WORKING PAPER

MATERIALS BALANCE FOR BROMINE, CHLORINE, SULFUR, AND NITROGEN IN EUROPE

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August 1988
WP-88-073

IIASA
International Institute
for Applied Systems Analysis

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PREFACE

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, and 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 about the fates of major industrial chemicals that have an impact on human health and the biosphere. These products that are ultimately dissipated into the environment during use, disposed of in land-fills, or burned as refuse. In most cases, detailed quantitative information regarding the spread or accumulation of these chemicals in the environment is non-existent, and chemical monitoring is totally enadequate 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 important inorganic chemicals, viz., bromine, chlorine, sulfur, and nitrogen.

The study is an application of the materials balance ideas of Prof. Robert Ayres, and I am grateful to him for writing the opening chapter on "Industrial Metabolism", which sets the stage for the remainder of the paper.

William M. Stigliani
Coordinator
Future Environments for Europe

ABSTRACT

An understanding of the flow of toxic materials through industry and into the environment is one of the major tasks for the IIASA Study, *The Future Environments for Europe: Some Implications of Alternative Development Paths.*

Toxic chemicals represent a great threat to the environment, and yet they are commonly used in industrial societies. A sustainable development path would require that usage and disposal of toxic chemicals be compatible with the long-term health of humans and the natural environment. Examining the current and past flows of these materials is a starting point for understanding options for management of their use and disposal, and the impact these options might have on the economy and society.

The method chosen to analyze this problem is a materials balance approach in which toxic chemicals are traced as they move through the industrial economy; from extraction to production to intermediate uses and finally to end uses. The methodology and its advantages and disadvantages are discussed in some detail in Chapter 2. The implementation of this approach will become apparent in Chapters 3 through 6 as four individual chemical elements are studied.

The four elements examined are bromine, chlorine, sulfur and nitrogen. These chemicals were chosen from a list of 15 which were of particular interest because of the exceptional biological activity of many of the compounds derived from them. The major goal of the project was to develop process-product flow diagrams for these elements showing their pathways through the industrial economy. Each of Chapters 3 through 6 contains a discussion of production processes, major uses, process-product flow diagram(s) and an Appendix with detailed information about the chemical transformations involved in each of the processes. In addition, further investigations including quantitative analysis and discussions of the applicability of this approach for a given element are included in some of the Chapters.

Chapter 3, Bromine, presents a detailed qualitative material balance and a more aggregated quantitative material balance for the Netherlands and the United States for 1978 and 1985. The selection of these two countries was based solely on available data. Although the U.S. is not formally part of the study, it is useful as it more closely represents the Western European consumption pattern on average than the Netherlands. While the quantitative analysis focuses only on two countries for two years, it does demonstrate both the qualitative and quantitative aspects of the material balance approach. Bromine consumption is an interesting case as it has been heavily impacted by the phase-out of leaded gasoline and strong market shifts are expected in the future.

Chapter 4, Chlorine, presents an in-depth qualitative materials balance and a look at the pathways of chlorine into the environment based on its pattern of end-use consumption. Currently, millions of tons of chlorine are produced each year for use as a disinfectant and in the organic and inorganic chemical industries. Many of the end-uses of chlorine result in eventual releases into the environment of various compounds which have a significant effect on environmental quality. Organic chlorine compounds are of great use to man because they are not readily biodegradable and they are chemically stable. However, because of these qualities they represent some of the most difficult disposal problems of any anthropogenic material.

Chapter 5, Sulfur, presents a thorough qualitative analysis of the industrial processes and an in-depth discussion of the applicability of the materials balance approach to sulfur. A large portion of anthropogenically mobilized sulfur is from the burning of fossil fuels and the smelting of ores, two processes where sulfur is not an intentional product, simply an unavoidable one. The bulk of scientific study of sulfur wastes is concentrated on these areas due to their contribution to the acid rain problem. The analysis presented here shows that over half of the total anthropogenic sulfur budget in Europe is from industrial sources other than fossil fuels and ore smelting. This is a fairly surprising result. Thus, the flow of sulfur through the industrial economy in Europe is significant and greater understanding of the eventual disposal of this sulfur is needed. In addition, sulfuric acid is the number one industrial chemical based on the tonnage of production. It is used in a myriad of industries where it is generally consumed in the process and not embodied in the end product. This presents difficulties in the implementation of the materials balance analysis for sulfur.

Chapter 6, Nitrogen, presents the process-product flow diagram for nitrogen. About 95% of the anthropogenically mobilized nitrogen is in the form of ammonia. Therefore, this chapter concentrates on the production and eventual end-uses of ammonia. While the process-product diagram is quite thorough, due to time constraints, further discussion and analysis of nitrogen is left as a future research topic.

This report is the first step toward completing the task of understanding the impact of toxic materials in Europe. Future analysts may use the process-product diagrams and the analysis presented in this report as a starting point for a historical reconstruction which then could be used for building future scenarios of chemical flows of toxic materials.

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MATERIALS BALANCE FOR BROMINE, CHLORINE, SULFUR, AND NITROGEN IN EUROPE

Vicky Norberg-Bohm, Janet Yanowitz and Jackie Prince

Chapter 1*

INDUSTRIAL METABOLISM

Man is a product of natural evolution and human societies exist in nature and depend upon it. So much has been clear since humans had leisure to observe and reflect. However, the tremendous energies released by the industrial revolution, and the accompanying population growth, have altered the situation in the critical respect. In the past century, the environment has been significantly modified by man. In some cases the modifications have been conscious and deliberate -- if not always, carefully controlled and limited. In other cases the effects have been essentially accidental and unexpected. Yet some changes may be irreversible. Changes in the ozone balance of the stratosphere, attributed to the use of chlorofluorocarbons (CFC's) were certainly unexpected. The rising CO_2 in the atmosphere is another case in point, and possibly a more serious one in the long run.

As a rough but reasonable generalization, human impacts on the environment can be attributed to:

1. Physical activities associated with agriculture and land settlement: forest clearing, grazing (and over-grazing), plowing, fencing, fires and fire prevention, irrigation, road-building, and so on.
2. Industry: the large-scale extraction, processing, refining, use and dispersion (in altered form) of fossil fuels, and minerals. Surface mining activities have caused major environmental disruptions, but they are largely of a local nature. It is the processing, use and disposal of wastes that produce subtler but more widespread and less easily controlled harms.

Figure 1.1 shows the economic system of man as a multi-stage materials-flow system, beginning with extraction, followed by physical separation, recombination, forming (into shapes) and final use (or "consumption"). At the end of the sequence the materials are returned to the environment in a degraded form of waste/refuse.

The industrialized economic system of today may (or may not) be in rough equilibrium in terms of supply/demand relationships, but it is very far from equilibrium in thermodynamic terms. The self-sustaining economy of small farms is a thing of the past, if not a textbook idealization. At present enormous quantities of "fossil" fuels and high quality minerals are being extracted each year to drive the economic engine. The economic system is stable only in the way a bicycle and its rider are stable: if (or when) forward mo-

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[*] Written by R.U. Ayres

tion stops, the system will collapse and fall down. Forward motion in the economic system is technological progress. Only by continuously discovering ways to exploit mineral and fuel resources that are ever more inaccessible, and/or lower in quality, can the system keep going. In the long run, it may be possible to utilize solar energy effectively to replace fossil fuels, but the technology is still undeveloped and it will be a very long time -- may decades at least, before the necessary infrastructure be put in place.

But even if human ingenuity develops a substitute for fossil fuels (which would eventually end the CO_2 build-up due to combustion), there is no long-term substitute for other minerals and metals. As the best quality ones are extracted and used up, the accessible and recoverable ore bodies decline in quality. The amount of physical and chemical processing needed to extract the useful and desirable materials from the useless waste materials will inevitably increase over time. Recycling will, of course, also increase as industrial wastes and municipal/household refuse become competitive in quality with natural ores. But as long as humans demand material goods (or services derived from material goods), the need for materials processing would grow steadily over time, ***even if the population were stable and the quantity of material output (of final goods) remained constant.*** If population and incomes continue to grow, the aggregate amount of materials to be processed must grow even faster.

The environmental stresses resulting from materials-processing arise primarily from the dispersion of biologically active materials such as toxic heavy metals (such as copper, lead, zinc, and arsenic), sulfur, halogens, and nutrients (phosphorus, nitrates). In natural systems the toxins are mainly locked up in minerals that are mobilized very slowly by leaching and volcanic action, or in non-reactive salts. Phosphorus is naturally recycled through the oceans at a very slow rate and nitrogen is naturally cycled through the atmosphere, with assistance from bacterial action. On the other hand, industrial activities have created new and incessant uses for many of these materials. Moreover, many of the uses are not amenable to complete recycling, ***even in principle.*** Obvious examples include solvents, reagents, catalysts, algicides, pesticides, herbicides, and fertilizers, paints, dyes and pigments, soaps and detergents, lubricants, flocculants, fuel additives (such as tetraethyl lead) and so on. In a word, many of the uses of materials in industrial society are inherently dissipative.

We need to know more about the "production-consumption cycle" of materials. The flows and uses -- especially inherently dissipative uses -- in our industrial system are not monitored by any government agency and have been studied only on an occasional 'ad hoc' basis by a few researchers.

The applicable methodology can perhaps best be called materials/energy balance accounting. More detailed description can be found in the subsequent chapters and bibliography.

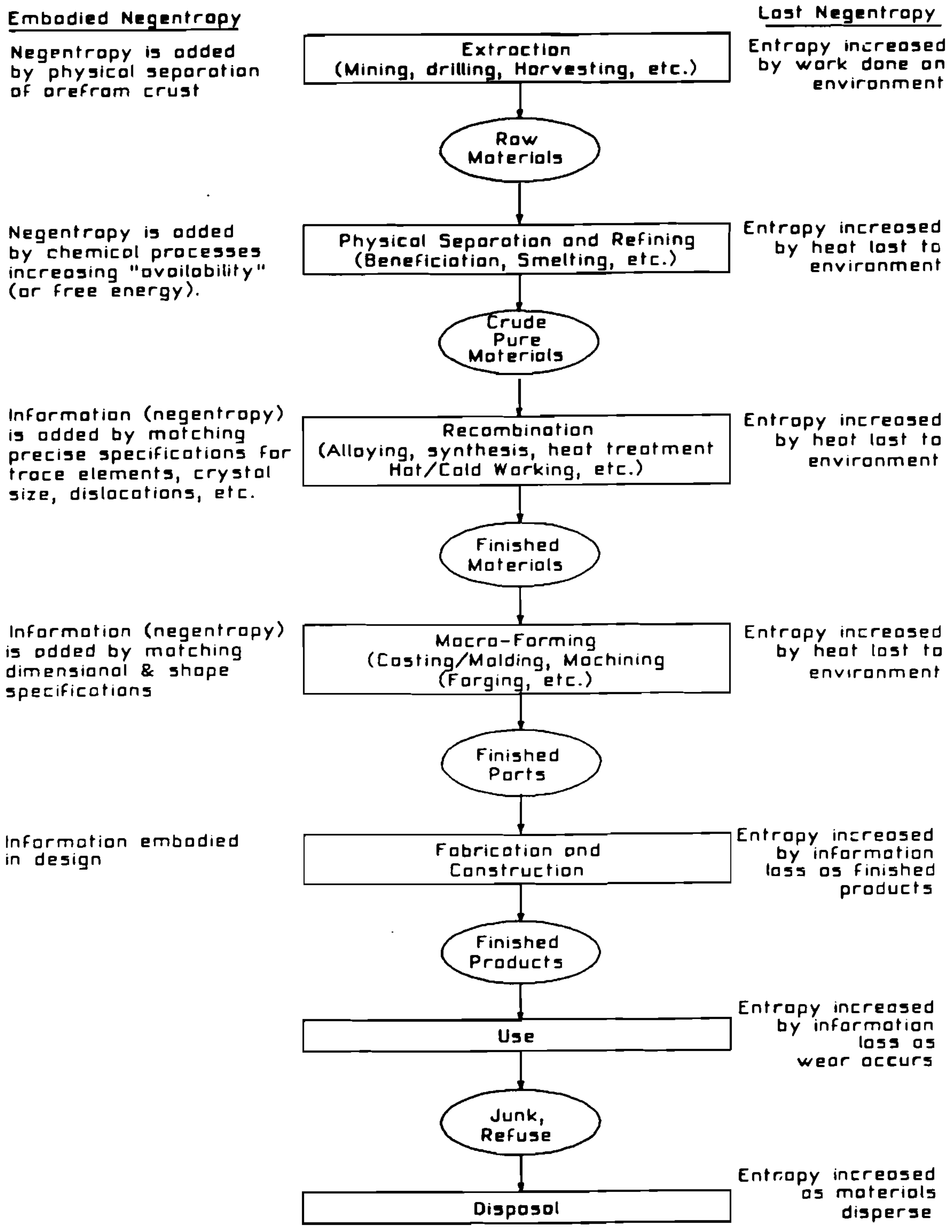

Figure 1-1: **Representation of the Economic System as Materials-Process-Product Flow**

Chapter 2*

APPROACH AND APPLICATION OF THE MATERIALS BALANCE METHOD TO ENVIRONMENTALLY RELEVANT CHEMICALS

Approach: A materials balance is an input-output analysis of the flow of mass through a system. Underlying all materials balance models is the assumption of conservation of mass, i.e. the rate of mass input to the system must equal the output plus the rate of accumulation within the system.

Based on the problem to be addressed and the availability of data, the following criteria must be considered in structuring a material balance.

Boundaries: Is a whole industry to be studied or only one factory? The whole world, one country, one region or the flow between several countries? What section of the geochemical cycle should be examined? Figure 2–1 shows the general structure of a global materials balance. Each of the rectangles in this figure represents a sector for which a materials balance could be applied. Of course, a narrower or broader scope may be more applicable to a particular problem. Also to be considered is the question of what time period to study: future, past or present, or some combination.

Level of Aggregation: Can certain materials be grouped together because they follow a similar path through the system, or because they have a similar impact on the issue under study? Greater aggregation will lead to a simpler model, with the resultant loss in detailed information, but with a saving in time and effort. This decision will rest on the level of aggregation and the accuracy required of the available data.

Dynamic vs. Static: The rate of change in the flow is sometimes of interest. The cycling of automobiles in Belgium by Billen, et al. (1983) is a good example of the use of a dynamic mode.

Qualitative vs. Quantitative: Normally, a qualitative balance is created first in order to discern what aspects of the balance should be explored more quantitatively.

Applications: The applications of the concept of materials balance are many and varied. Although the basic principle may seem obvious, an imaginative choice of the boundaries of the system, level of aggregation or model structure can lead to surprising revelations.

Our choice, and the choice of several past researchers (for example Ayres (1978), Ayers et al. (1985), Anzion and Feenstra (1980), Billen et al. (1983)) has been to trace the path of one chemical element at a time. This approach is particularly suited to the study of the geochemical cycling of environmentally active materials. The heavy metals and chlorine are perhaps the most obvious subjects for elemental materials balances because small quantities of these elements, contained in a vast range of industrial and consumptive materials, form a large percentage of environmentally active substances.

The primary aim of this type of materials balance is to determine the relative importance of the different paths to the environment of the substances of interest. A qualitative balance shows in what forms the element leaves the industrial economy to return to the environment. In some cases, for example zinc in steel, the metal is tied up in a form which will not be readily mobilized and thus presents little threat to the environment. However, zinc in tires is eventually dispersed into the environment and thus this use of zinc is of in-

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* Written by Janet Yanowitz

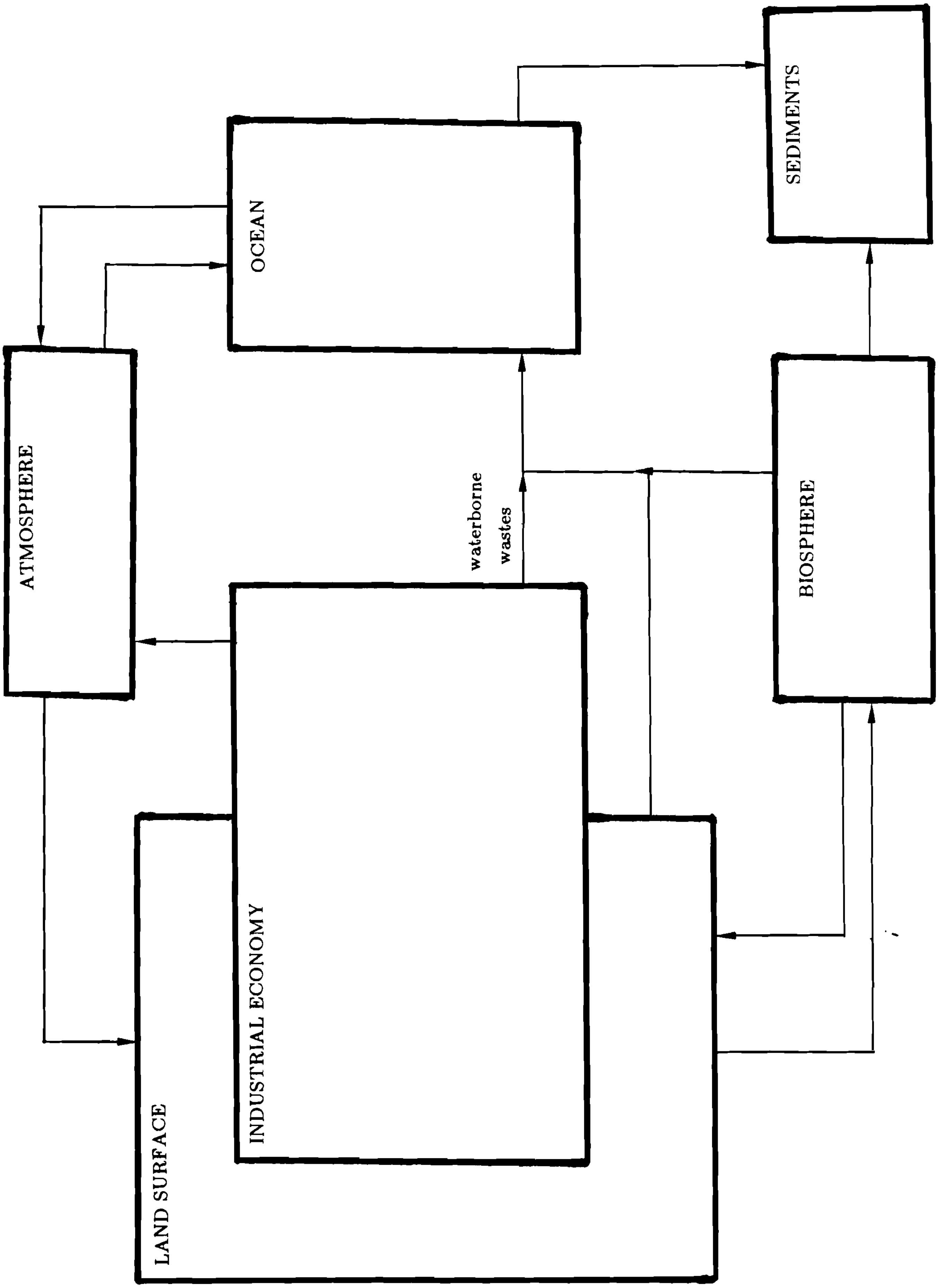

Figure 2-1: Generalized Structure of a Global Materials Balance

terest. A qualitative model can also suggest areas for future research concerning the fate of materials after consumption. For example, mercury is used in batteries. What happens to the mercury after the battery is disposed of?

A quantitative materials balance shows the end uses which are most significant in terms of amount. These end use quantities can be compared to often well-documented point source data in order to determine the relative importance of non-point sources and point sources of pollution. The materials balances constructed by Ayres, (1985) and Johnston, et al. (1979) (as well as many other balances) have underlined the significance of dissipative end uses of hazardous materials. Although, disposal is not always immediate, production creates an accumulation of materials that will eventually need disposal, recycling or will remain in the environment.

A fundamental problem in the use of materials balances is that in many cases the impact of environmentally active materials is dependent on concentration. Since many end uses of materials are dissipative in low concentrations, it is not always clear that such low-level sources of hazardous materials are significant.

Quantitative data on the anthropogenic sources of various materials is often available or can be deduced by a materials balance applied to the industrial economy. For example, mining data on metals are widely available and from this it is possible to make an estimate of the total amount of metal that is consumed. Unfortunately, production and end use data are often not as easily acquired.

Materials balances of industrial production provide a much needed understanding of the link between production and release into the environment. Many studies, such as the exposure commitment assessments of environmental pollutants by MARC (1981–1987), show the relationship between the presence in the environment and impact. By linking these two types of analyses, it is possible to show the health effects and impact on the environment of current production. In some cases the control of production may prove to be the best leverage point for modifying the impact of hazardous materials in the environment.

Materials balances can be used to account for the production and commerce in hazardous materials. If industries are known to buy a certain amount of highly toxic or carcinogenic material, they could be held accountable for safe destruction or disposal of the same amount of those materials. Other chemicals that are currently of only preliminary concern can be tracked so that if they eventually turn out to be problems, it will be possible to know their environmental pathways. Similarly, past production of hazardous wastes can be quantified and end uses identified. This analysis can then be used to trace these materials and estimate their potential environmental hazards.

Materials balances applied on a country-by-country basis give some indication of the flow of certain materials between nations. For example, the flow of valuable metals from Africa to Europe can be studied. As some of these metals are currently economically recyclable, and may become more so in the future, Europe is gradually accumulating a stock of these metals while the mines of Africa are becoming depleted. Conversely, Europe is accumulating a stock of toxic anthropogenic materials within its borders. Moreover, a materials balance approach can reveal whether consumption of a hazardous material or industrial processing of the material, is the major source of pollution. If consumption is the major source, then exporting the processing industries producing these materials will not help the local environment. Such an analysis would have strong implications for management strategies for controlling the material.

A materials balance on automobile use in Belgium applied over several decades indicates that the rate of consumption has increased. However, this is not due to an increase of cars in use, but rather to the shorter lifespan of more recent model automobiles (Billen, et al., 1983). In comparison to 40 years ago, when the lifespan of cars was 10 years, on average, the lifespan is now about 4 years.

In thinking about future material flows, it would be interesting to determine whether there is a more general trend toward the replacement of expensive and durable products by less expensive disposal ones. Ernsberger (1987) has noted that today's busy middle-income consumer is often willing to pay extra money to replace, rather than to repair an item. This preference has been accelerated by the combination of high repair costs, high levels of "disposable" income, and a societal norm that increasingly values convenience over conservation.

Manufacturers, noting this shift in preference, have already begun to exploit the rising demand for disposable items. The author cites three recent examples: disposable telephones (9 to 10 dollars with a life span of 6 to 12 months), disposable cameras (7 to 10 dollars for 24 exposures), and disposable contact lenses (2 weeks). Hospitals are potentially a large market for disposable telephones, selling them to patients anxious about using phones touched by previous patients (e.g. the misplaced fear of catching AIDS via contact with phones touched by AIDS patients). The market for disposable cameras is predominately young buyers, engaged in leisure-time activities, who have left their expensive cameras at home. Disposable contact lenses are appealing because they would be more convenient and sanitary than existing lenses, and obviate the need for heatings and disinfectants. Disposable items may also not be limited to small products. Ernsberger (1987) quotes the chairman of a product-research firm in New York who states that the "Yugo (a cheap, Yugoslavian small car) is practically a disposable automobile."

Chapter 3*

BROMINE: ANTHROPOGENIC SOURCES AND FLOW

Introduction

Information on sources, production, major uses, and consumption rather than emissions data provides the basis for re-creating the flow of bromine (Ayres et al., 1985). Using a simple conservation of mass principle, process-product diagrams have been developed to highlight the uses and potential releases of bromine in our economy and environment. These process-product diagrams are the first step in a materials balance approach; the second step involves a quantitative analysis of bromine usage based on process information and production and consumption data. Consumption data on the use of bromine in Europe is limited and, therefore, the quantitative analysis is incomplete. This chapter does conclude with a quantitative comparison of bromine use in the Netherlands and the U.S., which also demonstrates the use of a material balance approach. Where data are available, the use of bromine in other Western European countries is discussed.

Sources

Bromine is a halogen element with reactive properties intermediate between chlorine and iodine. Bromine 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 ppm bromine. Approximately 1 ton of elemental bromine (Br_2) can be extracted from 17,000 tons of processed seawater. Seawater continues to be a major source 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 1000 ppm. Furthermore, bromine can be produced as a by-product of alkali metal salt production (e.g. $MgCl_2$, KCl, $NaCl$ and $CaCl_2$) by first extracting bromine from the brines. Here, 1,000 tons of brine release approximately 1 ton of bromine. Other bromine sources include inland lakes and seas, with the Dead Sea as an especially rich source (5000 ppm bromine on average).

Bromine Production

Bromine was first produced in the United States in Freeport, PA 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 (Shreve, 1967).

Bromine production has been increasing steadily since 1900 when the world (mainly the U.S.) produced roughly 300 metric tons (Lyday, 1985). The changes over the years are shown in Table 3-1 for selected European countries, and the United States for comparison.

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* Written by Jackie Prince

Table 3-1 Bromine Production in Western Europe (metric tons)

	1900 (2)	1950 (2)	1960 (2)	1965 (2)	1970 (3)	1973 (2)	1978 (1,5)	1980 (4)	1983 (4)	1985 (5)
USA	236	44,691	77,132	124,578	158,600	189,769	202,586	170,347	166,670	158,800
U.K.					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
West Germany				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
World Total	300	50,400	103,500	150,000	224,800	270,200	361,207	340,588	358,468	381,300

Sources:

(1) Lyday, Phyllis A. (1978), p.4.
(2) Kirk, E. and Othmer, D.F. (1978), p.238.
(3) Anzion, C.M. and Feenstra, J.F. (1980), p.11.
(4) US Bureau of Mines (1984), p.177.
(5) Roskill Information Services, Ltd. (1986), p.6.

The U.S. continues to be the primary producer worldwide with approximately 70% of the total production during the 1960s and 1970s and roughly 45% today. US production has remained steady, but the increase in USSR and Israeli output has shifted the relative market shares (Roskill Information Service, Ltd., 1986). The major Western European producers are the United Kingdom (ca. 10%), France (ca. 6%), West Germany (ca. 1%), Italy (ca. 1%), and Spain (Anzion and Feenstra, 1980). The U.K., Italy, and Spain mainly produce bromine from seawater. France produces over 50% 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 West Germany. Italy produces bromine from waste bitterns and inland lakes. Since 1970, Western Europe has produced roughly 16-18% of the total world production with the U.K. and France as the two leading producers. However, 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 U.S.), but the bromine raw material is imported from Israel, France, Great Britain, and West Germany. In 1977, the Netherlands imported 3286 tons of bromine for use in the manufacture of bromine compounds.

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 (1000 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); and,

(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 Br 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:

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

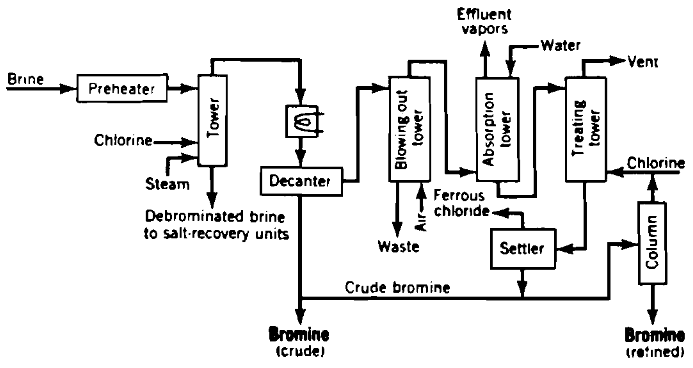
The stripped air is vented to the atmosphere. Finally, chlorine and steam are used to separate and purify the liquor: $2HBr + Cl_2 \rightarrow Br_2 + 2HCl$ (See Figure 3-1). The ratio of chlorine to bromine used in this process is roughly 2:1. Bromine recovery in the blowing-out process is 90-95%. The remaining 5-10% 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, 1 kg of chlorine will release 2.25 kg of bromine, but in reality more chlorine is needed to release 2.25 kg of bromine. 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 3-2). 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%. 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).

Figure 3-1: Bromine Blowing Out Process. Source: Faith et al, 1965.

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)

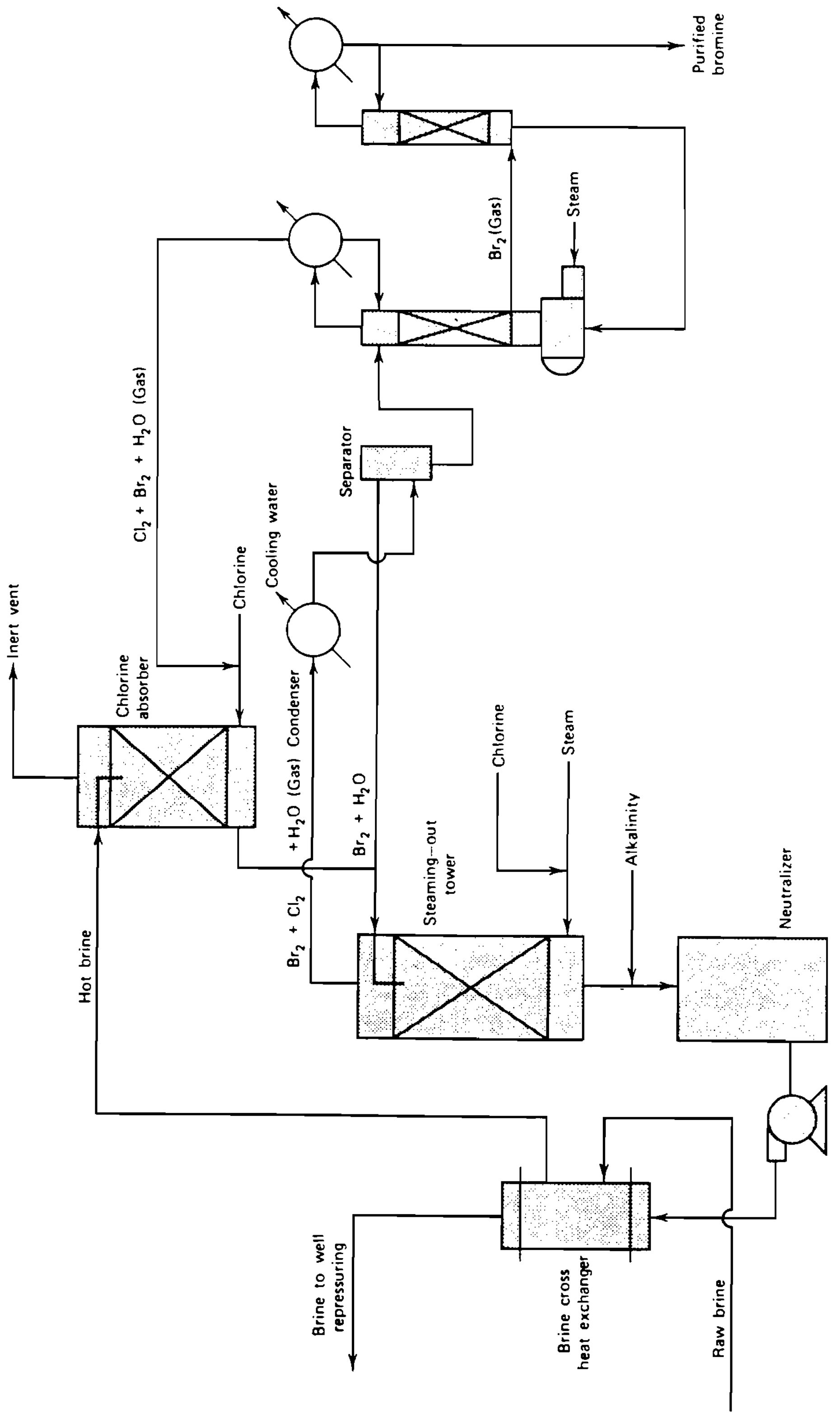


Figure 3-2: Bromine Steaming-Out Process Source: Kirk-Othmer, vol. 4, 1978.

Major Uses

Bromine is used primarily in the manufacture of organic and inorganic bromides and bromates. Only 17% 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 tetraethyllead as an antiknock agent in gasoline. Other organic bromine compounds are used in fumigants, insecticides, flame retardant agents, fire extinguishers, pharmaceuticals, solvents, gage 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 3-2 with a brief description of the specific uses. A more extensive list of organo-bromine compounds may be found in Kirk-Othmer (1978) which lists information on the use of 55 chemicals.

Table 3-2: 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_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.

Table 3-2 (Cont.)

Bromocyanide (BrCN):	Used as a fumigant.
3-Bromopropane: (CH_2CHCH_2Br)	Used as a fumigant.
Propylene Bromide: $(CH_3CHBrCH_2Br)$	Used as a solvent.
Acetylene Tetrabromide: $(CHBr_2CHBr_2)$	Used as a catalyst, gage fluid, and separation liquid.
Allyl Bromide: (CH_2CHCH_2Br)	Used as a fire retarding agent, primarily in 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.

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 desicant for air conditioning, as a catalyst and occasionally in bleaching with hypochlorites.
Silver Bromide (AgBr):	Used extensively in the photographic industry.

Table 3-2 (Cont.)

Potassium Bromide (KBr):	Also used in the photographic industry as a defogging agent during developing.
Alkali 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):	Finding growing use 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 gage and drilling fluid.
Calcium Bromide ($CaBr_2$):	Used in pharmaceuticals, as a catalyst, and in gage 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 in as a flour treating agent, in hair-wave preparations, and for shrinkproofing wool.

Process-product Diagrams

As discussed in the introduction, the first step in a materials balance approach is to recreate the flow of bromine in the economy and environment using information on production, intermediate uses, and end uses. The flow charts in Figures 3-3, 3-4, and 3-5 are intended to track, in detail, the flow of bromine in the industrial economy. Figure 3-3 is an overview showing bromine extraction, production, intermediates, and end uses. Figures 3-4 and 3-5 extend the flow chart and show the uses of hydrobromic acid (HBr) and bromine organics, respectively. In these charts, products are indicated by circles and ovals and processes are indicated by rectangles. The numbers in each box correspond to the numbers given for the process information (chemical reactions, etc.) presented in Appendix A.

The flow charts presented in Figures 3-3 to 3-5 qualitatively address the question of "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 looks at 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.

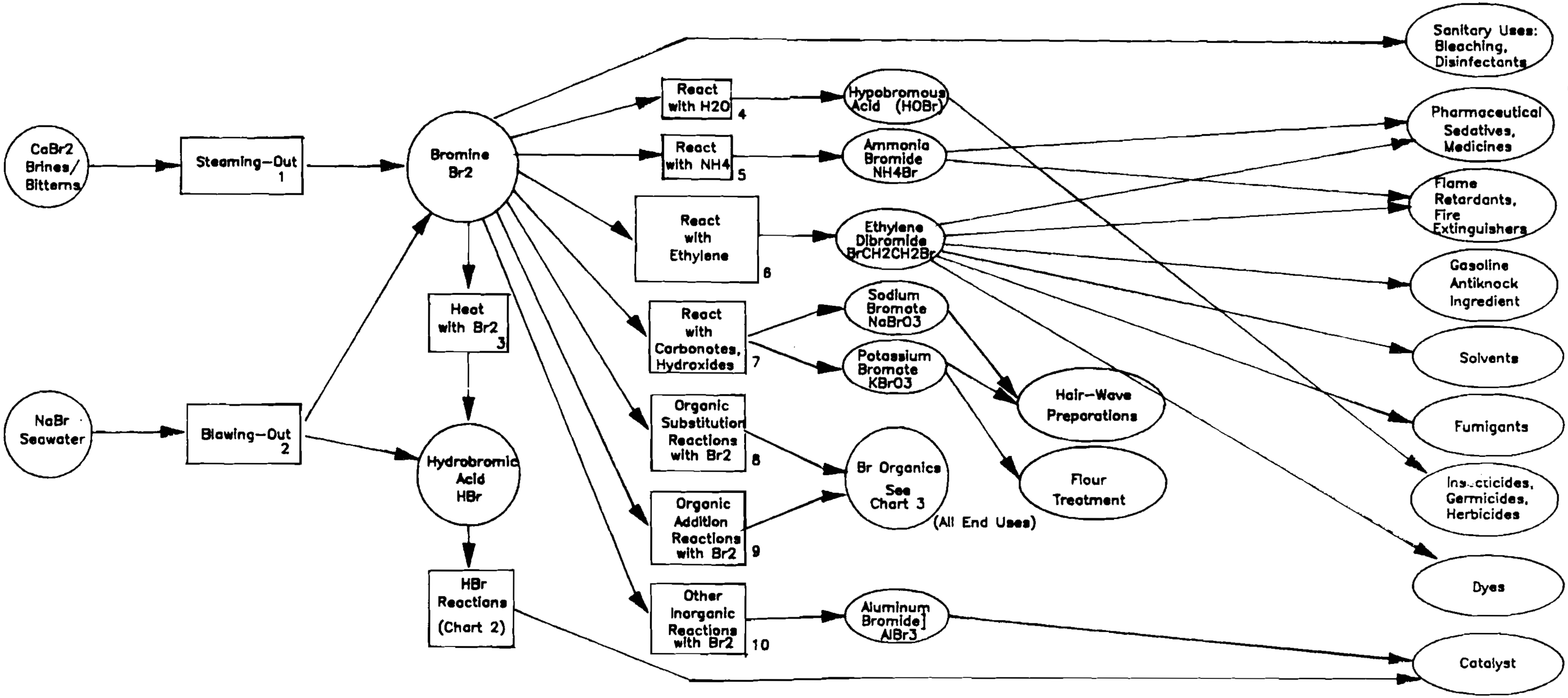


Figure 3-3: Bromine Compounds

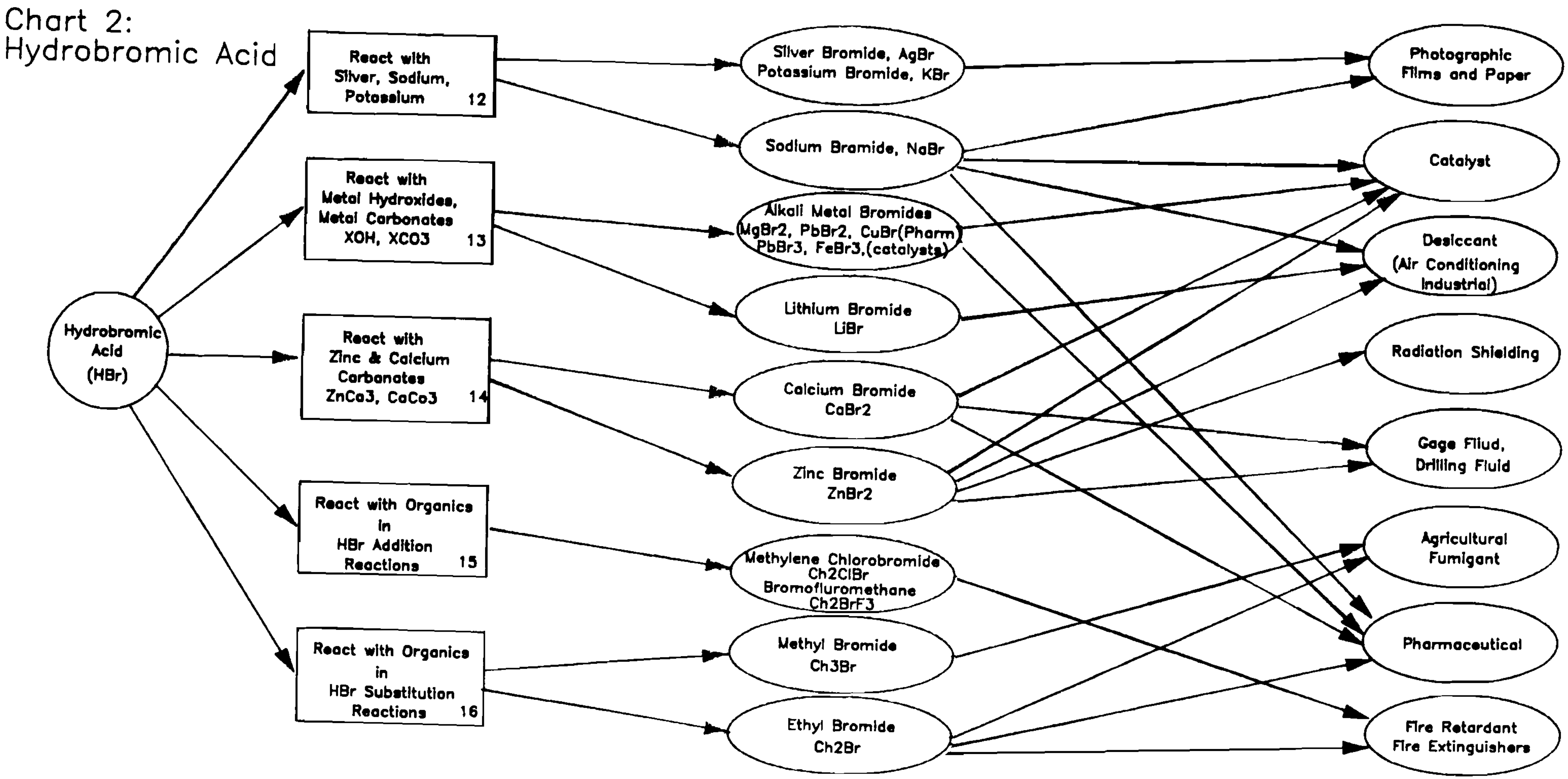
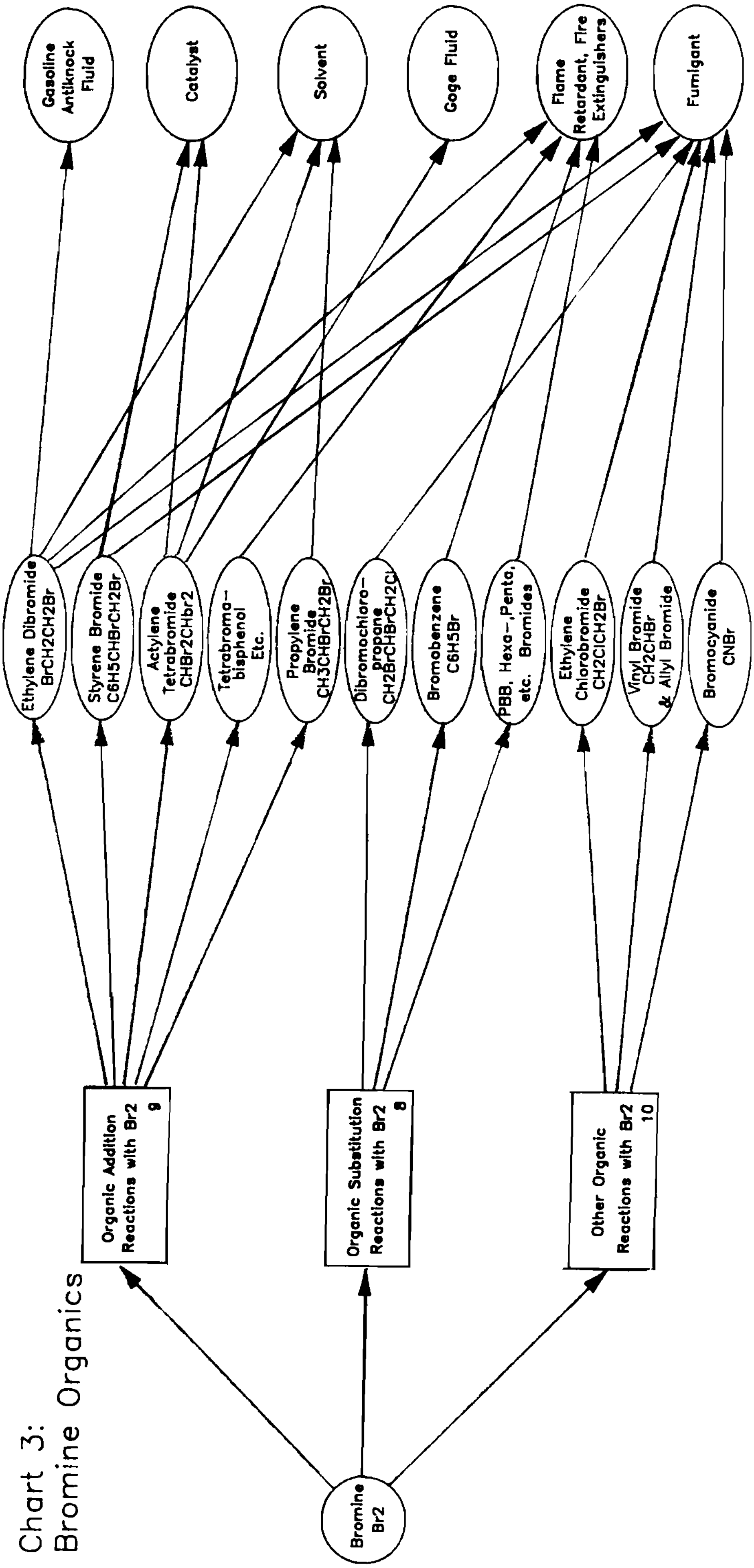


Figure 3-4: Hydrobromic Acid Compounds

Figure 3-5: Bromine Organics



Ethylene Dibromide

Traditionally, the primary end-use of bromine has been ethylylene dibromide (EDB) and, until recently, EDB represented approximately 70% of the total demand for bromine. About 95% of EDB is used as a gasoline additive, while the remaining 5% is used in pesticides and fumigants. Less than 1% is used as solvents in chemical synthesis (Anzion and Feenstra, 1980).

EDB acts as a lead scavenger in antiknock fluids and prevents lead build-up 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% of the total lead and bromine in gasoline leaves the engine system in this manner. The other 25% 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 fluid containing EDB, using the following information and simple calculations shown in (1) through (6) below.

(1) Composition of antiknock fluid (1975):

tetraethyl lead	61.5 %
or tetramethyl lead	50.8 %
ethylenedibromide (EDB)	17.85%
ethylenedichloride	18.85%

Antiknock fluids for aviation gasoline use pure EDB instead of a 1:1 ethylenedibromide:ethylenedichloride mixture.

(2) EDB composition: 86% elemental bromine.

(3) Bromine per gram of antiknock fluid:
(.1785 g EDB/g fluid)(.86 g Br/g EDB) = .1535 g Br/g fluid

(4) Bromine per liter (L) gasoline consumed:
(.1535 g Br/g fluid)(X g fluid/L gas) = Y g Br/L gas (where Y=.1535X)

(5) Air Emissions: (.75)(Y g Br/L gas)

(6) Bromine in waste oil: (.25)(Y g Br/L gas)

Assuming 75% 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 here and the amount of antiknock fluid per liter of gasoline varies according to year, gasoline grade, and country. The Netherlands have reported an average figure of .76 g/L (Anzion and Feenstra, 1980).

An alternative approach is to assume that 95% of all EDB produced is consumed in gasoline and calculate air emissions based on production data. For instance, Great Britain produces an average of 26,000 tons per year of EDB, exporting 24,000 tons (the U.K. is the major supplier of EDB for Europe (Anzion and Feenstra, 1980)). The following calculation gives a rough estimate of bromine air emissions in Great Britain assuming 2000 tons/year is the amount of EDB consumed:

(2000 tons EDB/yr)(.86 ton Br/ton EDB)(.95 gasoline use) =
(1634 tons of bromine consumed in gasoline)(.75)(1634 tons bromine/yr) =
1226 tons/year emitted to the air.

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 .15-.40 g Pb/L in gasoline. (National Energy Administration, 1984). Table 3-3 lists the maximum permitted levels of lead for Western European countries:

Table 3-3. Maximum Permitted Lead Content in Gasoline, 1984. (Roskill Information Services Ltd., 1986).

COUNTRY	LEAD CONTENT (g/L)
Austria	0.40 premium 0.15 regular
Belgium	0.40
Denmark	0.40
Finland	0.40
France	0.40
West Germany	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
U.K.	0.40

For present purposes, the assumption is made that the lead content varies from .15-.40 g per liter in gasoline in Europe. Therefore, the consumption of bromine per liter gasoline is .0579-.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 problematic as western countries are shifting toward unleaded gasoline at different rates. Scandinavia, Switzerland, and West 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% of the gas market used low-lead gasoline in Western Europe. By 1985, projections were for 32% of the market, still low when compared to 77% of the market use in the U.S. The EEC's objectives for the phase-out of leaded gasoline are as follows (Roskill Information Service Ltd., 1986):

(1) Freely available unleaded gasoline in West Europe by October, 1989.

(2) By 1989, all new models must run on unleaded gasoline.

(3) From October 1990, all new registration cars will run on unleaded gasoline, unless the manufacturer can prove that major re-engineering would be required.

The Netherlands decreased its maximum from .4 g Pb/L to .15 g Pb/L effective October, 1986. However, Shell reports that normal gasoline currently still contains .3 g Pb/L and premium contains $.38gPb/L$ (De Zoeten, 1987).

The impact of lead phase-out on bromine consumption is best illustrated by the U.S. example. Unleaded gasoline was first available in 1974 and regulations in 1983 decreased allowable levels to .66 g Pb/L for small refineries and .29 g Pb/L for large refineries. By 1986, levels must be down to .0264 g Pb/L ($.1gPb/gal$). (Lyday, 1985). As a result, EDB consumed only 55% of the total bromine produced in the U.S. in 1983 as compared to 77% in 1973; in 1987, EDB demand represented only 20% of the total bromine demand in the U.S. 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).

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% bromine while dibromochloropropane contains roughly 68% bromine. However, toxicological concerns regarding EDB and DBCP have resulted in the decline of agricultural use of these chemicals. In 1984, the U.S. suspended the use of EDB as a soil fumigant and subsequently banned DBCP. The U.K. 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 1870 tons of bromine in fumigants (20% 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 $75-100g/m^2$ to $40g/m^2$ 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 to the air during application or within several days thereafter. It is estimated that 85% of the methyl bromide applied to soil prior to 1985 in the Netherlands 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 (Mc Ewen 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 to 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.

Flame Retardants

Since the 1960s, flame retardants have been the largest growing use of bromine compounds. During 1986, 30% of all fire retardants used in the U.S. were bromide compounds, with 85% of those retardants being applied to plastics as compared to 14% in 1971 (McGraw-Hill Encyclopedia of Science and Technology, 1977; 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 3-2. There are two general categories of fire retardants: additive types with an average of 75% bromine and reactive types with an average of 66% bromine. Consumption of fire retardants is split roughly 50/50 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 ($CBrClF_2$) containing 53% bromine and bromotrifluoromethane ($CBrF_3$) containing 50% bromine. 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 flamestuffs, the product lifetimes and potential releases of these compounds should be examined.

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 to surface waters.

Pharmaceuticals

Pharmaceuticals have been a traditional use of bromides, particularly alkali and heavy metal bromides ($MgBr_2, SrBr_2, PbBr_2$, $CuBr$, and $HgBr_2$), sodium bromide ($NaBr$), calcium bromide ($CaBr$), and ammonium bromide (NH_4Br). Sedatives, anesthetics, and anti-spasmodic 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).

Photography

Silver bromide ($AgBr$) and small amounts of potassium bromide (KBr) and sodium bromide ($NaBr$) are used in the photographic and graphics industries and x-ray films due to their light-sensitive properties. Silver bromide contains roughly 75% 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% of the silver bromide while consumer end-uses consume 35% and graphic films consume 15% (Roskill Information Services Ltd., 1986). It is estimated that 100% of the bromides used in these categories is emitted to the environment in wastewater.

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% of all new oil and gas wells during 1977 to 1985. In Europe, drilling decreased by 6% in 1986 (Roskill Information Services Ltd., 1986). The U.K. is the largest consumer of calcium bromide in Europe with its North Sea oil activities.

Other Uses: Flour Treatment, Dyes, Catalysts

Potassium bromate ($KBrO_3$) is used in the treatment of flour to improve the leavening. However, France, Belgium, Luxembourg, the Netherlands, West Germany, Italy, and Spain do not allow bromate additives in traded wheat. The U.S. and the U.K. 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' dibromoindigo 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). Information on the use of bromine in dyes is limited.

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 provided information on a more aggregate level than the flow-charts in Figures 3-3 to 3-5. Therefore, the flow-charts used for the quantitative portion have eliminated much of the detail in the earlier charts and only focus on major compounds. Due to data restrictions, this section analyzes bromine consumption only for the Netherlands and the U.S. 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 U.S. Bureau of Mines is the primary source for U.S. production and consumption data. Although the U.S. is not part of the Future Environments for Europe case study, it provides a comparison to the Netherlands; in addition, the U.S. 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 3-4 below is a compilation of available consumption statistics for bromine compounds and illustrates the variations in use patterns. In 1976, worldwide consumption of bromine was estimated as follows: EDB, 55%; Agricultural chemicals, 17%; Flame retardants 9%; Dyes 7%; Photographic applications 3.5%; Pharmaceuticals 3.5%; and, Others 5% (Kirk and Othmer, 1978). However, in the U.S. and most of the western world, EDB use was much higher at roughly 70% of the bromine demand. In 1985, the consumption pattern in the western world had shifted to: EDB, 24%; Agricultural chemicals, 13%; Flame retardants 20%; Drilling fluids, 18%; and, Others 25% (Roskill Information Service Ltd., 1986).

Table 3-4: Bromine Consumption Patterns (in %)

YEAR	1965-75	1965	1970	1973	1976	1978	1983
COUNTRY	U.K.	USA	USA	USA	World	Netherlands.	USA
DATA SOURCE	(a)	(b)	(a)	(a)	(c)	(a)	(d)
EDB	78.8%	75%	71%	75%	55%	19.6%	27%
Pesticides	9.1%	6%		5%		56.9%	
			>14%		>17%		
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%; Misc., 5% for 1976
(f) Others = Drilling fluids, 27%; Misc., 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 3-6 and 3-7 are material balances for bromine consumption in the Netherlands and the U.S. in 1978; (numbers cited in parentheses indicate data gaps where assumptions and estimates have been made based on the other data in the flow- chart). Tables 3-5 and 3-6 summarize the salient information provided by the material balance: (1) the amount of bromine used in each category; and, (2) the potential environmental releases of bromine to the air, water, soil, permanent uses, or unclear endpoints during consumption. The statistics in these Tables demonstrate the usefulness of the material balance approach.

The second set of material balances focuses on the current consumption of bromine (1985) for the same two countries. Again, Figures 3-8 and 3-9 are the quantitative material balances with estimates cited in parentheses. Tables 3-7 and 3-8 summarize the key information provided by the material balance on percentages of bromine compounds consumed and percentages of estimated environmental releases. Finally, Figure 3-10 and Table 3-9 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.

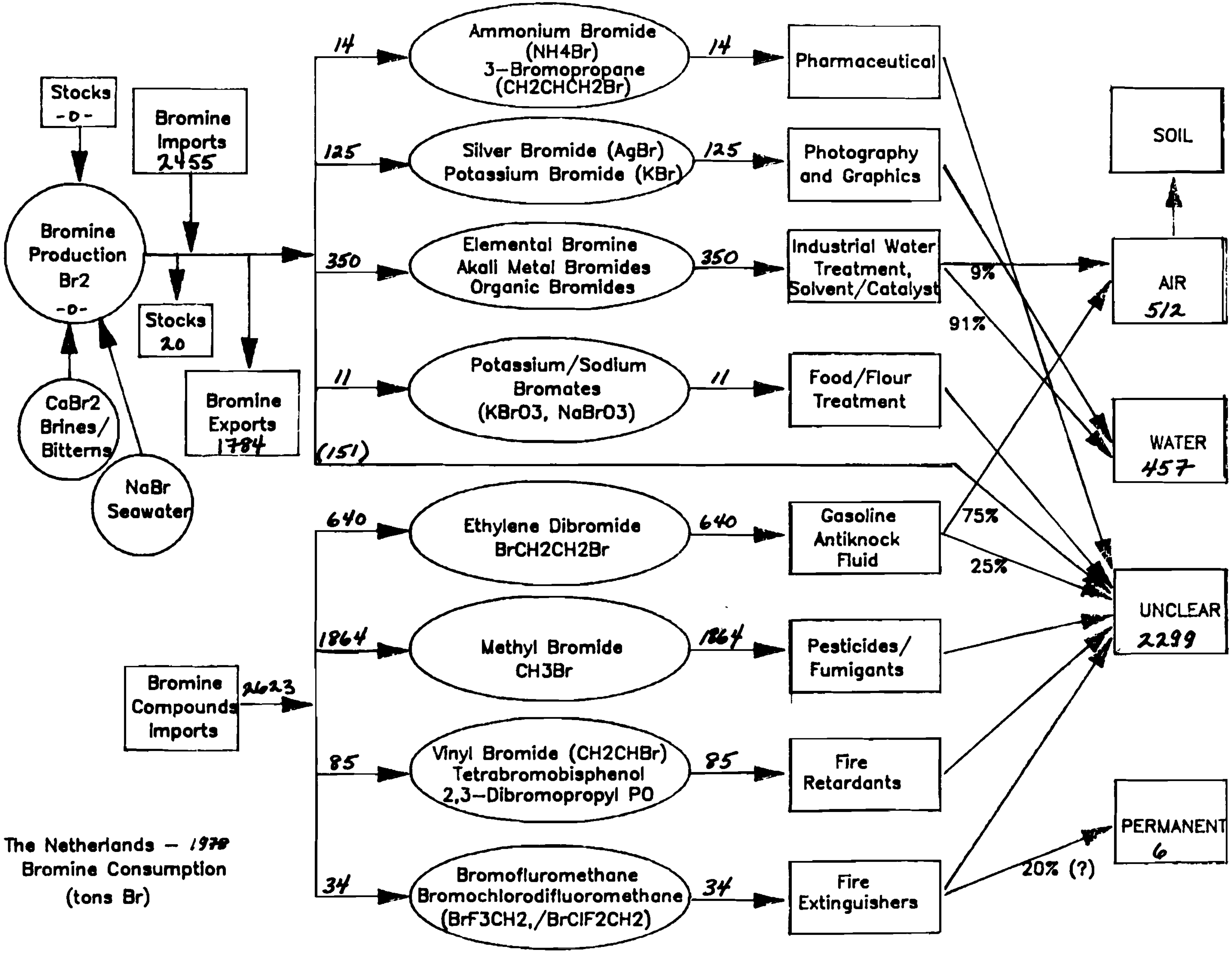


Figure 3-6: The Netherlands, 1978 - Bromine Consumption (tons Br)

Figure 3-7: U.S.A., 1978 - Bromine Consumption (tons Br)

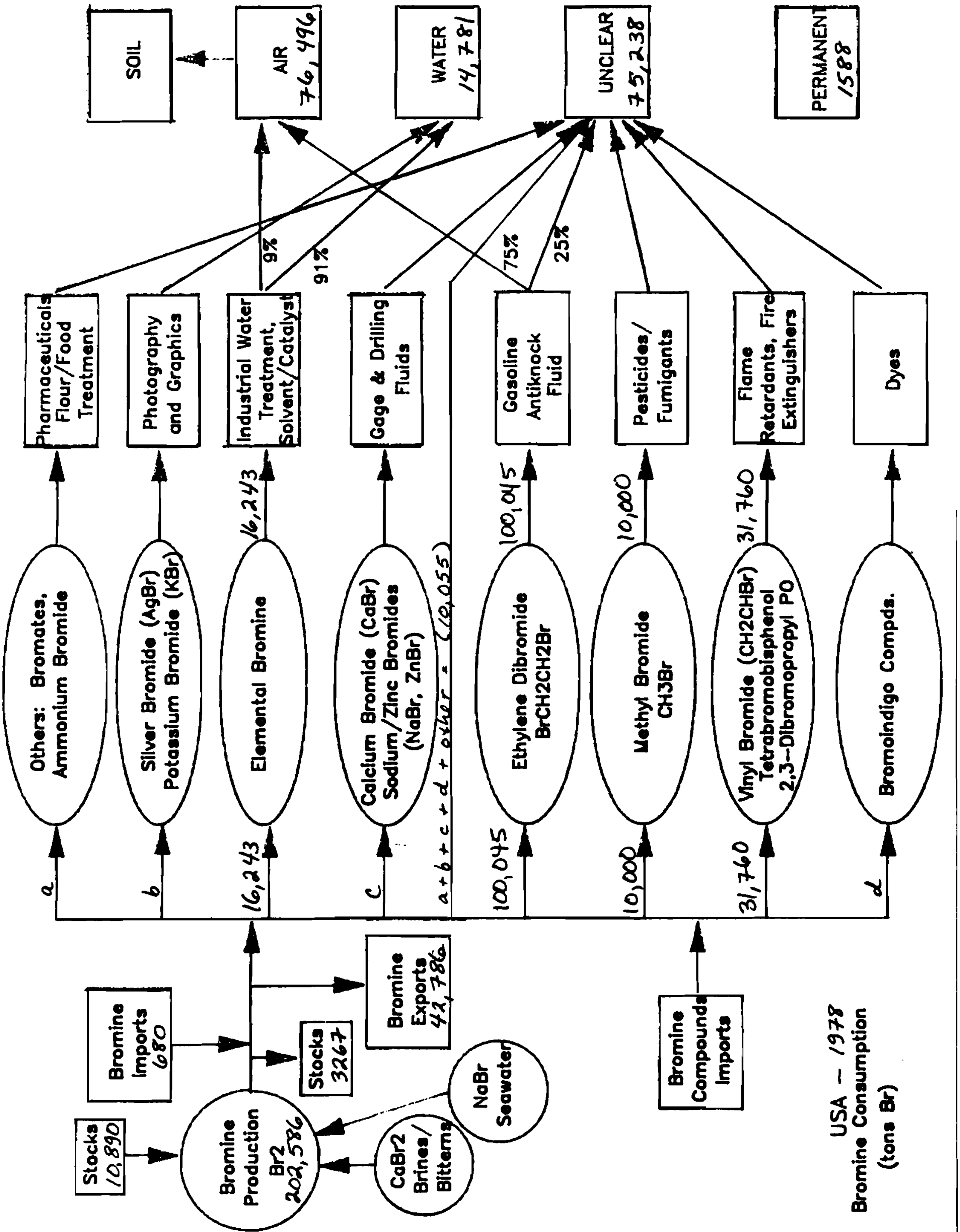


Table 3-5: Netherlands - 1978 (metric tons)

	AIR	WATER	PERMNT.	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
PHARMACEUT.		14		14	
DRILLING FLUIDS					
OTHER				162	162
TOTAL	512	457	6	2,299	3,274
% of TOTAL	15.64%	13.96%	0.18%	70.22%	100%

Table 3-6: USA - 1978 (metric tons)

	AIR	WATER	PERMNT.	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
PHARMACEUT.					
DRILLING FLUIDS					
OTHER				10,055	10,055
TOTAL	76,496	14,781	1,588	75,238	168,103
% of TOTAL	45.51%	8.79%	0.94%	44.76%	100%

Figure 3-8: The Netherlands, 1984/85 - Bromine Consumption (tons Br)

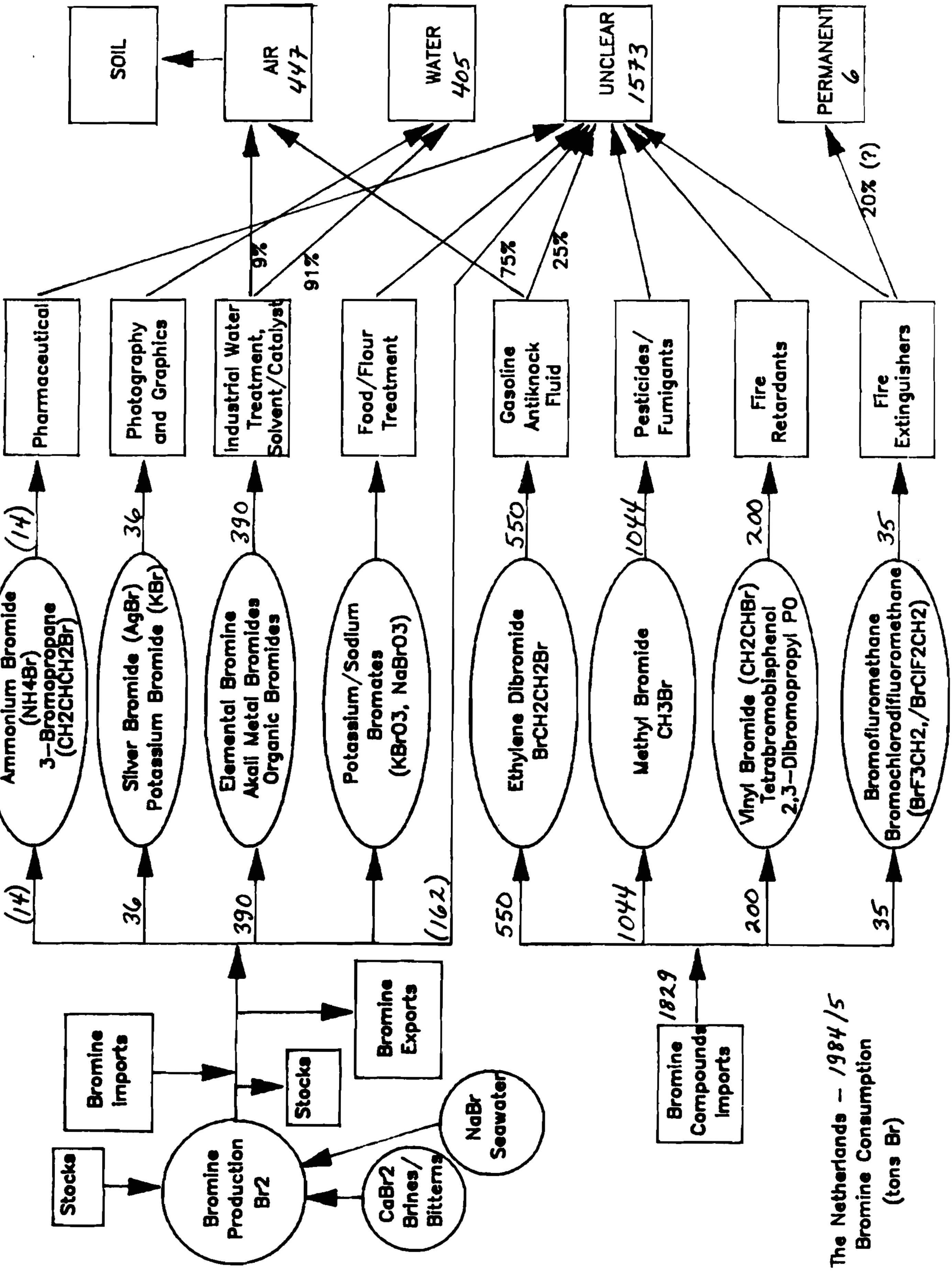


Figure 3-9: U.S.A., 1985 - Bromine Consumption (tons Br)

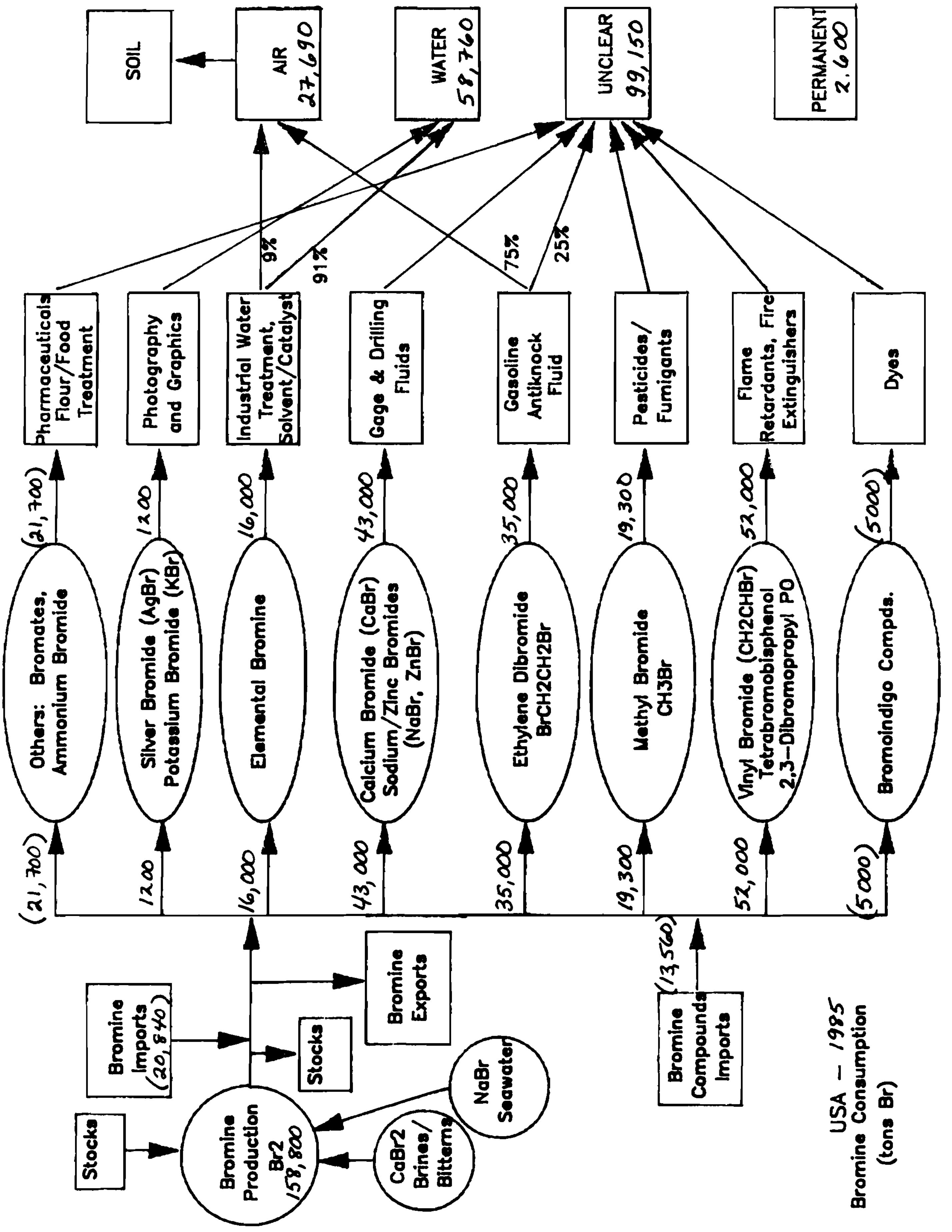


Table 3-7: Netherlands - 1984-5 (metric tons)

	AIR	WATER	PERMNT.	UNCLEAR	TOTAL	% 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%
PHARMACEUT.		14			14	0.58%
DRILLING FLUIDS					0	0.00%
OTHER				162	162	6.66%
TOTAL	447	405	6	1,573	2,431	100%
% of TOTAL	18.39%	16.66%	0.25%	64.71%	100%	—

Table 3-8: USA - 1985 (metric tons)

	AIR	WATER	PERMNT.	UNCLEAR	TOTAL	% 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%
% of TOTAL	14.33%	30.41%	1.35%	51.32%	100%	

Figure 10: Western Europe, 1985 - Bromine Consumption (tons Br)

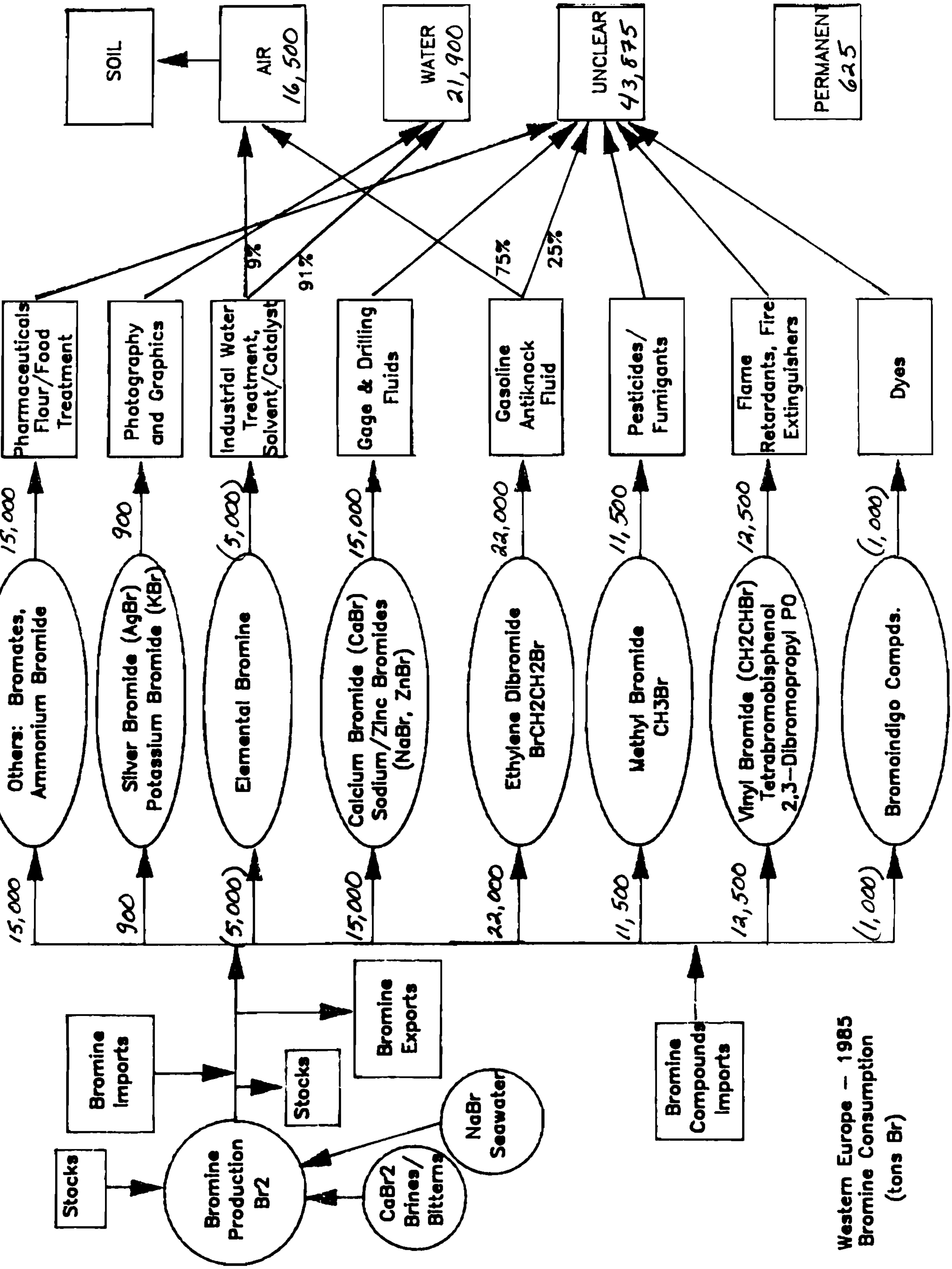


Table 3-9 Western Europe - 1985 (metric tons)

		AIR	WATER	PERMNT.	UNCLEAR	TOTAL	%of TOTAL
GAS (EDB)		16,500			5,500	22,00	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%
PHARMACEUT.	(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%
% of TOTAL		19.90%	26.42%	0.75%	52.93%	100%	----

NOTES:

(a) Varies 605 - 1200 tons

(b) Industry estimate based on very little data and unreliable

(c) Estimate based on worldwide use of 4000 - 8000 tons

(d) Estimate of "other" based on little data; includes dyes with usage of 30,000 worldwide

Conclusions

Clearly, during the 1950s, 1960s, and 1970s, the majority of bromine was used as a gasoline additive. As shown in Table 3-6, the U.S. consumed 60% of its bromine in the manufacturing of EDB during 1978, while sanitary and bleaching uses consumed 9.7%, fire retardants used 19%, and agricultural uses 6%.

The consumption patterns today are quite different as shown in Tables 3-7 and 3-8.

In the Netherlands, EDB continued to consume roughly 22.6% of the demand (550 tons in 1985 vs. 649 tons in 1978). But, use of methylbromide (CH_3Br) decreased from 1864 tons to 1044 tons (from 60% of the demand in 1978 to 43% in 1985). Use of bromine in firestuffs increased slightly from 119 to 235 tons representing 9.67% of the consumption while use in photography decreased to 1.5% of demand (36 tons down from 125 tons). Data was not available for the other use categories.

European consumption of bromine in 1985 was similar to the U.S. 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 U.S.. Fire regulations in Europe are expected to increase 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 U.S. market shift which took place in the late

1970s and early 1980s. The one exception is in the consumption of drilling fluids. Demand will be limited due to the low level of new drilling activity in Western Europe.

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% of the bromine is emitted to the air in the form of PbBr2 or other Pb-Cl-Br compounds, and 25% 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 10% 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 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; here, the only potential problem 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 to the air, water, and soil either directly or indirectly. Even so, the "unclear" category accounts for roughly 50% of all bromine consumed in the U.S. and Western Europe, and 65-70% of the bromine consumed in the Netherlands. The use of firestuffs, fumigants, and pesticides are 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 U.S. during the 1970s and earlier, at least 46% 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% of bromine consumed was released to 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 to water bodies were less than 15% 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 U.S. decreased its bromine air emissions by 2/3 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 have reduced their consumption of methyl bromide, which may impact 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) and appear preferable to EDB. 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 contribute the same net amount of bromine to the air, or water, or soil. The fundamental questions become: which compounds are most toxic, and are the shifting consumption patterns beneficial for the environment? And, 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.

Chapter 4*

CHLORINE: ANTHROPOGENIC SOURCES AND FLOWS

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 .15% 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.

Production

Chlorine was first produced as a pure material in 1774 by Carl Scheele who reacted MnO_2 with HCl to produced 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.

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 general in many parts of the developed and developing world. Chlorination has played a major part in virtually eliminating waterborne diseases from those areas in which it is practiced. Biological growth in industrial water supplies is commonly controlled using chlorine as an antifoulant treatment.

Although the amount of chlorine employed for bleaching and disinfecting has increased since its first use, the fraction of the total chlorine production used in these areas has declined due to 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, chlorinations are carried out by four general methods. The first uses molecular chlorine for substitution of hydrogens. These are chain reactions, initiated with UV light, catalysts or thermal scission of the Cl_2 molecule. The second method is Cl_2

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* Written by Janet Yanowitz

addition across an unsaturated bond. A third process utilizes HCl which also adds across an unsaturated bond or substitute on an alcohol. The fourth method, known as oxychlorination, requires HCl, 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 markets. Polyvinyl chloride is the most significant example. Several elastomers, or rubbers are made which incorporate chlorine in the product. Neoprene and hypalon are two examples.

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, tetramethyllead 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, which 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. They also have many industrial solvent applications.

A summary of the most important chlorine containing compounds and their major uses is provided in Table 4-1.

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 use is shown in three process-product diagrams in Figures 4-1,4-2, and 4-3. No quantitative data have been gathered. The reader may also refer to two materials 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 Appendix B.

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

There are several reasons for this chlorine based materials balance. 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

Table 4-1. Chlorine Compounds and Their Major Uses.

Important Chlorine Compounds	Major Uses
Cl_2 - molecular chlorine	disinfection of water, chlorination of hydrocarbons, bleaching of pulp and textiles
NaCl - sodium chloride	food additive, source of chlorine
HCl - hydrogen chloride	chlorination of hydrocarbons, pickling of steel, oil-well acidizing, food processing
KCl - potassium chloride	source of chlorine
ClO_2 - chlorine dioxide	disinfection of water
$Na(ClO_2)$ - sodium chlorite $Ca(ClO_2)_2$ - calcium chlorite $K(ClO_2)$ - potassium chlorite	bleaching of textiles, wood and paper pulp
Na(OCl) - sodium hypochlorite $Ca(OCl)_2$ - calcium hypochlorite	bleaching and disinfection
$KClO_3$ - potassium chlorate	fireworks, matches, explosives
$NaClO_3$ - sodium chlorate	weed killer
$KClO_4$ - potassium perchlorate NH_4ClO_4 - ammonium perchlorate	fuels for rockets and jet propulsion
$AlCl_3$ - aluminum chloride	catalyst in petroleum, drug and cosmetics industries
$TiCl_4$ - titanium chloride	smoke screen agent, sky writing
CH_3Cl - methyl chloride	solvent, intermediate in the production of silicone rubbers, tetramethyl lead and quaternary ammonium compounds, refrigerant
CH_2Cl - methylene chloride	solvent, intermediate in the production of fluorocarbons
$CHCl_3$ - chloroform	solvent, intermediate in the production of fluorocarbons
CCl_4 - carbon tetrachloride	solvent for dry cleaning and in industry
C_2H_5Cl - ethyl chloride	intermediate in the production of silicone rubbers, ethyl cellulose and tetraethyl lead
$C_2H_4Cl_2$ - ethylene dichloride	intermediate in the production of vinyl chloride, polysulfide rubbers and ethylene diamine

Table 4-1. Cont.

Important Chlorine Compounds	Major Uses
$ClCH_2CHOCH_2$ - epichlorohydrin	intermediate in the production of epoxy resins, polymerized to form epichlorohydrin rubbers
S_2Cl_2 - sulfur chloride	vulcanization of rubber
CCl_2CHCl - trichloroethylene	solvent for drycleaning and industrial degreasing and cleaning
CCl_2CCl_2 - perchloroethylene	solvent for drycleaning and industry, intermediate in fluorocarbon production
$COCl_2$ - phosgene	intermediate in the production of isocyanates for urethanes, fumigant, intermediate in the production of urea
$CH_2CHCHClCH_2$ - chloroprene	polymerized to neoprene rubber
$^{\sim\sim\sim}CH_2CHCHClCH_2^{\sim\sim\sim}$ - neoprene	adhesives, coatings, wire and cable insulations, automobile fittings and protective clothing
$^{\sim\sim\sim}C_3H_6CHClCH_2CHSO_2ClC_2H_4^{\sim\sim\sim}$ - hypalon	elastomer with high ozone and oxidation resistance, used in gaskets, wire and cable insulation, roof coatings, white sidewall tires and coated fabrics
CH_2CHCl - vinyl chloride	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

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 away from the sea coast except for 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 (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% of the ozone at an altitude of 40 km disappeared between 1978 and 1984. To explain the ozone decrease most hypotheses assume large concentrations of chlorine atoms in active forms that can catalyze 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 CFC-11 and CFC-12 are increasing at an astonishing rate of 5% per year. Studies have also shown that methyl chloroform and carbon tetrachloride are growing at rates of 7% and 1% per year, respectively. According to Pauline Midgely, technical liason at ICI Americas (a major manufacturer of chlorofluorocarbons (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 lifetimes in the atmosphere of about 75 and 110 years, respectively. Carbon tetrachloride has a lifetime of 50 years. Other CFC's are comparable (C&EN, 1986). The CFC's which we are currently producing will be in the atmosphere for a long time.

Chlorinated hydrocarbons 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 (PCB).) The most common method to detoxify and destroy 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 $500^o C$ are required to combust chlorinated hydrocarbons completely (Tsang and Shaub, 1982).

The thermodynamics of CHC combustion are complex. The formation of HCl and Cl_2 generally constitute the bulk of the chlorine bearing species in 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 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 can 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 one of water pollution. Even if all of the chlorine is present as recoverable HCl, the disposal of the HCl poses problems. Fully 90% of the HCl produced in the US in 1972 was the byproduct of

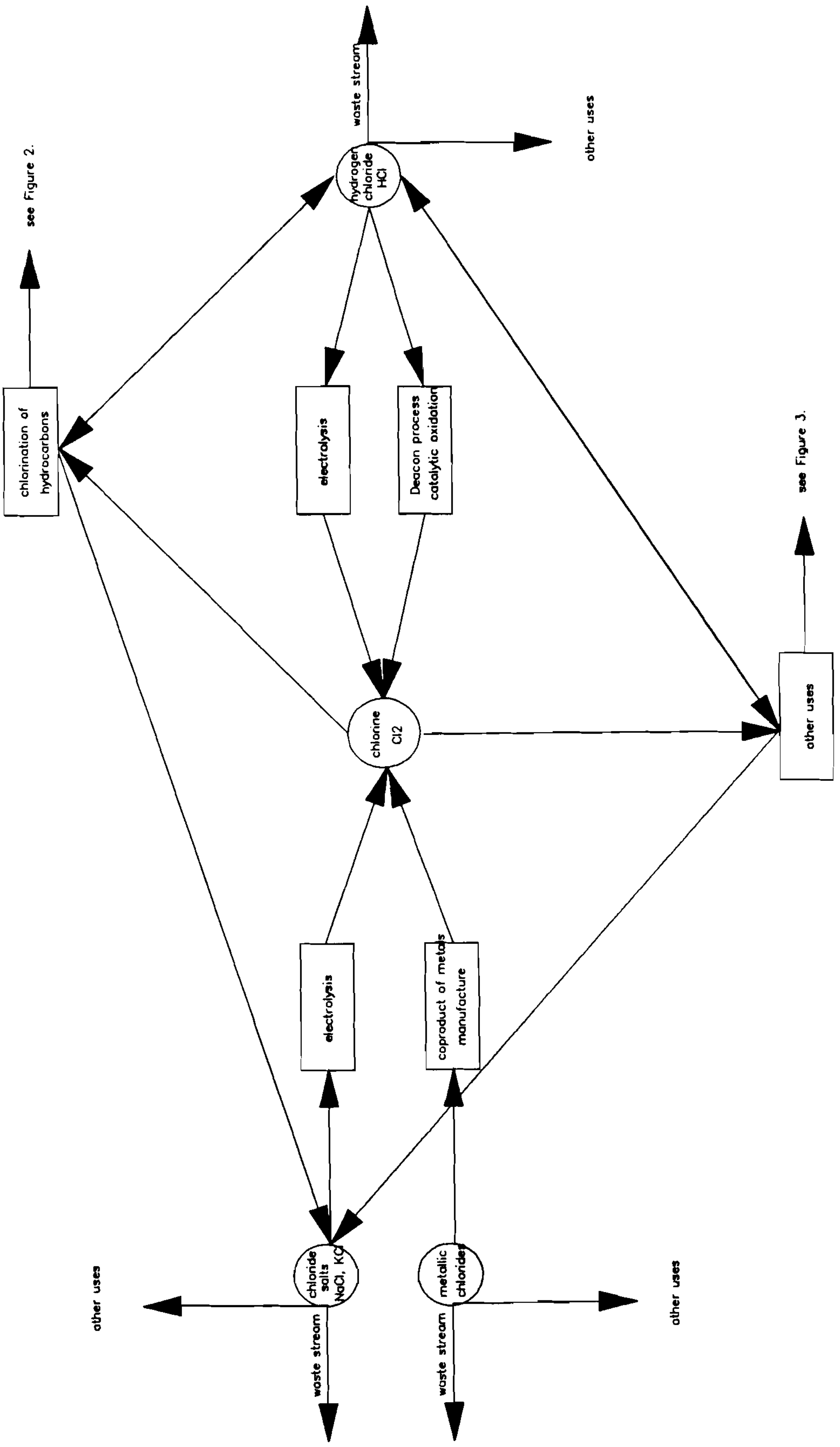

Figure 4-1: Materials Balance for Chlorine

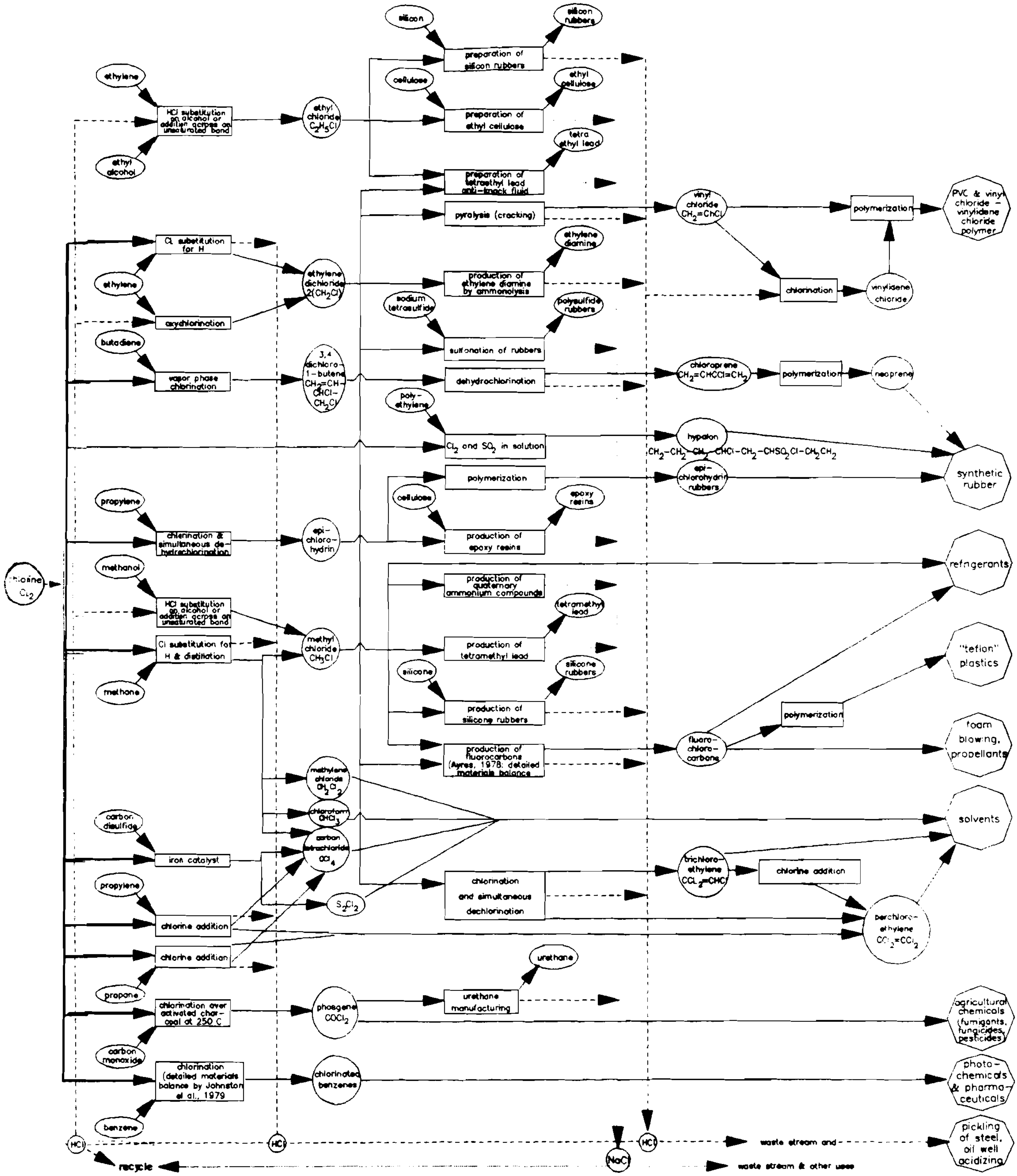

Figure 4-2: **Materials Balance for Chlorination of Hydrocarbons**

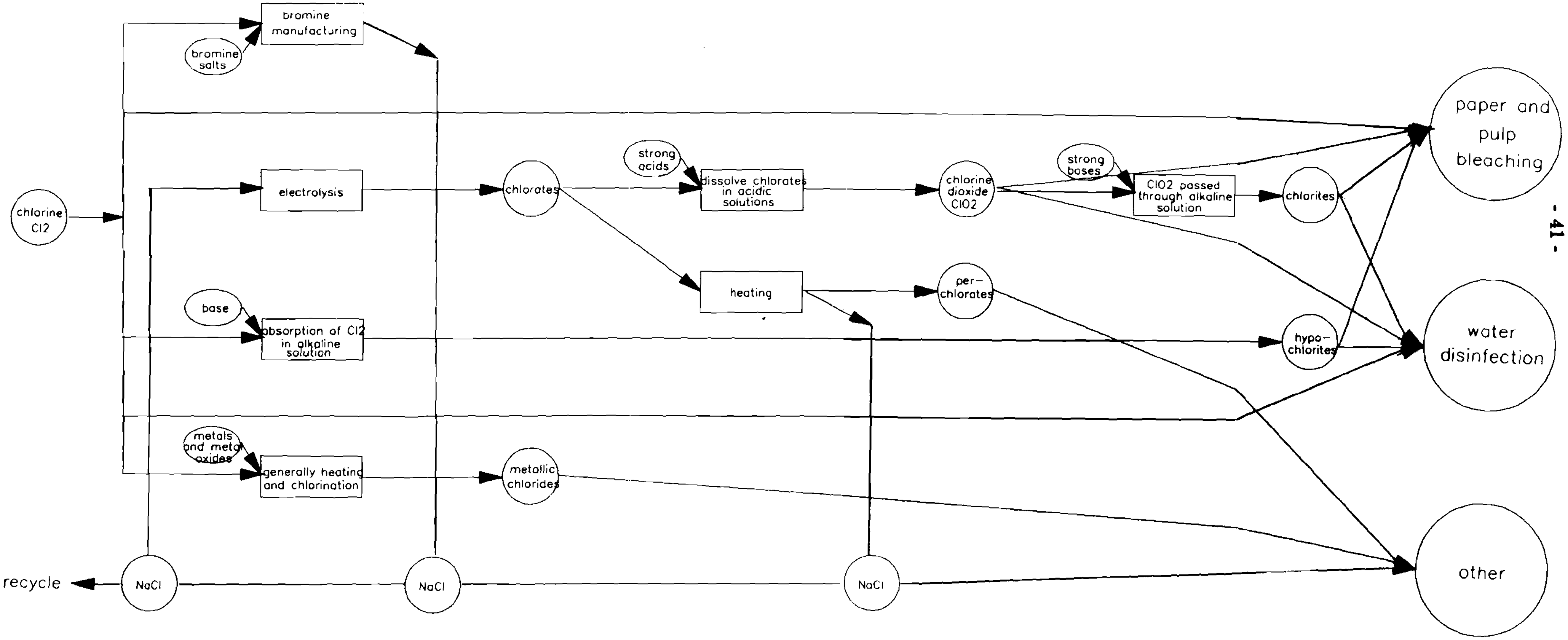

Figure 4-3: **Materials Balance for Inorganic Chemicals from Chlorine**

chlorinations (Current Industrial Reports, 1973). According to an NRC study (1976), byproduct hydrogen chloride is considerably in excess of what is recovered and reported and the disposition 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 added in bleaching and disinfecting operations. Both are highly corrosive. Chlorine is a strong oxidizing agent that can oxidize metals and other materials. It supplies a strong acid that can then 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 that aid in the solubilization and dispersion of corrosion products that, in its absence, might remain to form a passive barrier (NRC, 1976).

Claeys, et al. (1980) and Leach (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 become sedimentary materials or through microbial action be reintroduced into the watershed (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 2% 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 are not easily accomplished. Current production levels of these materials will therefore have a significant impact on the future concentration of chlorinated materials in the environment. The materials balance approach underlines that the production rate of these hazardous materials must be equal to the rate at which they are transformed into a new form plus the rate of accumulation. Production, instead of recycling, inevitably results in a flow of these materials into the environment. Many of these compounds are environmentally active, in the atmosphere, in water and in the living environment. Policy makers who wish to control the action of these materials in the biosphere need a better understanding of the production of these substances, because the control of production may be the simplest and most efficient way to manage the resulting environmental problems.

CHAPTER 5*

SULFUR: ANTHROPOGENIC SOURCES AND FLOWS

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.

Sources and Production of Sulfur and Sulfuric Acid

Worldwide, there are currently three major sources for the production of elemental sulfur and sulfuric acid; (1) native sulfur found in the limestone caprock of salt domes, volcanic deposits, or bedded anhydrite, (2) hydrogen sulfide present in "sour" natural gas, refinery gas and other fuel gases, and (3) ferrous and nonferrous metallic sulfides. 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-1970's, about 70% 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 investment needed for new mines. Production from secondary sources such as hydrocarbons is increasing due to stricter environmental regulations on atmospheric emissions.

Gypsum was formerly used in Europe as a source of sulfur. The method was developed by Germany during WWI to solve the problem of sulfur shortages. The process was refined and was a significant source of sulfur at least through 1959 (Duecker and West, 1959). The process is apparently no longer commercially viable, at least partially 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 which is recovered from emissions control technologies is used for by-product sulfur production; it is instead 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. Generally this is accomplished by heating to decompose the sulfuric acid to sulfur dioxide, oxygen and

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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 show in economic trade data.

Sulfuric acid is rarely used for its sulfur content but rather for its properties as an acid, catalyst, and a 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 for the manufacture of sulfuric acid. Since the advent of the contact process, it has declined in importance. By 1973, only 0.5% of the acid produced in the U.S. was by the chamber process. No new chamber plants have been built in the U.S. since 1956.

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

Major Uses

As mentioned above, sulfur and sulfuric acid are employed in an extremely large number of industrial processes. This is demonstrated in Table 5-1 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 5% of the total. A similar use pattern is seen in the breakdown of end uses in Table 5-2 from the U.S. Mineral Yearbook (1984). This use pattern shows phosphatic fertilizers accounting for 66% of the total sulfur use, petroleum refining products accounting for 7%, and all other uses accounting for 5% 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.

Three tables of important sulfur compounds are included with this report. The first, Table 5-3, is taken from Nriagu (1978) and is less detailed than the other two, Tables 5-4 and 5-5 from Fulton (1975). There is some overlap between these tables and also some differences. In addition, there were a few important sulfur compounds discussed by Lowenheim (1975) whose uses are not found on either chart. They are listed below.

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

Table 5-1: Distribution of Sulfuric Acid by End Use in the United States between 1950 and 1970[a] (Nriagu, 1978).

	Percent of Total		
Use	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.

Table 5-2: Sulfur and Sulfuric Acid Sold or Used in the United States, by End Use (U.S. Mineral Yearbook, 1984)

SIC	End Use	Elemental sulfur (1)		Sulfuric Acid (sulfur equivalent) (1)		Total		Total
		1983	1984	1983	1984	1983	1984	1984
102	Copper ores	-	-	175	341	175	341	2.6
1094	Uranium and vanadium ores	-	-	82	53	8253	0.4	
10	Other ores	-	-	45	63	45	63	0.5
20	Food and kindred products	W	W			W	W	W
26,261	Pulpmills and paper products	14	29	248	266	262	295	2.2
28,285,286, 2816	Inorganic pigments, paints and allied products, individual organic chemicals, other chemical products	115	127	125	109	240	236	1.8
281	Other inorganic chemicals	250	285	316	379	566	664	5.1
282,2822	Synthetic rubber and other plastic materials and synthetics	34[2]	65[2]	315	314	349[2]	379[2]	2.9
2823	Cellulosic fibers, including rayon	(3)	(3)	96	51	96	51	0.4
283	Drugs	-	-	28	24	28	24	0.2
284	Soaps and detergents	23	14	104	83	127	97	0.7
286	Industrial organic chemicals	-	-	367	307	367	307	2.3
2873	Nitrogenous fertilizers	-	-	52	85	52	85	0.6
2874	Phosphatic fertilizers	-	-	7,113	8,621	7,113	8,621	65.6
2879	Pesticides	-	-	28	23	28	23	0.2
287	Other agricultural chemicals	563	480	60	15	623	495	3.8
2892	Explosives	-	-	20	39	20	39	0.3
2899	Water-treating compounds	-	-	130	70	130	70	0.5
28	Other chemical products	-	-	67	132	67	132	1.0
29,291	Petroleum refining and other petroleum and coal products	142	278	677	676	819	954	7.3
30	Rubber and miscellaneous plastic products	W	W	31	W	31	W	W
331	Steel pickling	-	-	94	88	94	88	0.7
333	Nonferrous metals	-	-	11	16	11	16	0.1
33	Other primary metals	-	-	6	37	6	37	0.3
3691	Storage batteries (acid)	-	-	58	58	58	58	0.4
	Exported sulfuric acid	-	-	55	20	55	20	0.2
	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	

W Witheld to avoid desclosing company propriety data; included with "unidentified"

1 Does not include elemental sulfur used for production of sulfuric acid

2 Includes elemental sulfur used in cellulosic fibers

3 Included with "Synthetic rubber and other plastic materials and synthetics."

Table 5-3: Major Uses of Sulfur Compounds (Nriagu, 1978)

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
	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	See Table 5-5
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, pharmacetuicals, 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

Table 5-4:

Sulfur Derivatives and End Uses (Fulton, 1975)

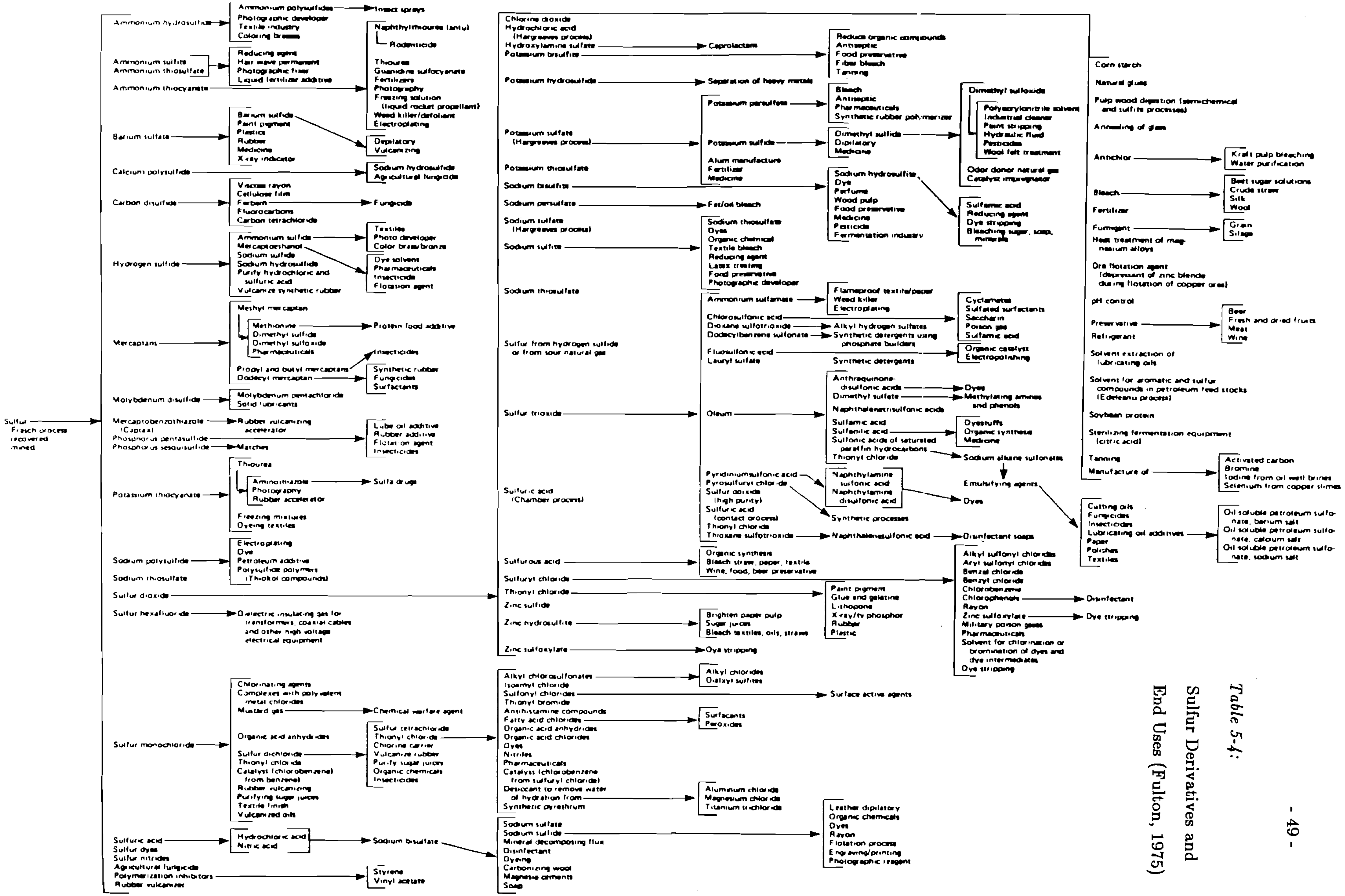
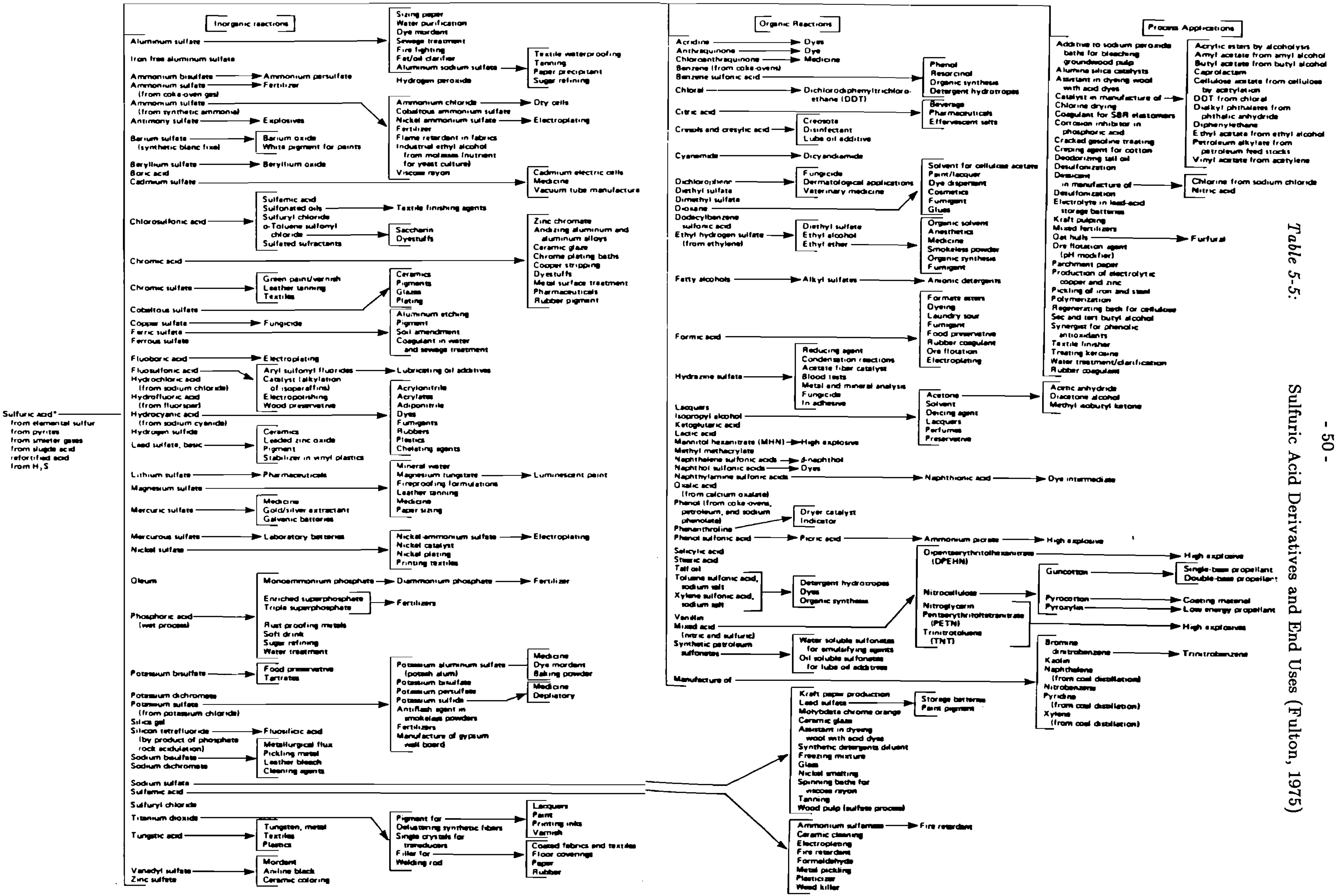


Table 5-5: Sulfuric Acid Derivatives and End Uses (Fulton, 1975)



* Varying strengths of sulfuric acid are used as processes require (sulfuric acids ~100% H_2SO_4, or oleum 100% H_2SO_4)

Source: Anon., 1967 (courtesy Stanford Research Institute).

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 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 5-1, 5-2, and 5-3. Figure 5-1 shows sulfur extraction and sulfuric acid production. Figure 5-2 shows processes, intermediary chemicals and end uses for sulfur. Figure 5-3 shows processes, intermediary chemicals and end uses for sulfuric acid. In these charts, products are indicated by circles and ovals and processes are indicated by rectangles. The numbers in the process boxes correspond to the numbers given for the process information presented in Appendix C.

In some cases there is incomplete process data and in other cases there is no information about a given process. Nevertheless, we began to examine the applicability of the materials balance method to sulfur and to determine what data are available. From this point forward, 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 Tables 5-3, 5-4 and 5-5. They basically indicate the end use categories as shown in the Minerals Yearbook, 1984. This is the level of detail for which one can find trade data in the U.S., and is an indication of what might be hoped for in Europe. (In addition, the Tables were not complete at the time the Appendix was being created.) The information in them may be useful for future development of the sulfur process-product diagram.

Two useful references were found just as this report was being completed. They are *Sulfur, Energy and Environment* by Meyer, 1977 and Industrial Minerals and Rocks edited by Lefond, 1975. Both of these contain some process information which has not been incorporated into this report.

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 5-4. Ivanov and Freney (1983) estimate that globally 113 Tg 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% 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 anthropogenically mobilized sulfur, they contribute a significant fraction and thus raise concern over the final environmental destination of this sulfur.

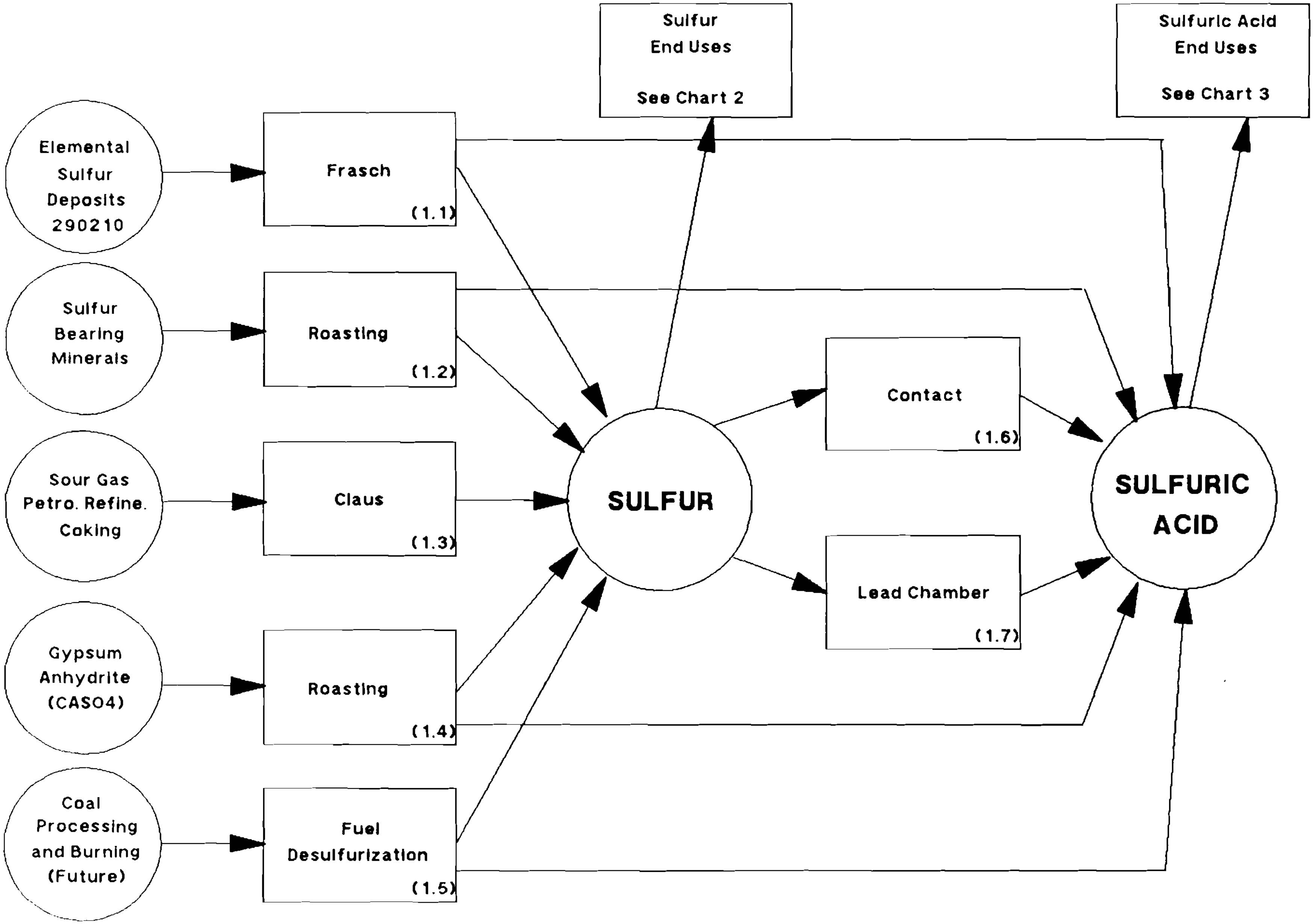


Figure 5-1: Sulfur Extraction and Sulfuric Acid Production

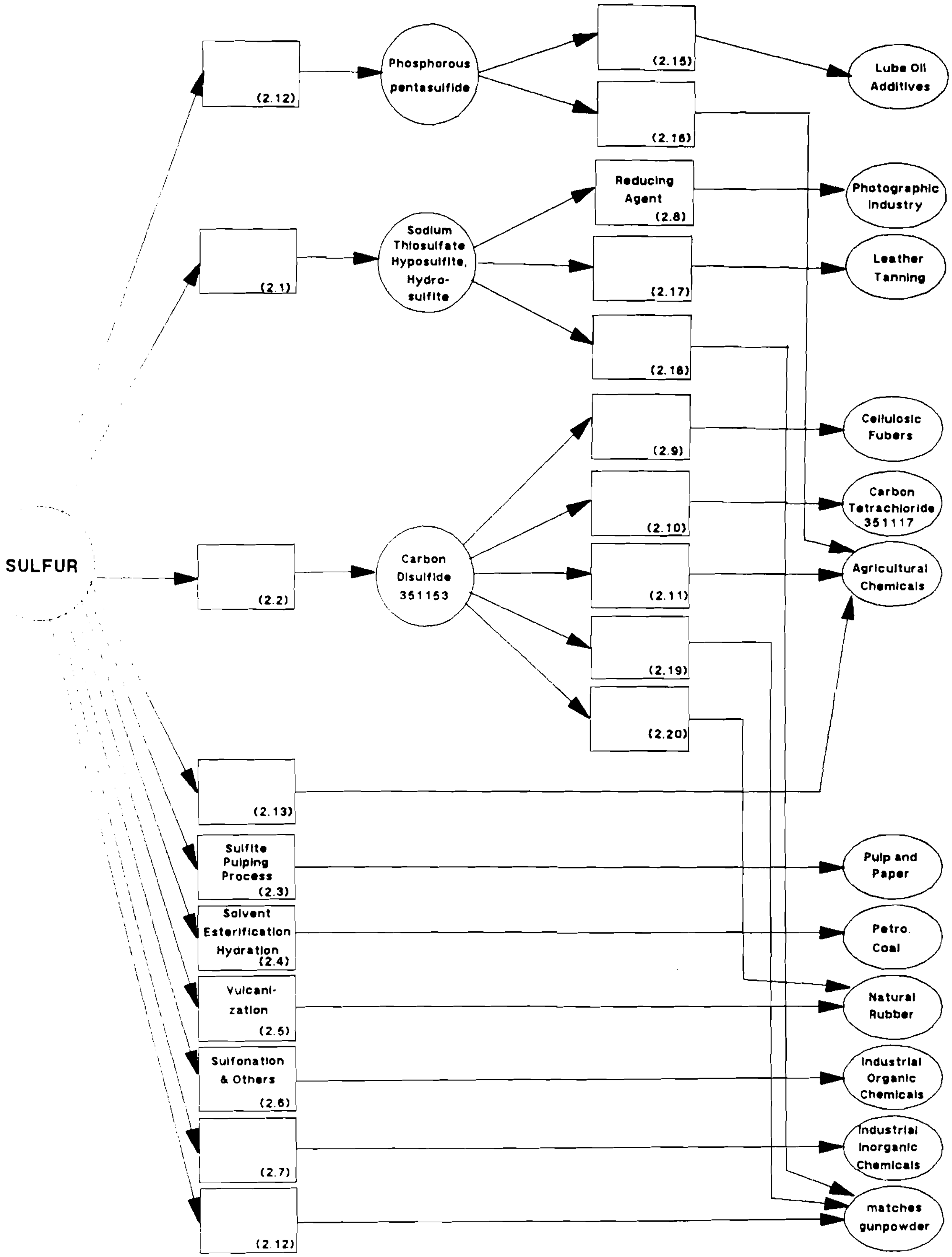


Figure 5-2: Sulfuric End Uses (Excluding Sulfuric Acid)

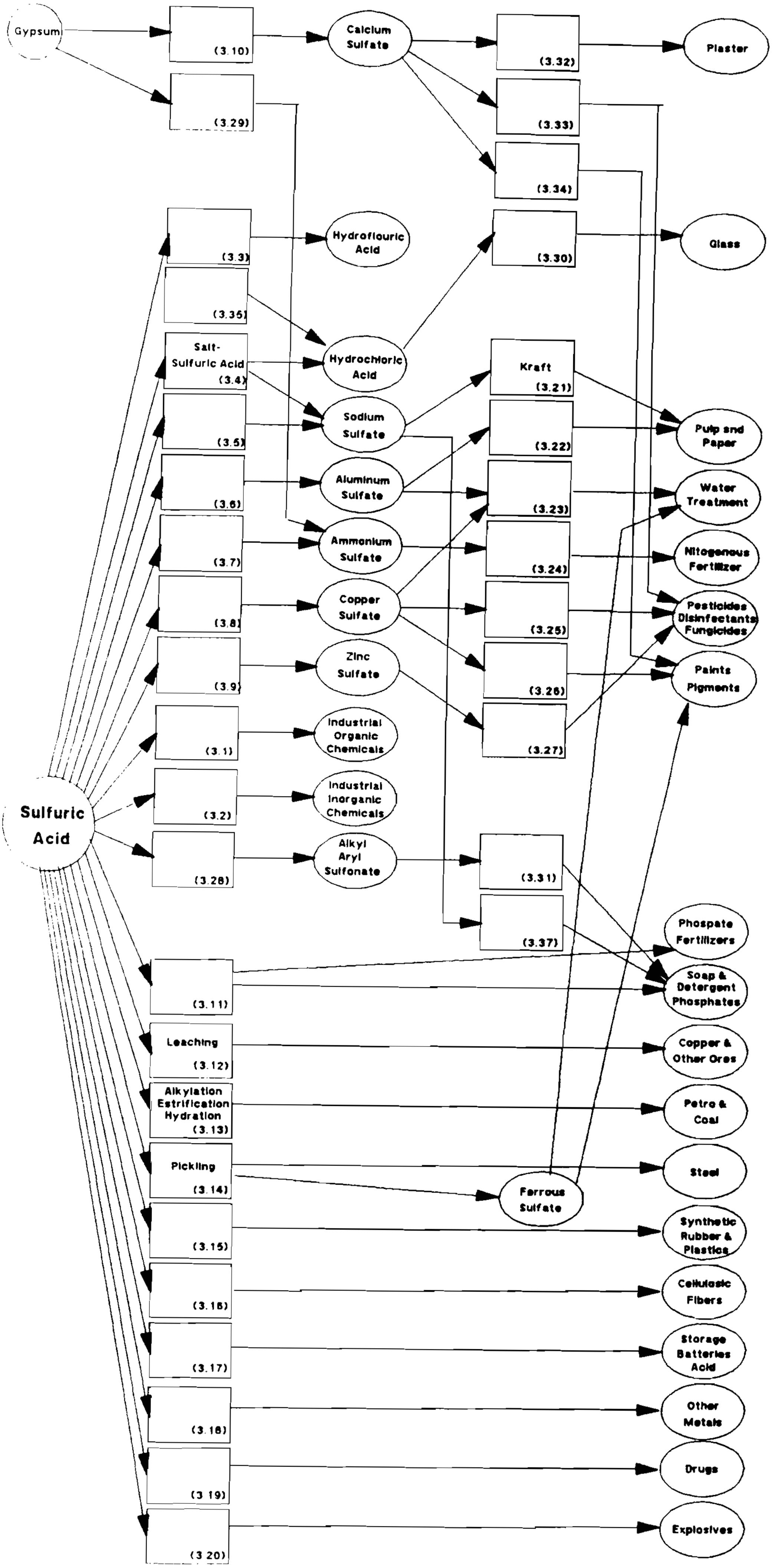
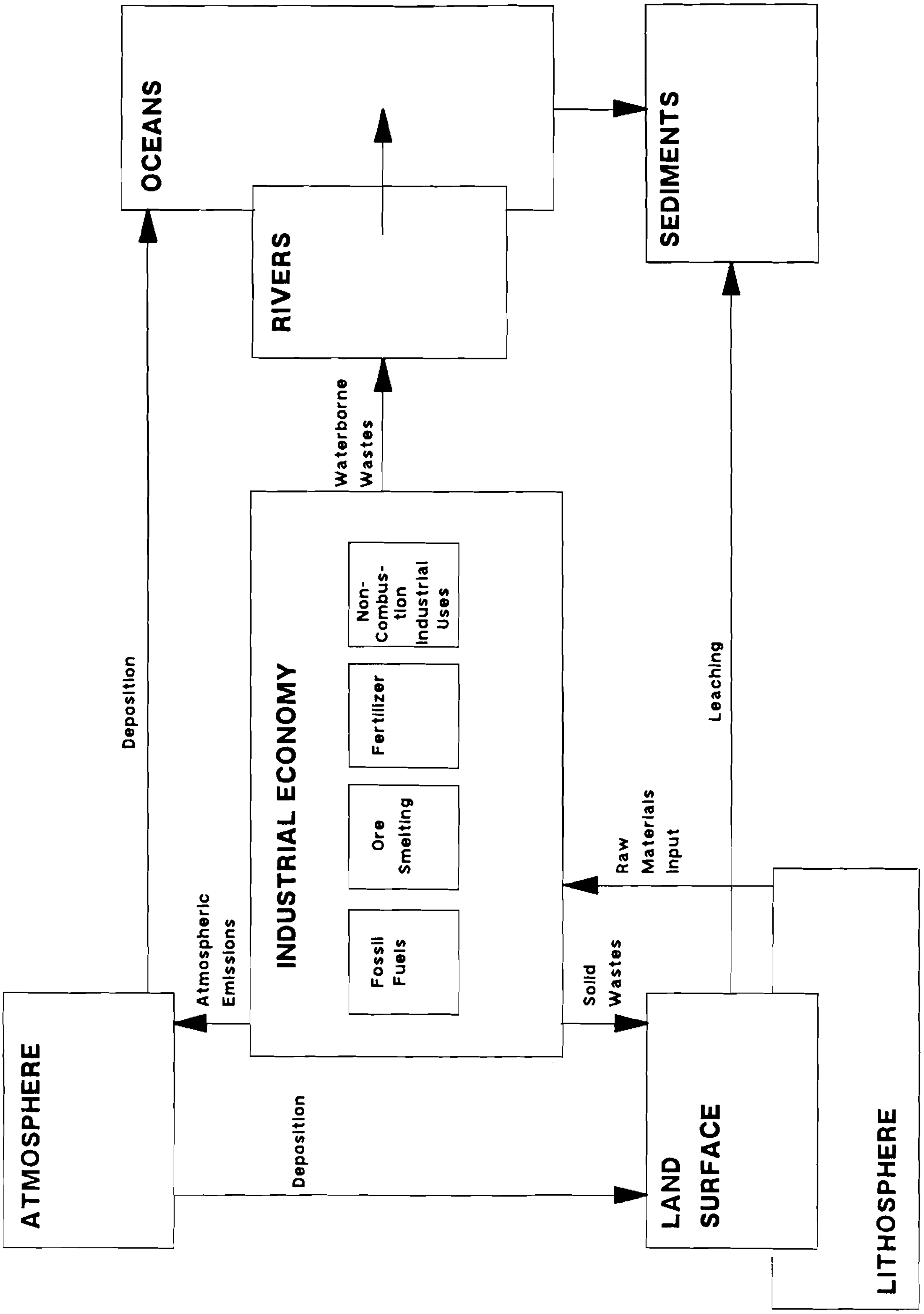


Figure 5-9: Sulfuric Acid End Uses

Figure 5-4: Anthropogenic Sulfur Cycle



Sulfur emissions are of greater importance on a regional than on a global scale. There are significant differences among European countries on the contribution of non-combustion industrial sources to anthropogenic sulfur emissions. When looking at Western Europe, the countries which have large pulp and paper industries and where relatively low amounts of fossil fuel are used for electricity generation show a much different picture than the global average. Tables 5-6 and 5-7 show the trend of emissions in Norway and Sweden. The emissions from industrial non-combustion sources in 1983 represent 52% and 32% of the total sulfur emissions for Norway and Sweden, respectively. Also, the percentage of total emissions from non-combustion sources have been increasing and are predicted to continue to increase. It is important to note that the above data for Norway and Sweden are for atmospheric emissions only, while the global estimate included all sulfur mobilized by the industrial economy. The percentages of airborne emissions from industrial sources in Norway and Sweden thus represent only part of the total sulfur which is cycled through the environment by industrial processes.

The sulfur mobilized by the industrial economy in Western Europe for non-combustive uses is compared to the atmospheric sulfur emissions from combustion and the total anthropogenic sulfur budget in Table 5-8. 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 5-6: Summary of the Emissions of sulfur for 1980, 1983 and 1985 and Estimated Emissions for 1993 and 2000 (Ministry of the Environment, Finland, 1986)

SOURCE OF EMISSION	EMISSION OF SO_2 THOUSAND TONS				
	1980	1983	1985	1993[1]	2000[1]
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		39%	36%	50%	59%

1) Estimated

Table 5-7: Sulphur Dioxide Emissions in Sweden (National Swedish Environmental Protection Board) (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

Table 5-8: Sources of Anthropogenic Sulfur, 1980 (KT S)

Country	Atmospheric Emissions - (a)			Sulfuric (b) Acid	Industrial (c) Sulfur	Industrial Sulfur/ Total
	Combustion	Industrial	Industrial/ Total	Consumpton	Consumption	Sulfur (d)
Austria	147	30	17%	101	119	45%
Belgium/Luxemburg	375	73	16%	792	932	71%
Denmark	226	1	0%	9	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	1512	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 Acid Rain Project. Combustion includes combustion from power plants, district heat generation, domestic and service sectors, transportation, and industry. Industrial 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 Acid Rain 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 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, the next question becomes, is it 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. That which 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 by and large 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 2 and 8 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 form of calcium sulfate and calcium sulfite. There is little in the literature on the land-based disposal of sulfur wastes from industrial processes. The lack of information in texts about sulfur and the environment (Ivanov & Freney, 1983, Nriagu, 1978, and 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):

> *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. (p. 161-162).*

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? And 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, 1984, and Morrison, 1982). These solid sulfur wastes pose three potential problems. One is simply waste disposal. The wastes are often in a sludge form which is difficult to dewater. In addition, the disposal of these wastes on land creates land which is then unusable for other purposes into the foreseeable future. The shear magnitude of wastes over the long term, say 100 years, will create disposal problems. 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 background concentrations. In addition, in the case of wastes from fuel emissions (and possibly some industrial processes) the leachate may also contain traces of heavy metals. The third problem is the possibility of sulfur gas emissions in the form of 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 is being disposed of on land and that we can expect this trend to continue and possibly increase. The possibility of countering this trend in the near future is for more sulfur to be recycled and less sulfur to be mined. Research and development into possible uses for the sulfur-bearing wastes from flue gas desulfurization continues. A promising use is in the cement industry (Ellison, 1984, and Chemical Marketing Reporter, 1984).

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 current use of a 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 will only be a solution of a current environmental problem but not a future one.

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 and the fact that the sulfur is not generally embodied in the end product complicate the use of the materials balance approach. The numerous diverse uses mean that the number of processes to be understood is huge. For example, only one use, fertilizers, has more than a 5% share of the sulfur end use in the U.S. The fact that sulfur is used for processing rather than being embodied in a product (i.e. it is a point source pollutant rather than a dissipative end use) 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 and what the final form of the sulfur is. What percentages of the sulfur are discharged to air, water or land? What is their chemical form? Thus, even if one were to decide that the materials balance approach could shed light on the problems of sulfur in the environment, it would be quite a task to gather the data necessary for a quantitative analysis.

Two arguments can be made in favor of a materials balance approach for sulfur. The first is that the industrial processes atmospheric emissions data for sulfur are considered unreliable and unverified for most of the European countries (Leen Hordijk, personnel communication, IIASA, 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 manufacture. In this way, it has identified one area where the materials balance approach is feasible.

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.

CHAPTER 6*

NITROGEN: ANTHROPOGENIC SOURCES AND FLOWS

Introduction

Nitrogen fixation is the conversion of dinitrogen (N_2) from the atmosphere to a form available for plants, animals, humans and industrial uses. Producton 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 or ammonia 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 number one petrochemical in production volume.

Sources and Producton of Nitrogen (Ammonia)

The first significant commercial source of ammonia, developed in the 1880's, was the by-product of the making of manufactured gas through the destructive distillation of coal. The next advance, developed by Fritz Haber in 1913, was the synthesis of 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 pressure and temperature. Karl Bosch adapted this process to industrial production, largely to meet the demand for ammonia for explosives during WWI. 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 °and 700 ° C.

Before WWII the major source of hydrogen for the synthesis of ammonia was the reaction of coal or coke and steam in the water-gas process. A small number of plants used water electrolysis or coke-oven by-product hydrogen. Since WWII 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. Sixty-five percent of these were from natural gas.

The source of nitrogen has always been air. Originally, the 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 the 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

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* Written by Vicki Norberg-Bohm

by chemical procedures. Because cheap electricity is a prerequisite for the industrial use of this process, 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 (1975).

Major Uses

It is estimated that ammonia and its derivatives are used in the manufacture of 2500 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 defoliation, pipe sealing, algae control, animal feeds, pest control, and bacteria control.

Worldwide, 80% of nitrogen is used in fertilizers and 20% in industrial chemical products. A breakdown of nitrogen consumption by end use for the United States is given in Table 6-1 (Slack, 1979). A breakdown of nitrogen consumption by major chemicals and three aggregated end use categories is given in Table 6-2 (Considine, 1974).

Major nitrogenous chemicals and their key end uses are shown in Figures 6-1 through 6-5 which are discussed in the next section.

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 6-1 shows the production of ammonia and three of its key derivatives; nitric acid, urea and ammonium sulfate. Figure 6-2 shows the production of fertilizers. Figure 6-3 shows the production of resins. Figure 6-4 shows the production of explosives. Figure 6-5 shows the production of other nitrogenous compounds and their key end uses. A more detailed presentation of the material presented in Figure 6-1 is shown in Figures 6-6 and 6-7 which are taken from Ayres (1985). In these charts, products are indicated by circles and processes are indicated by rectangles. The numbers in the process boxes correspond to the numbers given for the process information presented in Appendix C.

Table 6-1: Estimates of Total Producton 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, plastics	230	530	690	980	1,420	1,550
Chemicals	180	400	630	740	800	830
Pulp, paper	30	40	80	90	90	100
Metallurgy	30	40	60	70	80	90
Animal feeds*	60	150	290	440	540	640
Other**	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

* Primarily as urea.

** Refrigeration, rubber, water treatment, detergents, textiles, dyes, etc.

Table 6-2: Major Areas of Ammonia Consumption*

—	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

* Based on practice in the United States

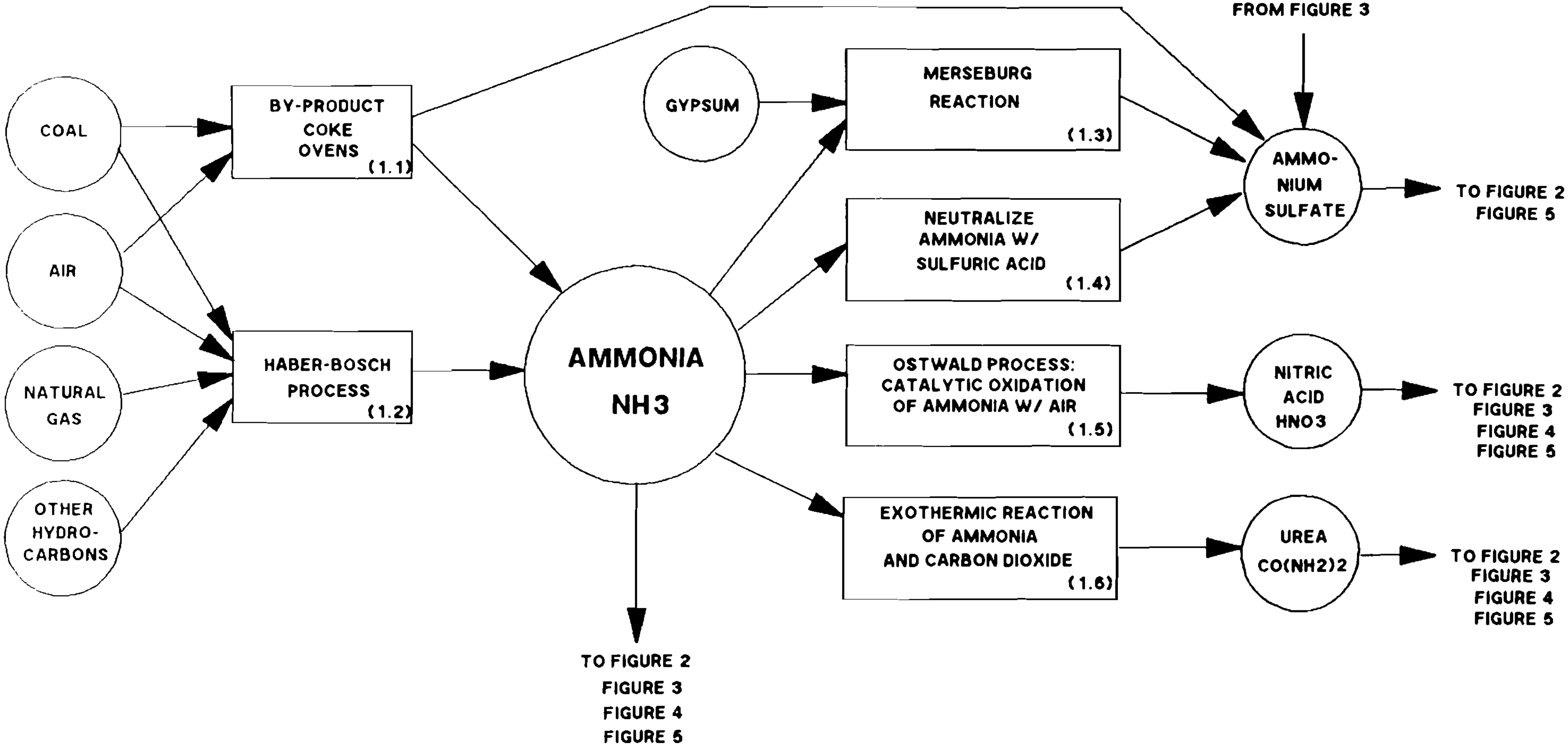


Figure 6-1: Production of Ammonia and Some Key Derivatives: Nitric Acid, Urea, and Ammonia Sulfate.

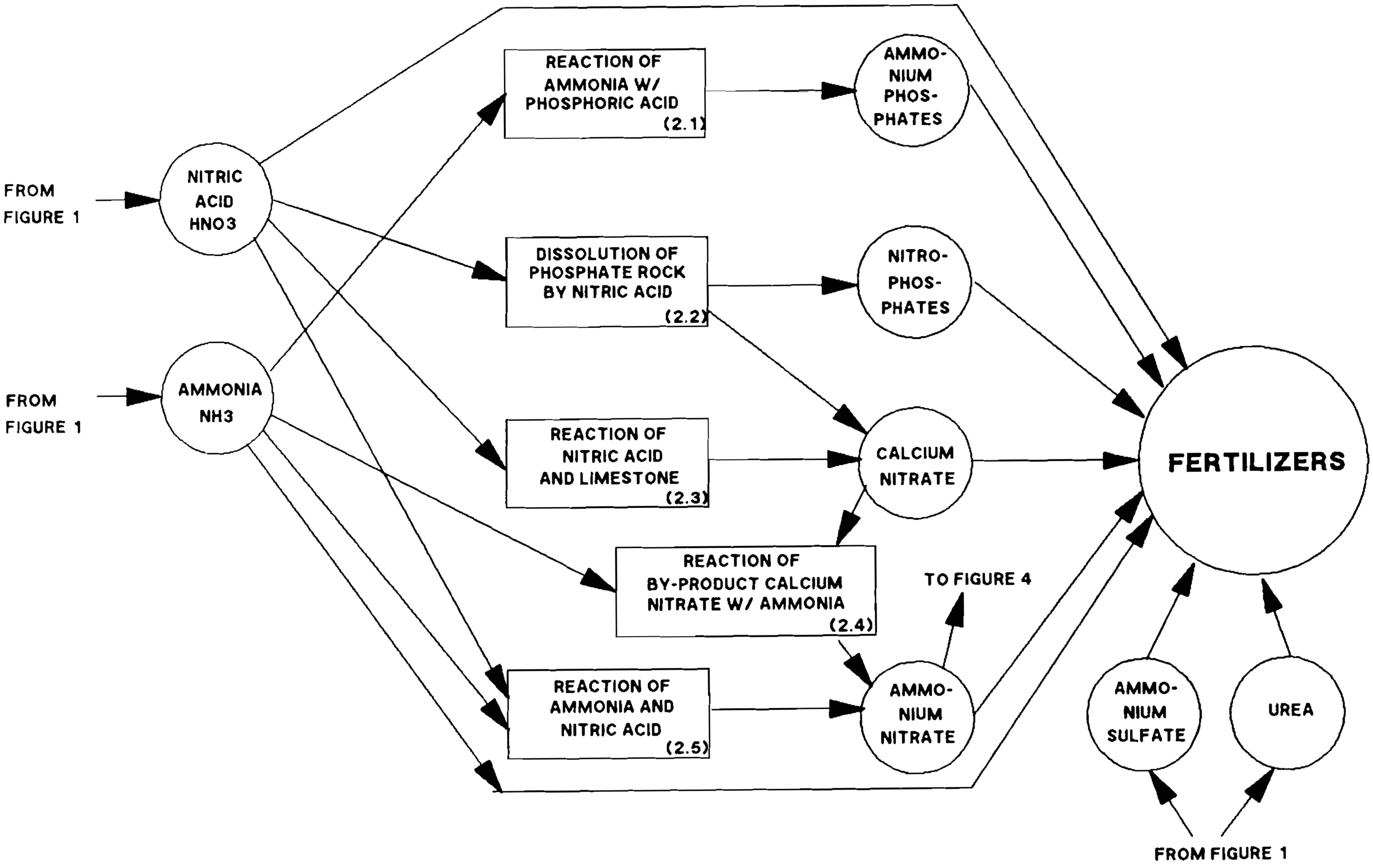
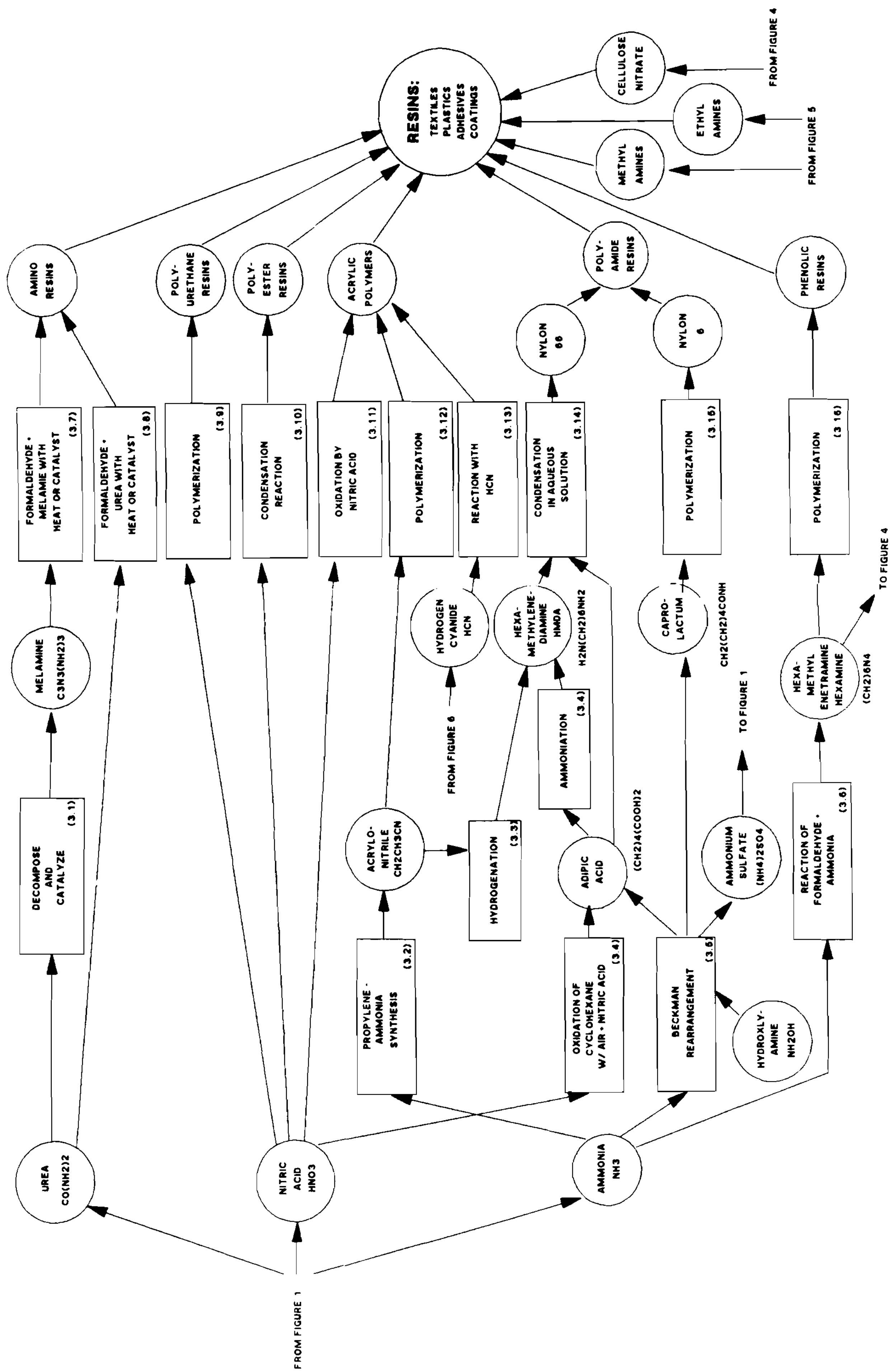


Figure 6-2: Production of Nigrogenous Fertilizers.

Figure 6-3: Production of Nitrogenous Resins.



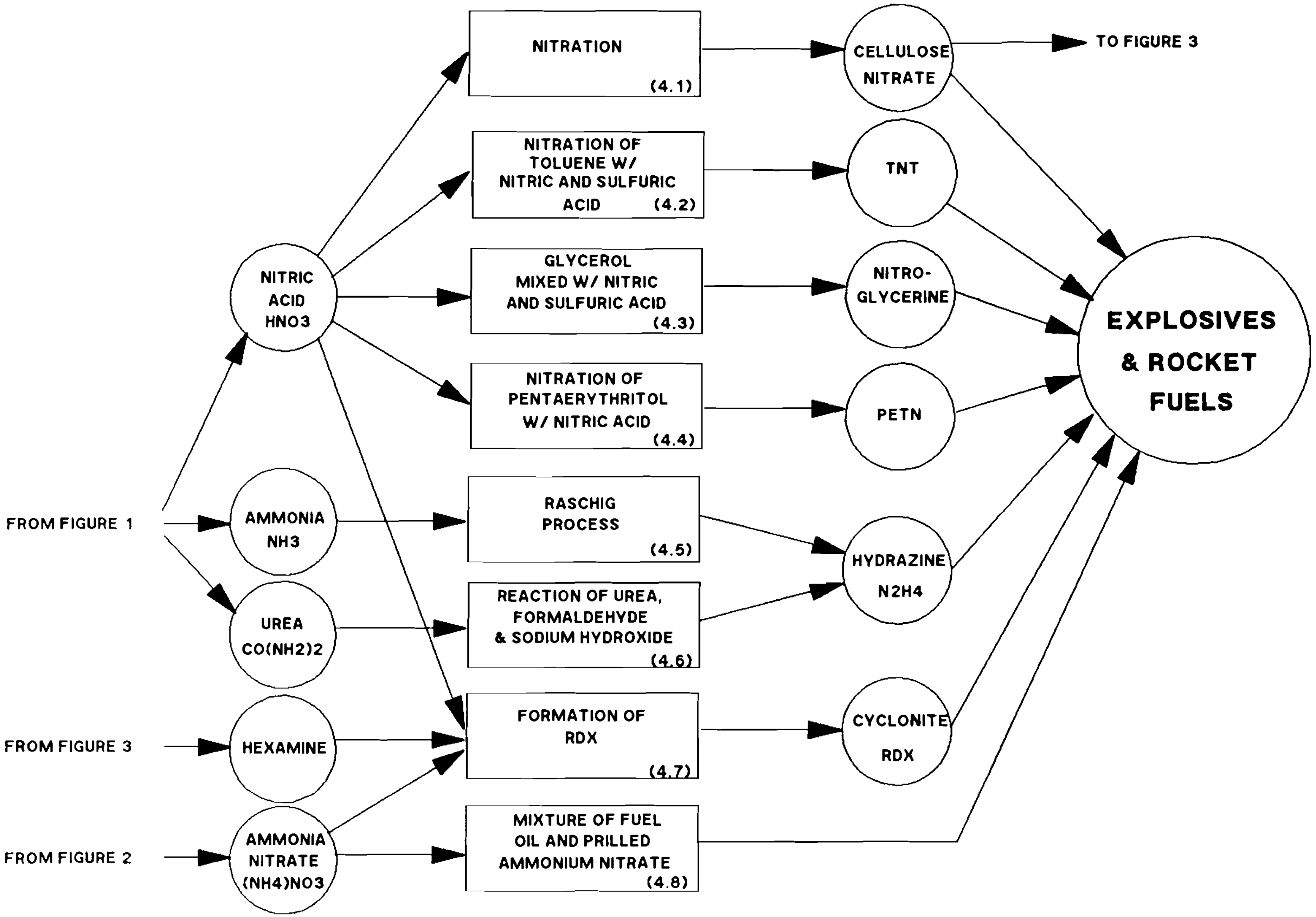


Figure 6-4: Production of Nitrogenous Explosives.

Figure 6-5: Production of Important Nitrogenous Compounds for End Uses Other than Fertilizers, Resins, and Explosives.

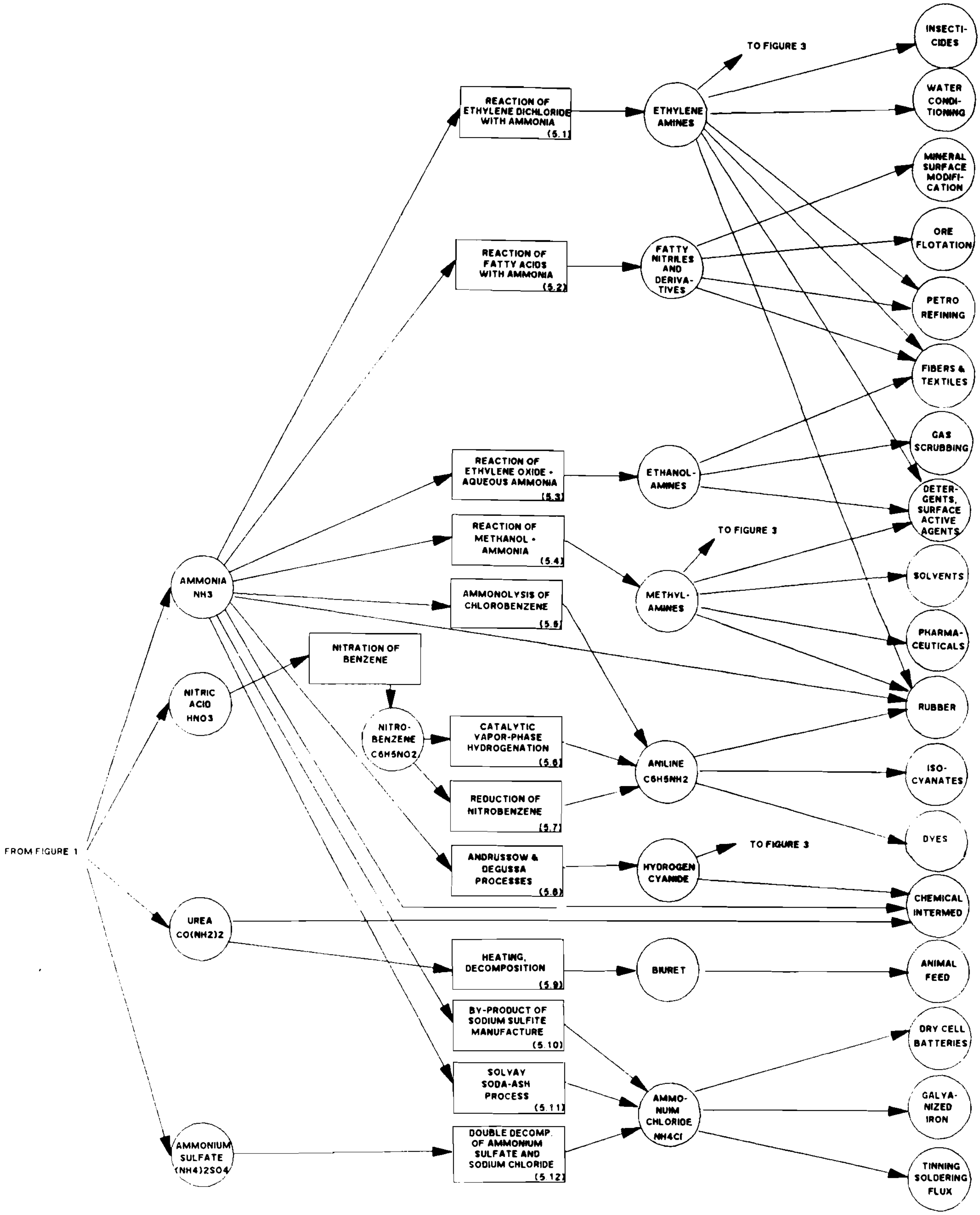


Figure 6-6: Materials Process Relationships for Ammonia Synthesis.

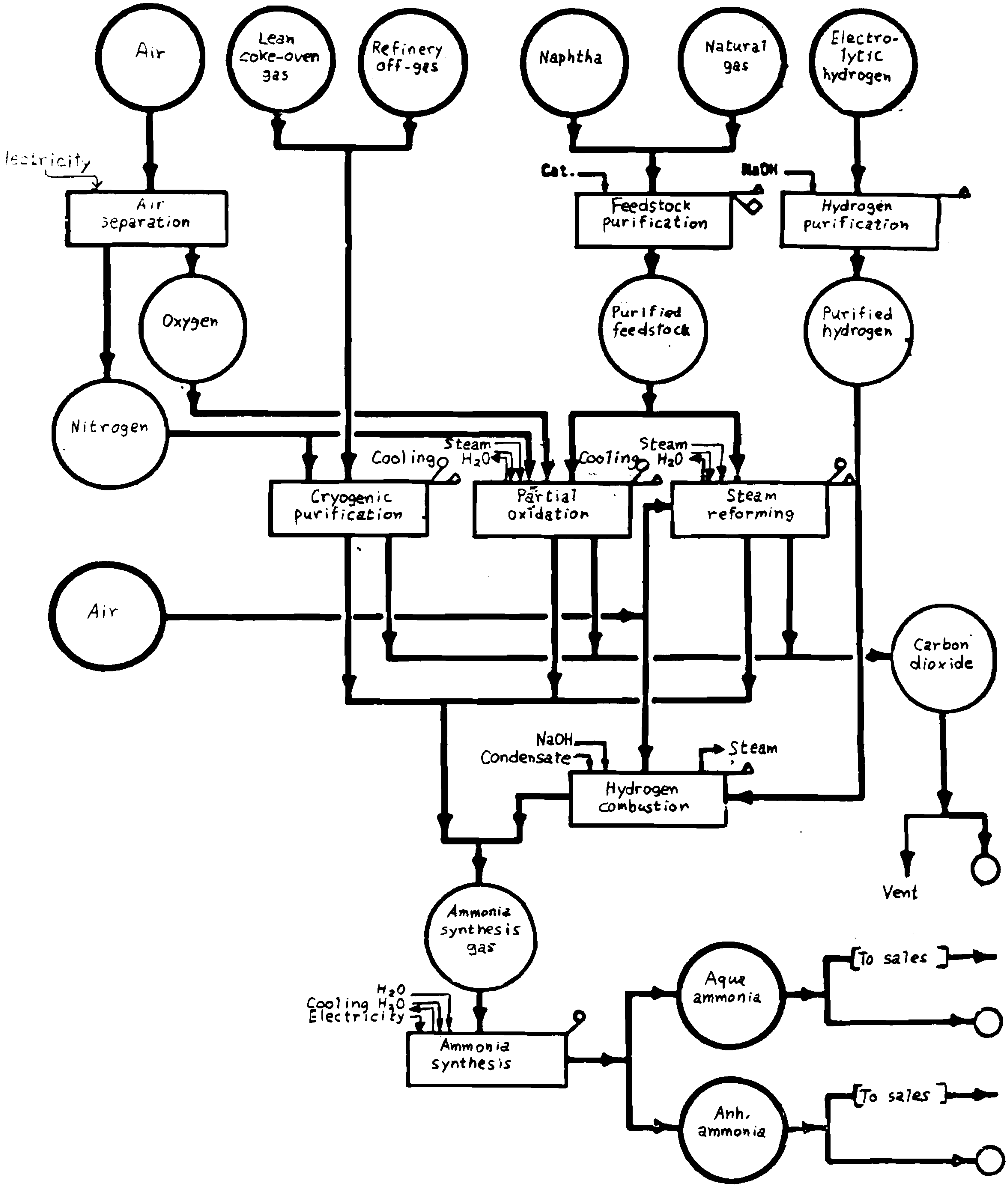
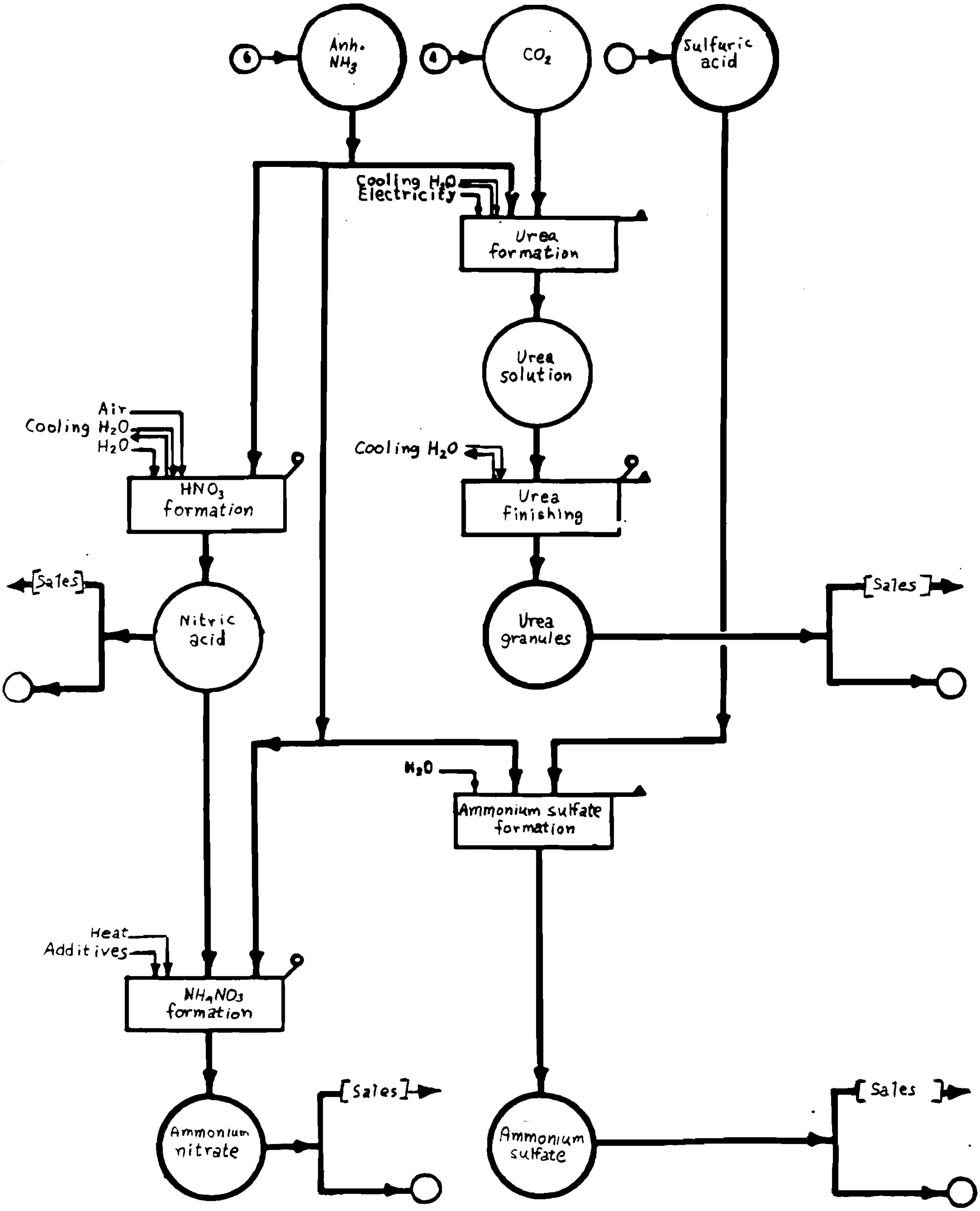


Figure 6-7: Materials Process Relationship for Ammonium Sulfate, Nitric Acid, Ammonium Nitrate and Urea.



Appendix A: Bromine Reactions

This appendix corresponds to the process-product flow charts for bromine. Each reaction is referenced by 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 .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 2 and 3 (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 .405 tons
H_2SO_4 (96%) 2.25 tons
SO_2 .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 U.S. 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:

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

Appendix B:

Table B-1.Chemical Equations for Figure 4-1.

$$2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH \qquad 1.$$
$$2KCl + 2H_2O \rightarrow Cl_2 + 2KOH$$

(Encyclopedia Brittanica, 1973)

$$2FeCl_3 \rightarrow 2Fe + 3Cl_2 \qquad 2.$$
$$TiCl_4 \rightarrow Ti + 2Cl_2$$

etc.

(McGraw-Hill, 1971)

$$2HCl \rightarrow H_2 + Cl_2 \qquad 3.$$

(McGraw-Hill, 1971)

$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O \qquad 4.$$

(McGraw-Hill, 1971)

Table B-2 Chemical Equations for Figure 4-2.

$$C_2H_4 + HCl \xrightarrow{AlCl_3} C_2H_5Cl \qquad 1.$$

or

$$CHCHOH + HCl \rightarrow C_2H_5Cl \ (McGraw-Hill, 1971)$$

$$C_2H_4 + Cl_2 \rightarrow ClCH_2 - CH_2Cl \ (McGraw-Hill, 1971) \qquad 2.$$

$$2C_2H_4 + 4HCl + O_2 \rightarrow 2ClCH_2 - CH_2Cl + 2H_2O \qquad 3.$$

(McGraw-Hill, 1971)

4. 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.

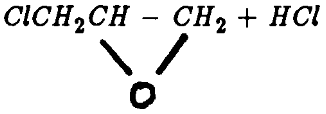
$$2C_4H_6+2Cl_2 \rightarrow CH_2=CH-CHCl-CH_2Cl+ClCH_2CH=CHCH_2Cl$$

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

(Witcoff and Reuben, 1980)

$$CH_3 - CH = CH_2 + Cl_2 \rightarrow ClCH_2CH = CH_2 + HCl \qquad 5.$$

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



$$ClCH_2CHOHCH_2Cl \rightarrow ClCH_2\underbrace{CH - CH_2}_{O} + HCl$$

(Witcoff and Reuben, 1980)

6.7 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)

$$CS_2 + 3Cl_2 \xrightarrow{Fe} CCl_4 + S_2Cl_2 \qquad 8.$$

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

(Witcoff and Reuben, 1980)

$$2C_3H_6 + 16Cl_2 \rightarrow Cl_2C = CCl_2 + 4CCl_4 + 12HCl \qquad 9.$$

(Witcoff and Reuben, 1980)

$$C_3H_8 + 8Cl_2 \rightarrow Cl_2C = CCl_2 + CCl_4 + 8HCl \qquad 10.$$

(Witcoff and Reuben, 1980)

$$CO + Cl_2 \rightarrow COCl_2 \qquad 11.$$

(Witcoff and Reuben, 1980)

$$Si + nC_2H_5Cl \rightarrow (C_2H_5)_n\,SiCl_{(4-n)} + (n-2)\,Cl_2 \quad (n = 1\text{--}4) \qquad 13.$$

$$(C_2H_5)_n\,SiCl_{(4-n)} + (4-n)H_2O \rightarrow$$

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

(Witcoff and Reuben, 1980)

$$CH_2ClCH_3 + \text{cellulose}polymer + NaOH \rightarrow \qquad 14.$$

$$\text{cellulose}-0-\text{C}_2H_5 + NaCl$$

(Considine, 1974)

$$4C_2H_5Cl + 4PbNa \rightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl \qquad 15.$$

(Herrick, et al., 1979)

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

$$ClCH_2 - CH_2Cl \rightarrow CH_2 = CHCl + HCl \qquad 16.$$

(Witcoff and Reuben, 1980)

$$ClCH_2 - CH_2Cl + 2NH_3 \rightarrow H_2N - CH_2 - CH_2 - NH_2 + 2HCl \qquad 17.$$

(Herrick, et al., 1979)

$$nClCH_2 - CH_2Cl + nNa_2S_4 \rightarrow \qquad 18.$$

$$(CH_2CH_2S_4)_n + 2nNaCl$$

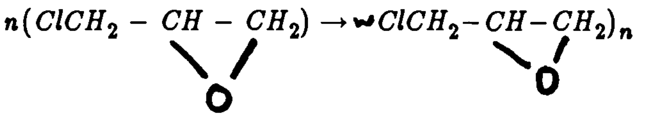
(Considine, 1974)

$$CH_2 = CH-CHCl-CH_2Cl \rightarrow CH_2 = CH-CCl-CH_2 + HCl \qquad 19.$$

(Witcoff and Reuben, 1980)

$$\sim\sim\sim\sim(CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2)_n + nCl_2 + nSO_2 \rightarrow$$
$$\sim\sim\sim(CH_2-CH_2-CH_2-CHCl-CH_2-CSO_2Cl-CH_2-CH_2)_n\sim\sim\sim\sim \qquad 20.$$

(Witcoff and Reuben, 1980)



$$n(ClCH_2 - \underbrace{CH - CH_2}_{O}) \rightarrow \sim ClCH_2-\underbrace{CH-CH_2}_{O})_n \qquad 21.$$

(Greek, 1986)

22. Epoxy resins are typically condensated of 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)

$$R-N-(CH_3)_2 + CH_3Cl + NaOH \rightarrow \qquad 22.$$
$$R-N^+-(CH_3)_3 + NaCl + OH^-$$

(Herrick, et al., 1979)

$$3CH_3Cl + 3PbNa \rightarrow Pb(CH_3)_3 + 2Pb + 3NaCl \qquad 24.$$

(Considine, 1974)

$$Si + nCH_3Cl \rightarrow (CH_3)_nSiCi_{(4-n)} + (n-2)Cl_2 \quad (n=1-4) \qquad 25.$$
$$(CH_3)_nSiCl_{(4-n)} + (4-n)H_20 \rightarrow$$
$$(CH_3)_nSi(OH)_{(4-n)} + (4-n)HCl$$

(Witcoff and Reuben, 1980)

$$ClCH_2 - CH_2Cl + 2Cl_2 \rightarrow CHCl = CCl_2 + 3HCl \qquad 27.$$
$$ClCH_2 - CH_2Cl + 3Cl_2 \rightarrow CCl_2 = CCl_2 + 4HCl$$

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

$$R(NH_2)_2 + 2COCl_2 \rightarrow R(NCO)_2 + 4HCl \qquad 28.$$

(Herrick, et al., 1979)

$$CHCl = CCl_2 + Cl_2 \rightarrow Cl_2C = CCl_2 + HCl \qquad 29.$$

(Witcoff and Reuben, 1980)

$$nCH_2 = CHCl \rightarrow \sim(CH_2CHCl)_n\sim\sim \qquad 30.$$

(Witcoff and Reuben, 1980)

$$CH_2 = CHCl + HCl \rightarrow CH_2 = CCl_2 + H_2 \qquad 31.$$

(Witcoff and Reuben, 1980)

$$nCH_2 = CH-CCl = CH_2 \rightarrow \sim(CH_2 = CH-CCl = CH_2)_n\sim\sim \qquad 32.$$

(Witcoff and Reuben, 1980)

Table B-3 Chemical Equations for Figure 4-3.

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2 \qquad 1.$$

(McGraw-Hill, 1971)

$$\begin{aligned} NaCl + 3H_2O &\rightarrow NaClO_3 + 3H_2KCl + 3H_2O \\ &\rightarrow KClO_3 + 3H_2 \end{aligned} \qquad 2.$$

(McGraw-Hill, 1971)

$$Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O \qquad 3.$$

(McGraw-Hill, 1971)

5.

$2Cl_2 + TiO_2 \rightarrow TiCl_4 + 0_2$
$3Cl_2 + 2Al \rightarrow 2AlCl_3$
$3Cl_2 + Al_2O_3 + 3C \rightarrow 2AlCl_3 + 3CO$
$3Cl_2 + 2Fe \rightarrow 2FeCl_3$
etc.

(McGraw-Hill, 1971, Encyclopedia Brittanica, 1973)

6.

$$2KClO_3 + 3H_2C_2O_4 \rightarrow 2ClO_2 + 2H_2O + 2CO_2 + 2KHC_2O_4$$

$$Ca(ClO_3)_2 + 4HCl \rightarrow CaCl_2 + 2ClO_2 + Cl_2 + 2H_2O$$

(Encyclopedia Brittanica, 1973)

$$4KClO_3 \rightarrow 3KClO_4 + KCl \qquad 7.$$

$$4NaClO_3 \rightarrow 3NaClO_4 + NaCl$$

(McGraw-Hill, 1971)

$$2ClO_2 + 2NaOH + H_2O_2 \rightarrow \qquad 8.$$

$$2NaClO_2 + O_2 + 2H_2O$$

(McGraw-Hill, 1971)

Appendix C: Sulfur Processes

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 U.S. 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 Frach process is used in Sicily, Poland and the U.S.S.R. 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. 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 99.9 - 99.0% pure. It may contain ash, moisture, H2SO4 and oil or carbanaceous material.

Waste Streams: The superheated water is recovered from bleeder wells. It 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, 1975 and Duecker and West, 1959).

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

Sulfide ores are burned in an oxidizing atmosphere to produce both sulfur dioxide 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, West 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 the copper. There are 3 types of roasts; partial, dead and sulfating.

Basic Chemical Reaction for Partial & Dead

$7FeS_2 + 6O_2 \rightarrow Fe_7S_8 + 6SO_2$
$Fe_7S_8 + O_2 \rightarrow 7FeS + SO_2$
$3FeS + 5O_2 \rightarrow Fe_3O_4 + 3SO_2$
$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$
$2Cu_2O + O_2 \rightarrow 4CuO$
$4Fe_3O4 + O_2 \rightarrow 6Fe_2O_3$

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).

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

This method is used by 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 and Lownheim, 1975).

1.4) Sulfur from Gypsum

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

$CaSO_4 + 2C \rightarrow 2CO_2 + CaS$
$CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2$
$3CaS + CaSO_4 \rightarrow 4CaO + 2S_2$
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 the Portland Cement and 9% SO_2 gas. The gas is used for making H_2SO_4. (Duecker and West, 1959).

1.5) 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.

1.6) 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:

1. 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.

2. From gaseous hydrogen sulfide (from sour gas, petroleum refining, and coking plants). This is basically the first half of the Claus process.
   $2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$

3. 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 on SO_2 to 99.7 - 99.9 %. (Considine, 1974)

Waste Streams: Oleum (pyrosulfuric acid, $H_2S_2O_7$) is used in the process and 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, 1975).

1.7) Chamber Process for Converting Sulfur to Sulfuric Acid

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

For information on the conversion of sulfur to sulfur dioxide, see notes under process 1.4.

Basic Chemical Reactions

$2NO + O_2 \rightarrow 2NO_2$
$NO2 + SO_2 + H_2O \rightarrow H_2SO_4 + NO$
98 - 99 % conversion
92 - 96 % yield sulfur

Waste Streams: Any remaining gases, including a small amount of SO_2.

(Lowenheim, 1975. More detailed chemical reactions can be found in Duecker and West, 1959).

2.1) 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, 1975).

2.2) Carbon Disulfide

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, 1975).

2.3) 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, 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 and Considine, 1974).

2.4) 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.

2.5) 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).

2.6) Industrial Organic Chemicals

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

$$RH + (HO)_2SO_2 \rightarrow RSO_2OH + H_20$$

2.9) 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 percent 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).

2.10) Carbon Tetrachloride

$$CS_2 + 3Cl_2 \xrightarrow{Fe\ catalyst} S_2Cl_2 + CCl_4$$
$$CS_2 + 2S_2Cl_2 \rightarrow 6S + CCl_4$$
$$6S + 3C \rightarrow 3CS_2$$

Carbon tetrachloride is also produced from hydrocarbons by chlorination. Its production from carbon disulfide is projected to decline.

2.11) Organic Fungacide from Carbon Disulfide

$$H_2NCH_2CH_2NH_2 + 2CS_2 \rightarrow HSCSNH\,(CH_2)_2\,NHCSSH$$
$$HSCSNH\,(CH_2)_2\,NHCSSH + 2NaOH \rightarrow NaSCSNH\,(CH_2)_2NHCSSNa + 2H_2O$$

2.12) Phosphorus Pentasulfide (P_4S_{10})

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

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

3.3) 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 evolved. The by-product is calcium sulfate. (Lowenheim, 1975).

3.4) 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, 1975).

3.5) 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 U.S.

From Rayon Spin Bath:

During the spinning process, 1.1 lb of sodium sulfate is produced for each pound 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, 1975).

3.6) 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 1 to 10 % Fe_2O_3. The iron is removed from the product by a reduction reaction using most often barium sulfide. Other reducing agents include sodium sulfide, hydrogen sulfide, sodium bisulfate or sulfur dioxide. (Lowenheim, 1975).

3.7) 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, 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 (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, 1975).

3.8) Copper Sulfate:

From copper oxide ores:

$CuO + H_2SO_4 + 4H_2O \rightarrow CuSO_4.\,5H_2O$
99% yield

This is often a byproduct 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, Keyes and Clark, 1965 and Lowenheim, 1975).

3.10) 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 U.S. (Considine, 1974).

3.11) 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 byproduct. It is discarded as waste.

3.12) 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).

3.12) Petroleum Refining and Petrochemicals

Sulfuric acid is used in the following processes:

1) Alkylation and dealkylation
2) Esterification of organic alcohols or acids, for example, ethyl acetate.
   $$CH_3CH_2OH + CH_3COOH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_2O$$
3) Hydration and hydrolysis
   An example of this is ethyl alcohol from the ethyl hydrogen sulfate method.
   $$3C_2H_4 + 2H_2SO_4 \rightarrow C_2H_5HSO_4 + (C_2H_5)_2SO_4 + aqua$$
   $$\rightarrow 3C_2H_5OH + aqueous 2H_2SO_4$$

(Considine, 1974).

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

3.14) 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. Steel pickling was looking (1975) at an HCl pickling process where the liquor was recyclable.

Some ferrous sulfate is produced as a by-product from the sulfate process for titanium dioxide. (Lowenheim, 1975).

3.21) 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. 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.

3.28) 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 U.S. 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, 1975).

3.29) Calcium Sulfate

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

Calcium sulfate is made by calcining gypsum rock to remove 3/4 of the water of crystallization.

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

3.35) 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 3.5. (Lowenheim, 1975).

Appendix D: Nitrogen Processes

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 WWII, 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, 1975, and Slack, 1979)

1.2 Ammonia by Catayltic Synthesus 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 degrees 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 gas, natural gas, fuel oil, catalytic reformer gases, or the electrolysis of water or brine. Since WWII the major source of hydrogen has been natural gas. (Lowenheim, 1975)

1.3 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 U.S. The calcium sulfate may be in the form of gypsum, anhydrite or phosphor gypsum from wet- process phosphoric acid production. (Lowenheim, 1975, Considine, 1974, and Slack, 1979)

1.4 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, 1975)

1.5 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, 1975 and Slack, 1979)

1.6 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, 1975, Considine, 1974, and Slack 1979)

2.1 Ammonium Phosphates:

Anhydrous NH_3 is reacted with H_3PO_4. Reaction ratios of NH_3 / H_3PO_4 are between 1 and 2, depending on the desired grade of product.

There are 3 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, 1979, Encyclopedia Britannica)

2.2 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 and Slack, 1979)

2.3 Calcium Nitrate from Limestone:

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

2.4 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.

2.5 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, 1975, Considine, 1974, and Slack, 1979)

3.1 Melamine from Urea:

Urea is heated in a fluidized bed and decomposes to ammonia and isocyanic acid which in the presence of a catalyst form melamine.

3.2 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, 1975)

3.3 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, 1975, Slack, 1979)

3.4 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, 1979)

3.5 Caprolactum $(NH(CH_2)_5CO$, (Aminocaproic Lactam) from Cyclohexanone (Beckman Rearrangement):

$$C_6H_{10}O + \frac{1}{2}(NH_2OH)_2\ H_2SO_4 \xrightarrow{(\frac{1}{2}H_2SO_4,2NH_3)}$$

$$C_6H_{10}NOH + (NH_4)_2SO_4 + H_2O$$

$$C_6H_{10}NOH \xrightarrow{(H_2SO_4)}$$

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

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 U.S. The newer processes produce less or no by-product ammonium sulfate. For details on these see Lowenheim (1975). Adipic acid is also a by-product of caprolactum production. (Lowenheim, 1975)

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

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

(Lowenheim, 1975 and Slack, 1979)

3.7 Melamine-Formaldehyde Resins:

This process is similar to that of urea-formaldehyde resins. See process (3.8).

$$\underset{(\mathit{Melamine})}{C_3N_3(NH_2)_3 +} \; \underset{(\mathit{Formaldehyde})}{3HCHO \rightarrow} \; \mathit{Trimethylolmelamine}$$

(McGraw-Hill)

3.8 Urea-Formealdehyde 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.

$$\begin{array}{lll} CO(NH_2)_2 + & HCHO \rightarrow & NH_2CONHCH_2OH \\ (\mathit{Urea}) & (\mathit{Formaldehyde}) & (\mathit{Monomethylolurea}) \\ CO(NH_2)_2 & 2CHHO \rightarrow & HOCH_2NHCONHCH_2OH \\ (\mathit{Urea}) & + (\mathit{Formaldehyde}) & (\mathit{Dimethylolura}) \end{array}$$

(Encyclopedia Britanica, McGraw Hill)

3.9 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, 1979)

3.10 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, 1979)

3.11 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, 1979)

3.12 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, 1979)

3.13 Acrylic Polymers by Reaction with Hydrogen Cyanide:

There are two different processes:

1. Ethylene oxide is reacted with basic hydrogen cyanide to form cyanohydrim which is reacted with the desired the alcohol to yield the acrylate.
2. 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, 1979)

3.14 Nylon 66:

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

$$Hexamethylenediamene + AdipicAcid \longrightarrow Polyhexamethyleneadipamide$$

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)

3.15 Nylon 6 from the Polymerization of Caprolactum:

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

(Considine, 1974)

3.16 Phenolic Resins from Hexamethylenetetramine:

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

4.1 Cellulose Nitrate:

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

(Slack, 1979)

4.2 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, 1979)

4.3 Clycerol Trinitrate (Nitroglycerine, NG) $CH_2NO_3CHNO_3\ CH_2NO_3$:

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

4.4 Petn, Pentaerythritoletranitrate:

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

4.5 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, 1975 and Slack, 1979)

4.6 Hydrazine from Urea:

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

(Lowenheim, 1975)

4.7 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, 1979)

5.1 Ethyleneamines:

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

5.2 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, 1979)

5.3 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, 1979)

5.4 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, 1979)

5.5 Aniline from Chlorobenzene by Ammonolysis:

$$C_6H_5Cl + 2NH_3(aqua) \rightarrow C_6H_5NH_2 + NH_4Cl(soln)$$

(Lowenheim, 1975)

5.6 Aniline from Nitrobenzene by Catalytic Vapor-Phase Hydrogenation:

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

(Lowenheim, 1975)

5.7 Aniline from Nitrobenezene by Reduction:

$4C_6H_5NO_2 + 9Fe + 4H_2O(HCl)4C_6H_5NH_2 + 3Fe_3O_4$

(Lowenheim, 1975)

5.8 Hydrogen Cyanide from the Andrussov and Degussa Processes:

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

Degussa Process: $NH_3 + CH_4 \rightarrow HCN + 3H_2$
This reaction takes place in the presence of a platinum catalyst. (Lowenheim, 1975)

5.9 Buiret:

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

5.10 Ammonium Chloride (Sal-Ammoniac) as a By-Producti 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, 1975)

5.11 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, 1975 and Slack, 1979)

5.12 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, 1975, and Slack, 1979)

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