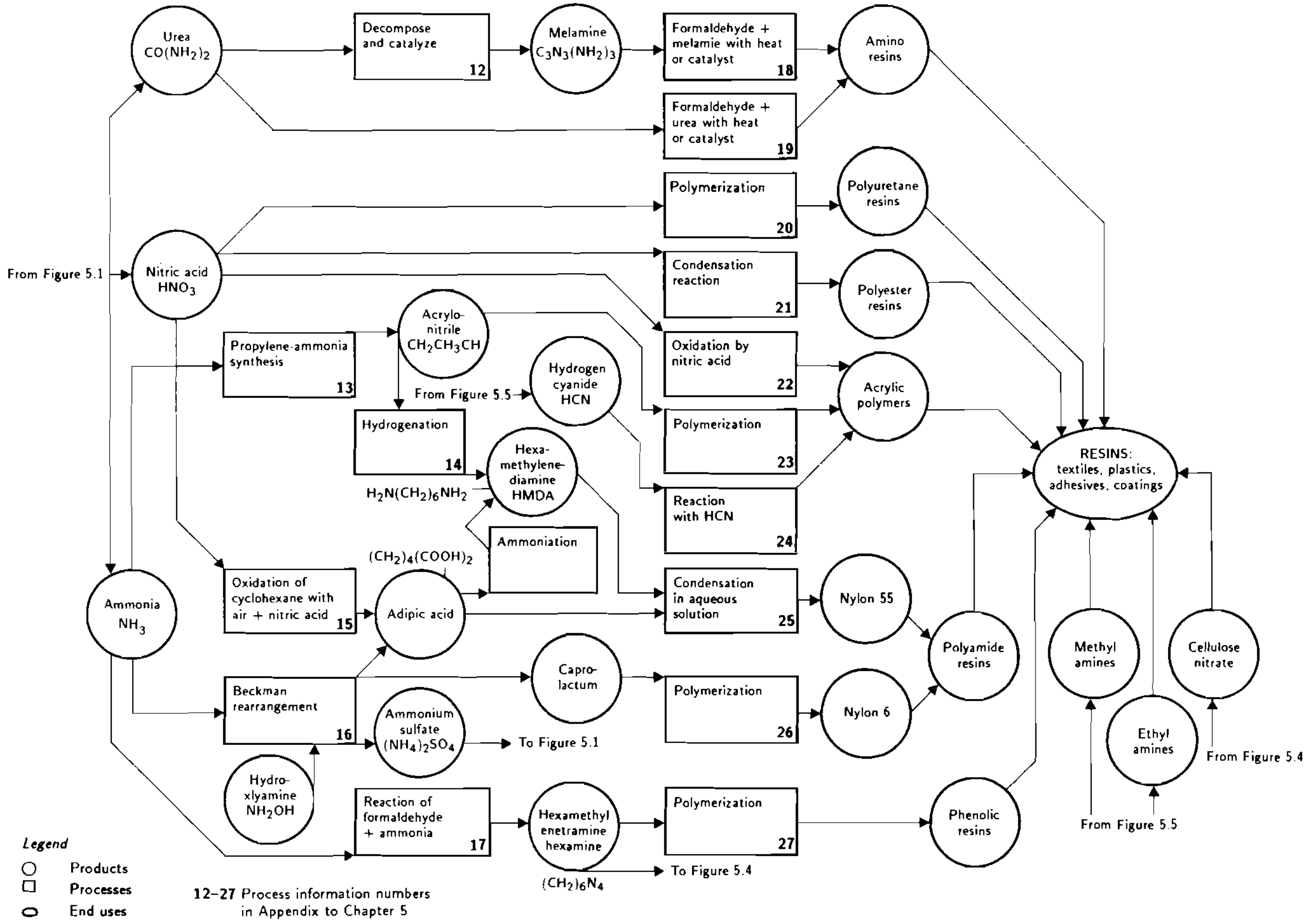

Figure 5.9. **Production of nitrogenous resins.**

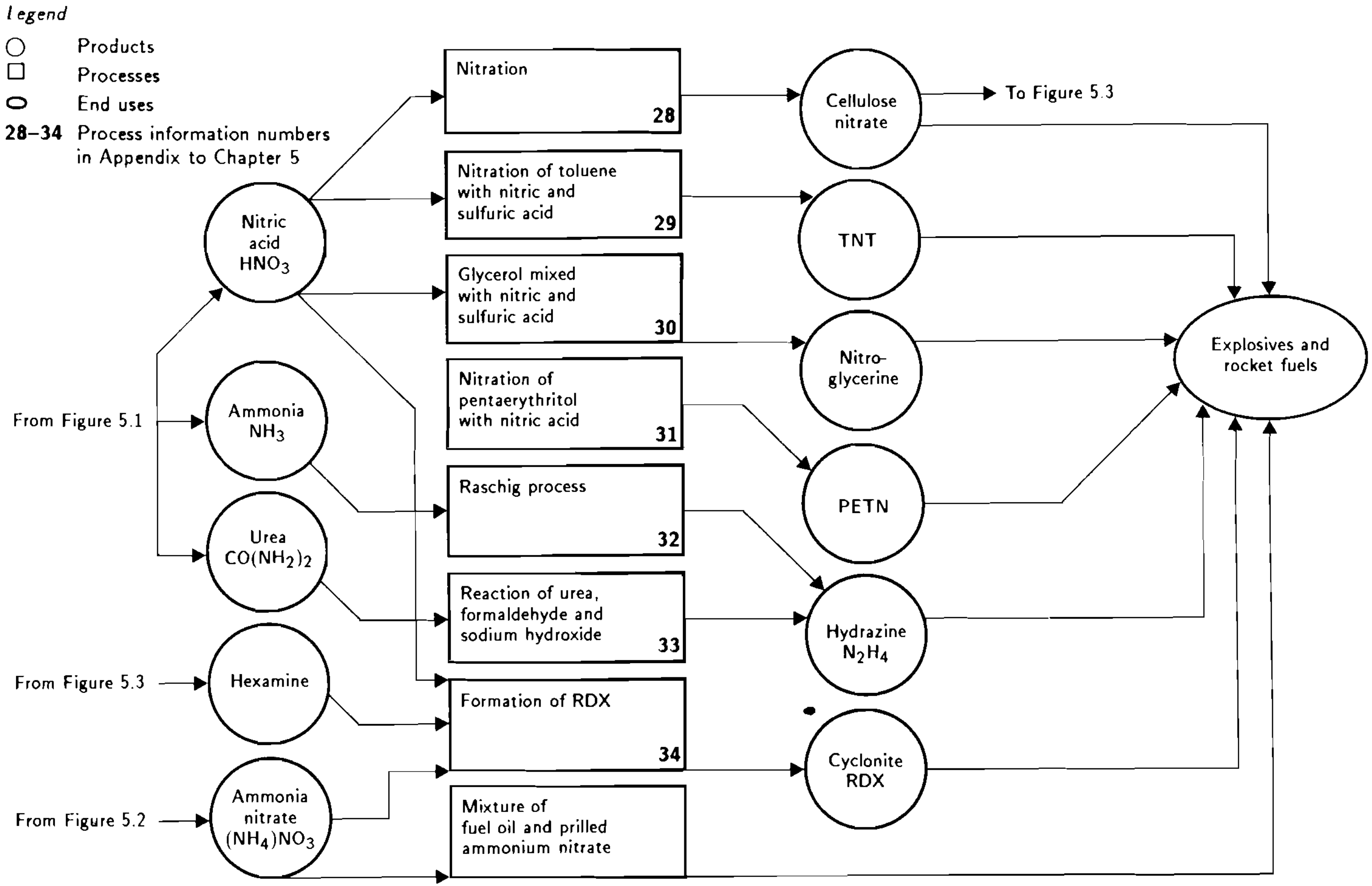

Figure 5.4. **Production of nitrogenous explosives.**

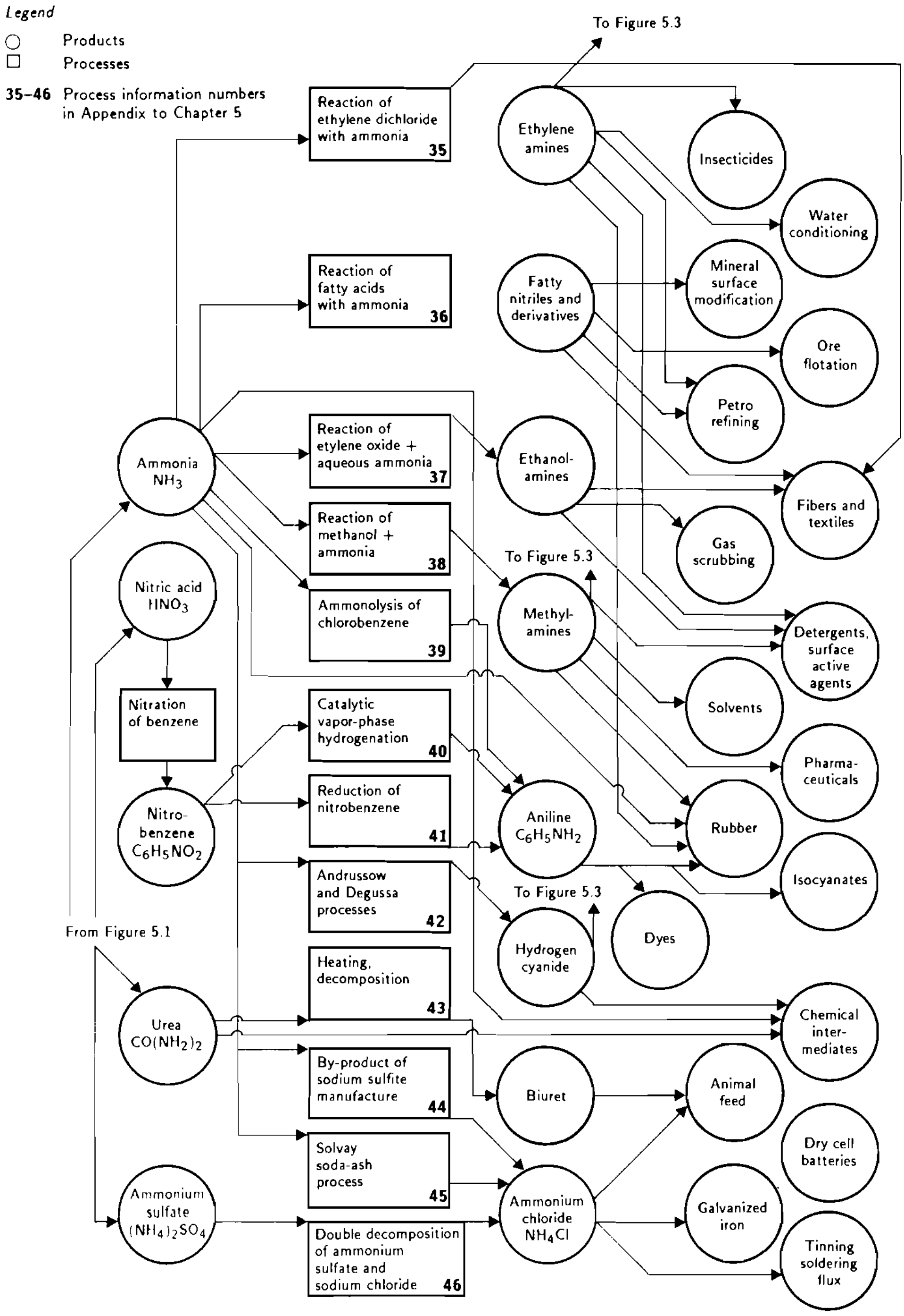

Figure 5.5. **Production of important nitrogenous compounds for end uses other than fertilizers, resins, and explosives.**

categories is given in *Table 5.2* (Considine, 1974). Major nitrogenous chemicals and their key end uses are shown in *Figures 5.1* through *5.5* which are discussed in the next section.

5.4. Process-Product Diagrams

The first step for using the materials-balance approach on a given element is to create a flow chart showing the pathways of that element through the industrial economy. The chart indicates primary production processes, intermediary processes and chemicals, and final end uses. *Figure 5.1* shows the production of ammonia and three of its key derivatives, nitric acid, urea, and ammonium sulfate. *Figure 5.2* shows the production of fertilizers; *Figure 5.3* shows the production of resins; *Figure 5.4* shows the production of explosives; *Figure 5.5* shows the production of other nitrogenous compounds and their key end uses (see Appendix to this chapter). A more detailed presentation of the material presented in *Figure 5.1* is shown in *Figures 5.6* and *5.7* and these are taken from Ayres (1978).

Appendix: Nitrogen Processes

This appendix corresponds to the process-product flow charts for nitrogen shown in *Figures 5.1* through *5.5*. Each reaction is referenced by a number on the flow charts.

Processes for *Figure 5.1*

(1) Ammonium and Ammonium Sulfate from Coal Gas:

Ammonia can be recovered from coke-oven operation, principally as aqua ammonia. Only a small amount of commercial ammonia, perhaps 1%, is from this source. The ammonia in the coal gas reacts with sulfuric acid. In the high temperature coking process, 15% to 20% of the nitrogen leaves the oven as ammonia. There are three general methods for manufacturing ammonium sulfate. In each of them the hot gases from the ovens are precooled and the gases are eventually passed through an acid bath saturator. About 25% of ammonium sulfate production is currently from this method. Until the middle of World War II, this was the major source of ammonium sulfate. An increase in demand for ammonium sulfate fertilizers during the war caused the development of the synthetic ammonium sulfate industry (Lowenheim and Moran, 1975; Slack and James, 1979).

(2) Ammonia by Catayltic Synthesis from Nitrogen and Hydrogen (*Haber-Bosch* Process):

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ + heat

Haber Process: Nitrogen and hydrogen react in a 1:3 ratio in the presence of a catalyst at high temperatures (200 to 700°C) and pressures (100 to 1000 atm.). The nitrogen is derived from the air by liquefication, the producer gas reaction or by burning out the oxygen in the air with hydrogen. The hydrogen is obtained from water gas, coke-oven

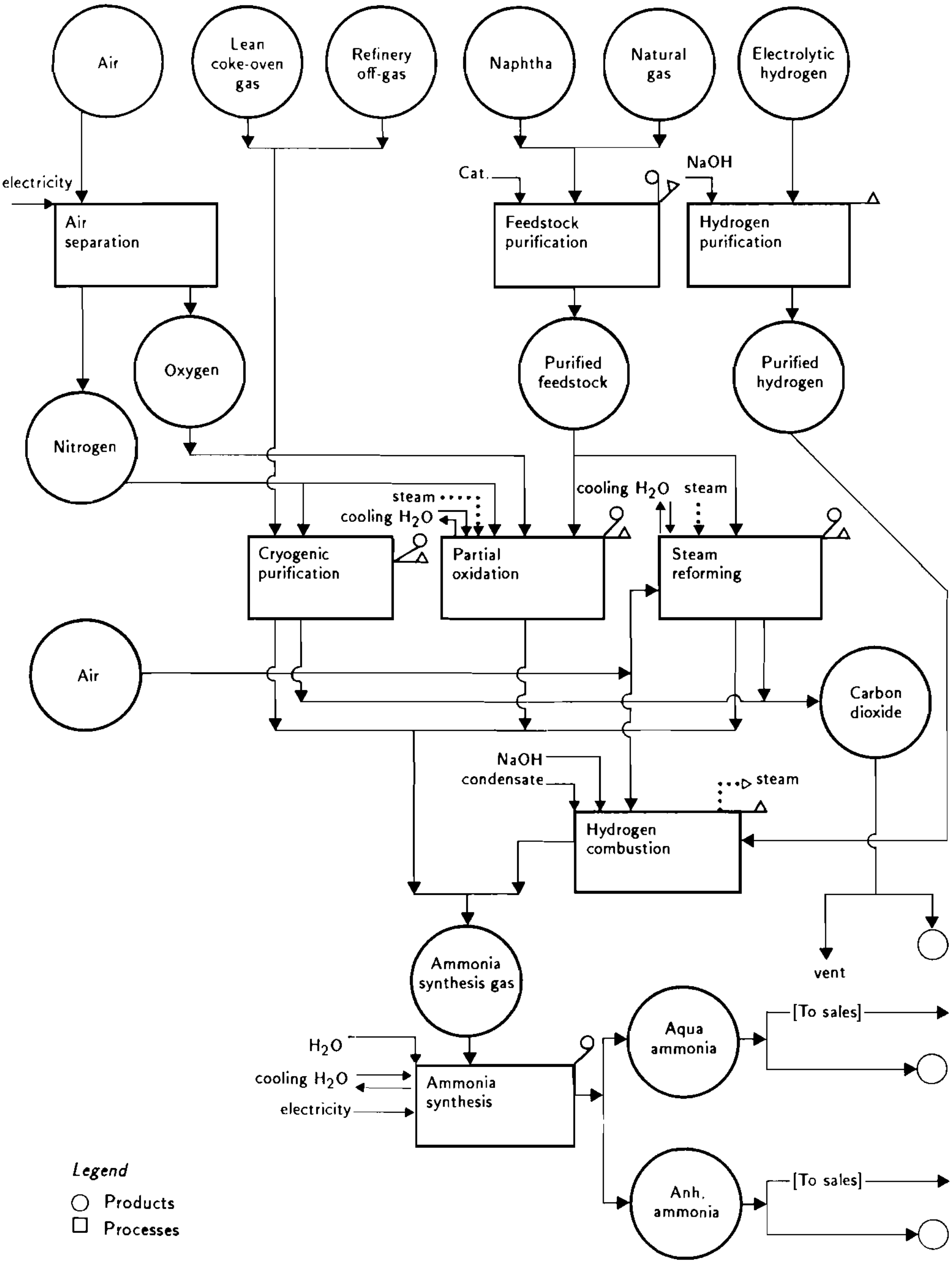

Figure 5.6. **Materials process relationships for ammonia synthesis.**

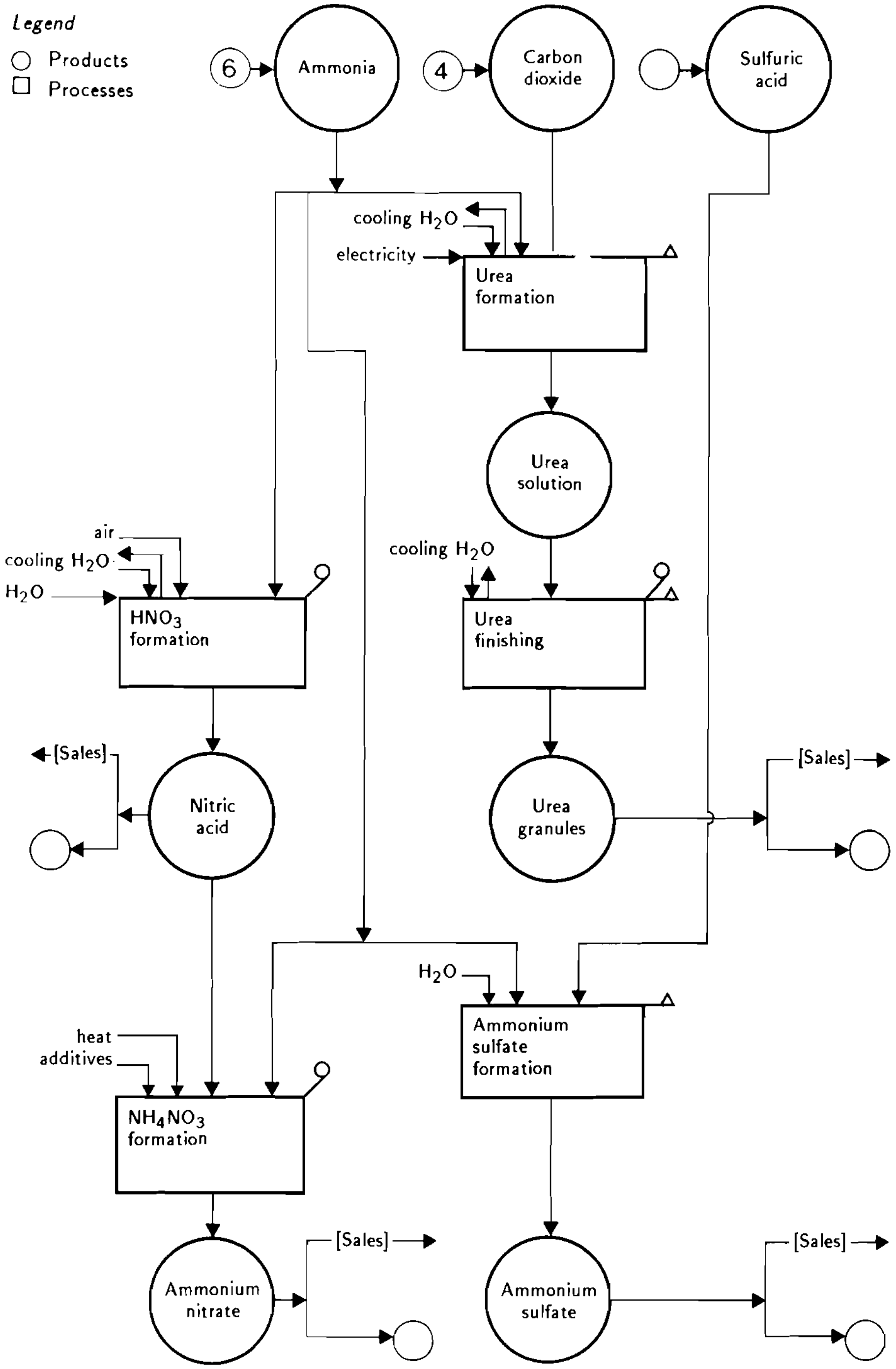

Figure 5.7. **Materials process relationship for ammonium sulfate, nitric acid, ammonium nitrate, and urea.**

gas, natural gas, fuel oil, catalytic reformer gases, or the electrolysis of water or brine. Since World War II the major source of hydrogen has been natural gas (Lowenheim and Moran, 1975).

(3) Ammonium Sulfate from Gypsum (Merseburg Reaction):

$$2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$$

$$(NH_4)_2CO_3 + CaSO_4\ 2H_2O \rightarrow (NH_4)_2SO_4 + CaCO_3 + 2H_2O$$

This is an important process outside the US. The calcium sulfate may be in the form of gypsum, anhydrite or phosphor gypsum from wet-process phosphoric acid production (Lowenheim and Moran, 1975; Considine, 1974; Slack and James, 1979).

(4) Ammonium Sulfate from Synthetic Ammonia and Sulfuric Acid:

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

Ammonia is directly neutralized with sulfuric acid, and water is removed by evaporation. The ammonium sulfate product is recovered by crystallization. About 75% of ammonium sulfate production is from this method (Lowenheim and Moran, 1975).

(5) Nitric Acid from Ammonia:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

The only current commercially important method for the manufacture of nitric acid is the catalytic oxidation of ammonia with air. The manufacture of nitric acid from sodium nitrate (Chile saltpeter) and sulfuric acid, historically the first commercial method, is now obsolete. The high temperature oxidation of atmospheric nitrogen in an electric arc (Berkeland-Eyle Process) is also not of commercial significance. Efforts to develop processes for making nitric acid directly from atmospheric nitrogen have not been successful (Lowenheim and Moran, 1975); Slack and James, 1979).

(6) Urea from Ammonia and Carbon Dioxide:

$$2NH_3 + CO_2 \rightarrow NH_2\ COONH_4 \rightarrow NH_2CONH_2 + H_2O$$

Anhydrous liquid ammonia and gaseous carbon dioxide are reacted at elevated temperature and pressure to form ammonium carbamate (NH_2COONH_4) which is then dehydrated to form urea. Conversion of carbamate is 50% to 75%. The remainder is decomposed to ammonia and carbon dioxide. There are many variations of the process, depending largely on the economical disposal of the waste gases. These waste gases can be partially recycled, totally recycled, or used to produce ammonium salts. The majority of current urea manufacturers use total-recycle processes (Lowenheim and Moran, 1975; Considine, 1974; Slack and James, 1979).

Processes for *Figure 5.2*

(7) Ammonium Phosphates:

Anhydrous NH_3 is reacted with H_3PO_4. Reaction ratios of NH_3/H_3PO_4 are between one and two, depending on the desired grade of product.

There are three types of ammonium phosphates: triammonium phosphate, $(NH_4)_3PO_4$, diammonium phosphate, $(NH_4)_2HPO$, and monammonium phosphate, $NH_4H_2PO_4$. Only mono- and di-ammonium phosphates are used for fertilizers, alone or in combination with other salts.

The reaction for producing monammonium phosphate is:

$$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4$$

The reaction for producing diammonium phosphate is:

$$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2HPO_4$$

(Considine, 1974; Slack and James, 1979; Encyclopedia Britannica, 1973).

(8) Nitrophosphates (Nitric Phosphates) and Calcium Nitrate from Phosphate Rock:

Phosphate rock is dissolved in nitric acid to produce mixtures of calcium nitrate, phosphoric acid and monocalcium phosphate, according to the amount of acid used. One example is:

$$3Ca_3(PO_4)_2CaF_2 + 22HNO_3$$
$$\rightarrow 4H_3PO_4 + CaH_2(HPO_4)_2 + 11Ca(NO_3)_2 + 6HF$$

(Considine, 1974; Slack and James, 1979).

(9) Calcium Nitrate from Limestone:

This involves the direct reaction of limestone and nitric acid. This method is in limited use at present.

(10) Ammonium Nitrate from By-Product Calcium Nitrate:

$$Ca(NO_3)_2 + 2NH_3 + CO_2 + H_2O$$
$$\rightarrow 2NH_4NO_3 + CaCO_3$$

By-product calcium nitrate from nitrophosphate plants is reacted with ammonia and carbon dioxide.

(11) Ammonium Nitrate from Ammonia and Nitric Acid:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

Ammonia and nitric acid are reacted to form ammonium nitrate in either solution or in a molten form. From here it is processed to a crystal or granular form. The concentration of the nitric acid is typically 57% to 60% but can range from 40% to 65%. Processes differ mainly in the method used to remove the solid phase from solution. Five processes in use today are the prilling process, the continuous vacuum crystallization process, the Stengel process, open pan graining, and pan granulation (Lowenheim and Moran, 1975; Considine, 1974; Slack and James, 1979).

Processes for *Figure 5.3*

(12) Melamine from Urea:

Urea is heated in a fluidized bed and decomposed to ammonia and isocyanic acid, which in the presence of a catalyst forms melamine.

(13) Acrylonitrile from Propylene (Sohio Process):

$$C_3H_6 + NH_3 + 3/2O_2 \rightarrow CH_2 = CHCN + 3H_2O$$

Acrylonitrile is produced by the catalytic reaction of propylene, ammonia, and air. A variation of this process uses a mixture of propylene and nitric oxide in stoichiometric amounts highly diluted with nitrogen. Two former processes, from ethylene cyanohydrin and from acetylene and hydrogen cyanide, have not been used commercially for many years (Lowenheim and Moran, 1975).

(14) Hexamethylenediamine [HMDA, 1,6-Diaminohexane, $(CH_2)_6(NH_2)_2$] from Adiponitrile by Hydrogenation:

$$CN(CH_2)_4CN + 4H_2 \xrightarrow{(NH_3)} (CH_2)_6(NH_2)_2$$

Hexamethylenediamine is produced from adiponitrile by hydrogenation. Adiponitrile is produced from acrylonitrile, butadiene, or adipic acid [Lowenheim and Moran (1975); Slack and James (1979)].

(15) Hexamethylenediamine [HMDA, 1,6-Diaminohexane, $(CH_2)_6(NH_2)_2$] from Cyclohexane and Nitric Acid:

Cyclohexane is oxidized with air and nitric acid in separate successive steps to yield adipic acid. Part of the adipic acid is used later for the nylon 66 condensation, the rest is ammoniated to ammonium adipate which is successively dehydrated and hydrogenated to yield HMDA [Slack and James (1979)].

(16) Caprolactum [$NH(CH_2)_5CO$, (Aminocaproic Lactam)] from Cyclohexanone (Beckman Rearrangement):

$$C_6H_{10}O + \frac{1}{2}(NH_2OH)_2H_2SO_4 \xrightarrow{(\frac{1}{2}H_2SO_4, 2NH_3)} C_6H_{10}NOH + (NH_4)_2SO_4 + H_2O$$

$$C_6H_{10}NOH \xrightarrow{(H_2SO_4)} C_6H_{11}NO\ H_2SO_4 \xrightarrow{(2NH_3)} C_6H_{11}NO + (NH_4)_2SO_4$$

Cyclohexanone is a key intermediate in the majority of caprolactam processes. Cyclohexanone is derived from phenol or cyclohexane. Caprolactam is produced via Beckmann rearrangement by the addition of hydroxylamine sulfate to cyclohexanone. Ammonia is used to neutralize the acid solution producing ammonium sulfate as a by-product. As of 1975, there were several new processes that were not used in the US. The newer processes produce less or no by-product ammonium sulfate. For details on these see Lowenheim and Moran (1975). Adipic acid is also a by-product of caprolactum production (Lowenheim and Moran, 1975).

(17) Hexamethylenetetramine (Hexamine, HMTA) from Formaldehyde and Ammonia:

$6CH_2O + 4NH_3 \rightarrow (CH_2)_6N_4 + 6H_2O$

(Lowenheim and Moran, 1975; Slack and James, 1979).

(18) Melamine–Formaldehyde Resins:

This process is similar to that of urea–formaldehyde resins. See process (19).

$C_3N_3(NH_2)_3$ + 3HCHO →
(Melamine) (Formaldehyde) Trimethylolmelamine

(McGraw-Hill, 1971).

(19) Urea–Formaldehyde Resins:

Formaldehyde and urea are reacted to form a water soluble methylolurea. The addition of heat or a catalyst causes the methylolurea to form a hard, insoluble, infusible resin. The urea–formaldehyde ratio is between 1:1.5 and 1:2.5, depending on the end use.

$CO(NH_2)_2$ + HCHO → $NH_2CONHCH_2OH$
(Urea) (Formaldehyde)(Monomethylolurea)
$CO(NH_2)_2$ 2CHHO → $HOCH_2NHCONHCH_2OH$
(Urea) + (Formaldehyde) (Dimethylolura)

(Encyclopedia Britannica, 1973; McGraw Hill, 1971).

(20) Polyurethane Resins:

Polyurethane resins are produced by reacting di- or polyhydroxyl compounds with di- or polyisocyanates, preferably aromatics. The isocyanate is generally 2,4- or 2,6-toluene diisocyanate (TDI) or a mixture. Nitric acid is used to nitrate the isocyanate (Slack and James, 1979).

(21) Polyester Resins:

Polyester resins are formed by the condensation reaction of polyfunctional acids and alcohols. Nitric acid is used in the oxidation of the cyclic poly-acids used in the manufacture of polyester resins (Slack and James, 1979).

(22) Acrylic Polymers from Oxidation by Nitric Acid:

Isobutylene is oxidized with nitric acid to hydrooxyisobutyric acid which reacts with methyl alcohol to yield the methacrylate (Slack and James, 1979).

(23) Acrylic Polymers from Acrylonitrile:

Acrylonitrile is dehydrated to the acrylamide using sulfuric acid. The acrylamide is reacted with alcohol to yield the acrylate. Ammonium sulfate is produced as a by-product (Slack and James, 1979).

(24) Acrylic Polymers by Reaction with Hydrogen Cyanide:

There are two different processes:

- Ethylene oxide is reacted with basic hydrogen cyanide to form cyanohydrin which is reacted with the desired the alcohol to yield the acrylate.
- Acetone is reacted with hydrogen cyanide to form acetone cyanohydrin which is dehydrated with sulfuric acid to methyl methacrylamide. The methyl methacrylamide is reacted with the alcohol yielding the methyl methacrylate. This is the most widely used process (Slack and James, 1979).

(25) Nylon 66:

$nNH_2(CH_2)_6NH_2 + n(CH_2)_4(COOH)_2 \rightarrow [NH(CH_2)_6NHCO(CH_2)_4CO]n + 2nH_2O$

Hexamethylenediamene + AdipicAcid → Polyhexamethyleneadipamide

Nylon 66 is produced by the condensation of adipic acid and HMDA in an aqueous solution adjusted to pH 7.8 with acetic acid (Considine, 1974).

(26) Nylon 6 from the Polymerization of Caprolactum:

$nNH(CH_2)_5CO \rightarrow [NH(CH_2)_5CO]n$
(E-Caprolactam) (Polycaprolactam)

(Considine, 1974)

(27) Phenolic Resins from Hexamethylenetetramine:

Hexamethylenetetramine is used in the second stage polymerization of the phenolic monomer (Slack and James, 1979).

Processes for *Figure 5.4*

(28) Cellulose Nitrate:

$C_6H_{10}O_5 + xHNO_3 \rightarrow C_6H_{(10-x)}O_{(5-x)}(ONO_2)_x + xH_2O$

(Slack and James, 1979).

(29) Trinitrotoluene (TNT):

$CH_3C_6H_5 + 3HNO_3 + H_2SO_4 \rightarrow CH_3C_6H_2(NO_2)_3 + 3H_20$

Toluene + Nitric Acid + Sulfuric Acid → TNT

(Slack and James, 1979).

(30) Glycerol Trinitrate (Nitroglycerine, NG) $CH_2NO_3CHNO_3$ CH_2NO_3:

Produced from glycerol and a mixture of nitric and sulfuric acid (Slack and James, 1979).

(31) PETN, Pentaerythritoletranitrate:

Produced by batch nitration of pentaerythritol with nitric acid (Slack and James, 1979).

(32) Hydrazine (N_2H_4) from Ammonia and Sodium Hypochlorite (Raschig Process):

$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$

$NH_2Cl + NH_3 \rightarrow N_2H_4 + HCl$

(Lowenheim and Moran, 1975; Slack and James, 1979).

(33) Hydrazine from Urea:

$(NH_2)_2CO + NaOCl + 2NaOH \rightarrow N_2H_4 + NaCl + Na_2CO_3 + H_2O$

(Lowenheim and Moran, 1975).

(34) RDX (Cyclonite, Trimethylenetrinitramine):

Hexamine is reacted with 50% nitric acid yielding a dinitrate. Ammonium nitrate, dissolved in 100% nitric acid is added. The crude RDX is precipitated, separated, and recrystallized from acetone. The product contains 10% tetramethylenetetramine (HMX), also an explosive (Slack and James, 1979).

Processes for *Figure 5.5*

(35) Ethyleneamines:

Ethyleneamines are produced by the reaction of ethylene dichloride with ammonia vapor or aqueous ammonia under varying temperatures and pressures (Slack and James, 1979).

(36) Fatty Nitriles and Derivatives:

These are produced by the reaction of fatty acids (tallow, coco, cottonseed, soya, tall oil, etc.) with ammonia at elevated temperatures and pressures in the presence of a metallic oxide catalyst. Their basic formula is RCN, where R is an odd-numbered, straight-chain alkyl group in the C_7 to C_{21} range (Slack and James, 1979).

(37) Ethanolamines:

These are produced by the pressurized reaction of ethylene oxide and aqueous ammonia at moderate temperatures. Their chemical formulas are:

Mono: $NH_2CH_2CH_2OH$
Di: $NH(CH_2CH_2OH)_2$
Tri: $N(CH_2CH_2OH)_3$

(Slack and James, 1979).

(38) Methylamines:

These are produced by the reaction of NH_3 and methanol in the presence of metallic oxide catalysts (AL_2O_3,SiO_2) or phosphoric acid or phosphate salt dehydration catalysts (Slack and James, 1979).

(39) Aniline from Chlorobenzene by Ammonolysis:

$C_6H_5Cl + 2NH_3(aqua) \rightarrow C_6H_5NH_2 + NH_4Cl(sol'n)$

(Lowenheim and Moran, 1975).

(40) Aniline from Nitrobenzene by Catalytic Vapor-Phase Hydrogenation:

$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$

(Lowenheim and Moran, 1975).

(41) Aniline from Nitrobenezene by Reduction:

$4C_6H_5NO_2 + 9Fe + 4H_2O \xrightarrow{(HCl)} 4C_6H_5NH_2 + 3Fe_3O_4$

(Lowenheim and Moran, 1975).

(42) Hydrogen Cyanide from the Andrussov and Degussa Processes:

AndrussovProcess: $2NH_3 + 3O_2 + 2CH_4$
$\rightarrow 2HCN + 6H_2O$.sp 0.5
This reaction takes place in the presence of a platinum-rhodium catalyst.

DegussaProcess: $NH_3 + CH_4 \xrightarrow{HCN} + 3H_2$

This reaction takes place in the presence of a platinum catalyst (Lowenheim and Moran, 1975).

(43) Buiret:

Formed by heating aqueous urea solutions at atmospheric pressure (Considine, 1974).

(44) Ammonium Chloride (Sal-Ammoniac) as a By-Product from the Manufacture of Sodium Sulfite:

$2NH_3 + H_20 + SO_2 \rightarrow (NH_4)_2SO_3$

$(NH_4)_2SO_3 + 2NaCl \rightarrow Na_2SO_3 + 2NH_4Cl$

This is a minor source of ammonium chloride. Ammonium chloride can also be manufactured from ammonia and hydrochloric acid, but the process is not usually economic (Lowenheim and Moran, 1975).

(45) Ammonium Chloride (Sal-Ammoniac) as a By-Product from the Ammonia-Soda Process:

$CaCl_2 + 2NH_3 + CO_2 + H_2O \rightarrow 2NH_4Cl + CaCO_3$

This is the major source of ammonium chloride (Lowenheim and Moran, 1975; Slack and James, 1979).

(46) Ammonium Chloride (Sal-Ammoniac) by Reaction of Ammonium Sulfate and Sodium Chloride Solutions:

$(NH_4)_2SO_4 + 2NaCl \rightarrow Na_2SO_4 + 2NH_4Cl$

This is a major source of ammonium chloride (Lowenheim and Moran, 1975; Slack and James, 1979).

CHAPTER 6

Conclusions and Further Applications of the Materials-Balance Approach

William M. Stigliani and Robert U. Ayres

6.1. Implications for Monitoring and Early Warning of Chemical Pollution

A comprehensive, global materials-balance data base may be critically important for the early warning and assessment of the impacts of low-volume chemicals with the potential for broad-scale harm to the environment. For example, Bruehl and Crutzen (1987) have identified the currently unregulated brominated halons (CF_2ClBr and CF_3Br) as potential threats to the stratospheric ozone layer. These compounds are even more potent ozone depleters than chlorofluorocarbons (CFCs). Moreover, BrO, derived from the halons, may react synergistically with ClO, derived from CFCs, in a new catalytic cycle that efficiently depletes ozone. Similar to CFCs, the halons have an atmospheric half-life in the order of decades. Hence, there may be a decades-long time lag between the release of these chemicals into the troposphere and their ultimate effect on stratospheric ozone. Atmospheric concentrations of $CBrClF_2$ and $CBrF_3$, measured over France and Central India at an altitude of 10–15 km, are of the order of two parts per trillion by volume (concentrations of CFCs are two orders of magnitude greater), and appear to be increasing by 12 percent and five percent per year, respectively (Singh *et al.*, 1988).

The halons are used almost exclusively as nontoxic fire extinguishers. They are widely used where extinguishers based on water and carbon dioxide are not desirable. These include computer installations, portable systems in ship cabins, automobiles, and aircraft (de Zoeten, 1987). Fire extinguishing systems have estimated lifetimes of up to 40 years. Releases to the atmosphere might occur during fire extinction, discharge during routine maintenance, or from disposal and leakage. Once released, they have lifetimes in the atmosphere estimated to be between 60 and 110 years for CF_3Br (Fabian, 1986), and between 30 and 40 years for CF_2ClBr (Lal *et al.*, 1985).

However, because there is no information on worldwide release rates of these halons into the atmosphere or on global production figures, it is not clear why their stratospheric concentrations are increasing so rapidly. Is it because production and use are rising? Or is it because of increased emissions from older fire extinguishers as they are disposed of or recharged? Estimating the pool of halons stored in fire extinguishers is extremely important. If this pool is growing rapidly, then the amounts released in the future could be substantial, even if use of the chemicals is banned.

Thus, there is an urgent need to compile statistics on the production and use of halons, not only from the present, but also from past years. There is no apparent coordination beween the bromine/fire extinguisher industries, who are the experts regarding the production and use of the chemicals, and environmental scientists calculating their effects on stratospheric ozone. Because of the critical importance of preserving the ozone layer, such a coordinated effort is urgently needed.

Extensive programs for monitoring the chemical composition of the atmosphere are already in place, and most probably, the atmosphere will be monitored even more extensively in the next decades. Such programs, however, should be complemented by a global-wide data base that gives annual production and consumption statistics for manufactured gaseous chemicals with the potential for influencing the natural chemical balance of the atmosphere, particularly those with a tendency to accumulate. A little appreciated fact, first noted by Ayres (1978), is that estimates of trace chemicals in the environment may be more accurately obtained from production and use statistics, than from chemical monitoring. Indeed regarding the halons, Singh *et al.* (1988), note that their estimates of annual stratospheric growth rates may not be very accurate because they are based on only a few measurements, and because the concentrations of the halons are low with respect to the measuring capability of their analytical eequipment. If there were detailed production and consumption data that could be compared to the measured estimates, the rates of growth of these gases in the stratosphere could be stated with more confidence.

6.2. Elucidation of Broad-Scale Sources of Pollution

End-of-the-pipe monitoring systems have indicated that materials such as cadmium, chromium, mercury, arsenic, and various organic chemicals often appear as major sources of pollution in river and estuary systems (Rothmann *et al.*, 1987). What is usually not apparent, however, are the sources of such pollutants. Public perception and environmental managerial reoccupation has been mostly focussed on industry, toxic waste dumps, coal-fired power plants and other point sources as the major causes of polluting emissions. However, the important findings of Ayres *et al.* (1985), and Ayres and Rod (1986), where the material-balance approach is applied in the Hudson-Raritan basin in the northeastern United States, suggest that since the 1980s *dissipative consumption* is by far the major source of pollution for the eight heavy metals and the 11 pesticides and herbicides studied. In Chapters 2 to 5 of this report, the analyses demonstrate the same results for bromine, chlorine, and nitrogen, although for sulfur, point sources of pollution still dominate.

If these findings are generally true for most river basins and other types of ecosystems, the implications for public policy are enormous. Control of pollution must not only focus on emissions from point sources, but also on emissions emanating from consumer use. This is not a new idea. Public pressure was probably largely responsible for reducing emissions of phosphate in phosphate-containing detergents, and the partial ban on the production of CFCs. But these represent only two cases. Effective control of other deleterious chemicals in the future will require much more public awareness of pollution caused by the use of commercial and domestic goods and products. Such awareness might spawn the promotion of *environmentally friendly* alternatives to common chemical products found to be environmentally harmful.

6.3. Constructing Comprehensive Materials-Use Forecasts

One fundamental requirement for achieving ecologically sustainable development of the biosphere is a better understanding of the linkages between development activities and the environment. These linkages must be elucidated in terms of past, present, and future trends.

Models for predicting environmental responses to given chemical inputs, although far from perfect, provide a methodological framework within which the *environmental* side of the linkage may be estimated. On the *development* side we need methods for estimating plausible scenarios in four broad sector: population; energy use; land use; and materials use. While scenarios for population and energy use have been the focus of numerous analyses over the last several decades, comparatively few analyses have been attempted for land and materials use.

One appropriate starting point for developing materials-use scenarios might be the methodology set forth in a landmark study published in 1963 by Resources for the Future, Inc. (RFF), (Landsberg *et al.*, 1963). This work included projections of resource uses and requirements for the US for the period 1960 to 2000. The analysis was based on *top down* extrapolations, applying projections of Gross Domestic Product (GDP) and its major components (with high, medium, and low scenarios). It then derived demands for specific materials and fuels by a kind of hybrid physico-economic model based on physical input–output coefficients for materials and energy use per unit output of various consumption categories.

In retrospect this analysis appears somewhat naive. It relied too much on simple growth-rate extrapolations and made too little allowance for substitutions and technological changes. Subsequently, the projections did not match the actual reality very well. Since the 1960s, there have been a number of attempts to build large-scale models for energy-economic analysis and various other purposes. *World modeling* became something of a fad in the early 1970s. However, it is only fair to note that virtually all of these efforts have been subsequently labeled as failures. This is because the complexities (and non-linerarities) of the real world have proven to be far beyond the grasp of any modeler. Nor is there any source of reliable data for many of the factors one would like to quantify.

Yet past model-building efforts might have been judged worthwhile had they not focussed on revealing the actual future trajectory of the national or world economy, but rather, on exploring the dynamic consequences of some of the complex assumptions, interconnections and linkages. Had the RFF model, or others, been computerized and available on personal computers for analysts to use as a tool for scenario building, by *experimenting* with a variety of political, economic, technological, and other assumptions on-line, they might have had a greater impact.

Today, the computer and modeling technologies are available for just this sort of *computer-aided scenario-building.* The complexity of the real world is not a sufficient reason to avoid building models. On the contrary, it is such that without some assistance in organizing this complexity, decision makers are increasingly helpless and forced to make decisions without any real idea of their consequences.

The area of materials use, and the environmental consequences thereof, would be a good starting point. Whereas many socio-economic relationships are inherently fuzzy, sometimes to an extreme degree, the materials/energy balance relationships between resource extraction, processing, use, and environmental disposal are inherently quite precise. Data may be incomplete, and technologies may change, but the sources of uncertainty are less great than in some other areas that have been tackled by modelers.

Without a clearer vision of how materials flow through the industrial economy and their effects on the environment now and in the future, management strategies will continue to work mostly by trial and error, i.e., as a reaction to some already discovered environmental problem caused by chemical pollution that was not anticipated. Far more preferable would be the development of models that would generate a range of plausible scenarios describing the chemical flows (i.e., quantities, types of usage and products, and geographical distribution) of selected chemicals potentially harmful to the environment. These scenarios would provide inputs to the environmental models, which could estimate environmental effects for a given scenario. Decision makers would thus be informed of the environmental implications of alternative development paths for a given chemical use. In order to build such a model of chemical flows, it will be necessary to adopt the materials-balance approach discussed in this report.

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