# Sulfur, Energy, and Environment

BEAT MEYER

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# Preface

In 1612 Rulando listed sixteen types of sulfurs which he assigned to two classes: "The lifegiving sulfurs," and those "which are and remain enemies of all metals." Today we know far more about sulfur, but the basic division remains between the viable sulfurs needed in agriculture and industry, and the corrosive and polluting sulfurs which constitute a nuisance for both the electric power industry and the public.

In talking with researchers and practitioners in any of the twenty-five fields listed in Table 1.1, one might easily gain the impression that sulfur is twenty-five different materials. It is the goal of this book to describe the properties of elemental sulfur and its three more important compounds, and to review the production, use, and recovery of sulfur in relation to energy production and environmental protection.

It is the purpose of this book to serve as a guide to the literature in fourteen areas which the author considers most important. Each chapter contains a short review, references to recent specialist reviews, and many key references to original research papers. Thus, the reader can choose the depth of his involvement, and, hopefully, the text is equally useful to both specialists and non-specialists. During the last fifteen years some 15,000 articles have dealt with sulfur. Despite Chemical Abstracts, it has become increasingly difficult to find access to basic new facts, not only because of the diversity of the areas involved, but because of changes in the publication styles. Obviously, a full coverage of the field would fill fifteen volumes rather than fifteen chapters, and a full set of references alone would fill an entire book. There is a definite need for such an encyclopedia on sulfur research, use, and recovery. In contrast, this book is intended to serve merely as a reference guide so that readers can quickly establish whether material is relevant to their work. Thus, several fields had to be omitted or neglected. For example, the entire field of pulp and paper chemistry has been totally ignored. Sulfur production, shipment, and other equally important fields receive abbreviated and incomplete treatment. Flue gas desulfurization is only described from a basic chemical viewpoint, and engineering considerations—no matter how important—have been neglected. Thus, this book does not contain one single process diagram, even though they constitute important information and are valuable aids. Likewise, only one out of ten references could be included in the bibliography to keep it manageable. This necessitated some quite arbitrary cuts in order to keep perspectives in a very large field which is still quickly developing.

The Introduction correlates traditions and trends in the fields of sulfur, energy use, and environmental attitude, and delineates the role of chemistry. Chapter 2 sketches a short history of sulfur chemistry. Chapter 3 reviews the chemical properties of the element and some of its most important compounds. Chapter 4 indicates common analytical methods and some problems encountered in their use. Chapter 5 provides a short list of sulfur sources and reserves. Chapter 6 reviews recent work on the four most important sulfur cycles. Chapter 7 summarizes sulfur production methods, and Chapter 8 describes coal combustion chemistry and flue gas desulfurization efforts. Chapter 9 describes some of the problems which occur at the interfaces of science, industry, and society. Chapters 10 through 14 deal with the use of sulfur in medicine, agriculture, chemical industry, the plastics industry, and in other applications. The final Chapter discusses possible future trends in sulfur production, use, and recovery, and the role of chemistry, government, and education in these areas.

This book reflects personal views based on my training and experience. My interests in sulfur were stimulated by Prof. E. Schumacher in Zürich, who showed me a paper by F. O. Rice on trapped sulfur vapor, and guided my Ph.D. research. Prof. Leo Brewer in Berkeley introduced me to high temperature and combustion chemistry, and showed me the challenges of conducting independent research in an applicable field. Furthermore, he brought me into contact with many leading scientists. There is not sufficient room to thank all those in academe, industry, and government who have been instrumental in my learning about sulfur. Dr. J. R. West and Dr. R. Coleman introduced me to many outstanding people in the industry, and to Mr. P. N. Kokulis, who practices a special art which makes it possible to efficiently translate basic scientific and innovative ideas into practical applications while protecting the interests of all sides.

The preparation of this book was greatly aided by Prof. L. Brewer who has regularly provided key references in basic and applied chemistry. My wife and daughter helped search, copy, and collect references; Harry

Weeks traced several dozen difficult to find references in the UC Berkeley library; Christal Shaskey Rosenlund helped research the history chapter and collected references dealing with the sulfur cycle. Phyllis Ayer helped with the literature search, the bibliography, the preparation of figures, and the indices. Carey Julian typed and edited Chapters One and Nine and helped with the bibliography. Special thanks belong to Mrs. Marilee Kapsa who coordinated the production and assembly of the text. She assisted in searching the literature, typed the text, edited and proofed the entire manuscript, and prepared the camera copy in Aldine Roman type.

This book is dedicated to all those in industry, government, and at universities who work with sulfur and help sound scientific methods find acceptance. If they should ever get discouraged, they should remember that Hermann Frasch struggled for many long years, and that, shortly before his sulfur production method finally succeeded, a prominent man promised him that he would eat every ounce of sulfur produced by his method.

Beat Meyer

*Seattle, Washington*
*March 1977*

# Contents

*Chapter 1*

# Introduction

This book deals with elemental sulfur. It describes the chemical properties of sulfur and their relation to the production, use, and recovery of the element. Both basic chemistry and industrial use of sulfur influence energy production and the extent to which the environment can be protected. Thus, sulfur is an important parameter in the choice of new technology and in determining practically enforceable environmental laws. The purpose of this book is to delineate the role of sulfur at a time when technological transitions and social adjustments are setting the framework of society for the next hundred years.

In 1976 almost fifty million tons of sulfur were produced worldwide. Most of this was used to manufacture sulfuric acid, which is unchallenged as the leading industrial chemical. Its production steadily increased from 5 tons in 1750 to 110 million tons in 1976. However, this smooth overall growth does not properly reflect development, which was marked by stagnant as well as dynamic periods. In the 18th and 19th Centuries sulfur production was centered in Sicily. Frasch's development of a clean and cheap sulfur production process made the Sicilian industry obsolete, and within ten years Louisiana and Texas had become the world centers for sulfur production. They retained this position unchallenged for 60 years, until 1960, when production of sour natural gas made Canada and France major producers of sulfur. With this development, an initially unwanted by-product became the major source of the leading industrial chemical. Currently, and for at least the next ten years, oil production in the Middle East will yield important quantities of sulfur, probably equalling the stepped-up production in Poland, which is implementing increasingly modern techniques based on traditional production methods.

Sulfur production from sour gas and oil is based on the Claus process, which was patented in 1882. Even before that time, the manufacture of sulfuric acid had reached essentially the present stage of chemical art. Since then sulfur chemistry and industrial inorganic chemistry have remained almost stagnant in comparison to other fields of basic chemistry and other sciences which have proceeded through a period of unique growth. Only during the last fifteen years has sulfur chemistry slowly revived. Recent progress has indeed been surprising: twelve new solid allotropes of the element have been synthesized, some 20 components of elemental sulfur vapor have been identified, and substantial progress has been made in the understanding of liquid sulfur.

At the same time, energy consumption has increased at a similarly spectacular rate. During the dynamic 1960's, when all progress and values were re-examined, the public suddenly became aware that involuntary release of sulfur dioxide from coal burning power plants–mainly into the air of the northern hemisphere–equaled the intentional world sulfur production. The public became fearful of the enormous quantities of efferent sulfur, because it did not realize that the total sulfur involved in all of man's recorded activities is smaller than the sulfur dioxide emission resulting from any of the large volcanic eruptions of Mt. Katmai in Alaska in 1912, Mt. Hekla in Iceland in 1947, or Mt. Agnug in Bali in 1963. The conflict between consumption and conservation brought into the open the emotional origin and the political potential of technical terms such as power, waste, and pollution, and an increasing government effort to regulate industries and abate pollution was demanded.

Today, a large number of highly competent and skilled specialists in industry, government, and education struggle to translate the results of a hundred years of progress in diverse fields of science into technology acceptable under the new standards of society. It is the goal of this book to help these researchers find their way through the increasingly incoherent literature of the last ten years, and gain access to work related to their fields. It is too early at this time to gain a full overview, but this book constitutes an effort to make a modest start and point out the direction of developments which are under way. It is hoped that it can support those working in the field as well as newcomers in their momentous task, which will determine the chemical basis for the large scale technology to be used during the next hundred years. This task will also influence the role of sulfur, and the nature and quality of human life. Since the work involves coordinating results from a variety of divergent sciences, it seems reminiscent of the task of salvaging the Tower of Babel.

*Changing Traditions*

A hundred-fifty years ago, sulfur was widely used in industry and in the chemistry lab, and could be found in the medicine cabinet of every home. Sulfur alone filled a third of the inorganic chemistry texts. During the following decades it maintained its position as the leading industrial chemical, but it disappeared from public view, from chemistry labs, and finally from college chemistry textbooks. One of the three leading U.S. college general chemistry textbooks of 1970 contains only six sentences on sulfur, of which two are incorrect. During the same time academic interest in sulfur also waned; ten years ago at the 20 academically highest ranking U.S. universities, a total of only three inorganic or physical chemistry professors conducted research focussing on sulfur. Most of the progress resulted from basic research which was conducted as a side activity by a small group of little-noticed but outstanding industrial scientists whose main responsibility was supervising plant production.

In the meantime oil, gas and sulfur production became cheaper, and abundant energy became available to exploit technology developped during recent wars for mass production. This, and the rapidly growing influence of media and international communication fostered a hunger for consumption of manufactured goods, which in turn caused quick economic growth. Sputnik caused demand for quick implementation of new technology and instant mass education. This proved to be socially disruptive, because democracy and free enterprise depend on equilibrating forces which require more time than was available.

At the time when manufacturers, in response to earlier trends, used linear extrapolation to compute anticipated needs, perfected better process methods, and finished building larger manufacturing facilities, products became obsolete. Industry responded by diversifying and intruding into each other's established fields in order to survive. By this time, education had caught up with the fifties, and had geared up for large scale improvement of traditional structures. Mass education in obsolete academic and scientific fields began. This caused frustration among graduates and insecurity among students. The unleashed anxiety and fears increased awareness of previously ignored complaints beyond the threshhold of political inactivity. The sudden change in the public attitude caught industry at an economically unfavorable time. Universities abolished traditional paths of study, and everybody rushed to explore new laws, policies and academic fields.

Table 1.1
ACADEMIC FIELDS WITH PROGRAMS OF SULFUR STUDY

| Field of Study | Subject |
|---|---|
| Law | Air quality legislation |
| Business management | Impact of $SO_2$ control |
| Economics | Electric rate structure |
| Political science | Distribution of abatement burden |
| Social science | Impact of $SO_2$ abatement |
| Medical epidemiology | Urban excess of morbidity & mortality |
| Clinical physiology | Symptoms of $SO_2$ exposure |
| Oceanography | Sedimentary sulfur cycle |
| Atmospheric science | Atmospheric sulfur cycle |
| Meteorology | Effect of sulfate particulates on climate |
| Soil science | Fertility of sulfur soils |
| Agricultural science | Effect of sulfur on crop yields |
| Veterinary science | Inorganic sulfur in feed of non-ruminants |
| Forestry | Effect of $SO_2$ on forest growth |
| Geochemistry | Artesian sulfur and pyrite |
| Environmental science | Effect of excess sulfur on climate |
| Biochemistry | Sulfur-containing proteins |
| Combustion chemistry | Sulfur chemistry in flame |
| Metallurgy | Corrosion of high temperature steels |
| Mining | Mechanical properties of high sulfur coals |
| Civil engineering | Sulfur dioxide monitoring |
| Mechanical engineering | Sulfur in construction materials |
| Physics | Optical properties of sulfur dioxide |
| Chemistry | Analytical chemistry, kinetics, etc. |

Today, in response to the political and social events of the last 15 years, interest in pollution abatement is well established, and every major U.S. university has sulfur specialists in at least 20 different academic fields (table 1.1).

Every government has a branch dealing with sulfur emissions, each government branch has sulfur specialists, and even businesses which neither buy nor sell any sulfur or sulfur-containing materials have pollution specialists.

Needless to say, academic chemists have also rediscovered sulfur; about a third of all research proposals from chemistry departments now deal with sulfur in connection with energy or pollution. Furthermore, technical, semi-popular and general literature is full of articles on subjects connected with sulfur. Even today, however, those who deal professionally with sulfur find it difficult to acquire basic chemical facts. As a rule, their specialized educations did not permit study of chemistry beyond the freshman level, and chemical education has adjusted slowly. Most college freshman classes deal with sulfur superficially, if at all, and often discuss the social impact of man on the environment instead of explaining basic sulfur chemistry. Introductory and general chemistry textbooks still focus on computer modeling, atomic physics and quantum theory, and ignore experimental chemistry and chemical facts in applicable fields. Even those who major in chemistry have a hard time learning about sulfur, as it is only superficially treated even in advanced texts, and less than one in six inorganic chemistry professors in North America knows the properties of gypsum, the structure of the bisulfite ion, or the composition of elemental sulfur vapor. This is a result of the fact that the subject was not taught when they acquired their own general chemical knowledge, and information explosions in their own specialties have prevented them from following progress in the field of sulfur. The burden of basic sulfur chemistry, then, rests with only a few professors, and primarily with industrial chemists and engineers, who have continued through the confusion to provide sulfur as needed. They are now aided in their research by highly competent government scientists.

Those attempting to gain access to the field are confronted with the results of the information explosion. Chemical Abstracts currently quotes over 10 articles connected with sulfur per day, and more than one patent per day. Anyone trying to read the original literature finds it difficult, as an increasing fraction of important data is in government reports or other articles which are published outside the traditional literature and may be difficult to procure. The traditional U.S. literature clearly suffers from lack of research funds; it is rich in general discussions and computer modeling, which is cheaper and quicker than experimental work. The most interesting work is frequently buried in unusual journals which don't levy publication charges, or in long and difficult to read papers derived from Ph.D. theses. Furthermore, professional literature increasingly uses a "modern" technical language in which structure and grammar are replaced with strings of often incomprehensible and artificial technical nouns, which undoubtedly would have aroused jealousy among the masters of the trade guilds of the middle ages.

Table 1.2

SULFUR CONTENT OF VARIOUS MATERIALS

| Material | Wt. % | Material | Wt. % |
|---|---|---|---|
| Cosmos | 0.002 | Colza cabbage | 0.98 |
| Crust of the earth | 0.052 | Alfalfa | 0.50 |
| Coal | 1-14 | Oats | 0.41 |
| Oil | 0.1-14 | Barley | 0.30 |
| Gas | 0.1-40 | Beef meat | 0.1 |
| Gypsum | 18.6 | Cow milk | 0.08 |
| Soil | 0.01&0.05 | Human brain tissue | 1.1 |
| Human body | 1.1 | Human dietary need | 0.5[a] |

a) Grams per day.

It is the goal of this book to help specialists cross interdisciplinary barriers and increase awareness of the relationship and importance of their own work to that being done in other fields.

*Sulfur, Chemistry and Engineering*

Table 1.2 illustrates that sulfur is more ubiquitous than is generally assumed. If the concentration of sulfur involved is modest, the total amount is certainly not trivial. Sulfur participates in numerous important reactions. Here are some examples which reflect its diverse role.

Phosphate rock and sulfuric acid yield fertilizer:

$$3Ca_3(PO_4)_2 \quad + \quad 6H_2SO_4 \quad \rightarrow \quad 3Ca(H_2PO_4)_2 \quad + \quad 6CaSO_4$$

This reaction constitutes the largest use of sulfur. Sulfur acts as an acid to solubilize the rock, and part of it remains in the product, serving as a plant nutrient. This process is fully described in Chapter 2. The quantities and values involved are described in the next section.

Sulfate is essential for plant growth:

$$\text{Soil} \quad + \quad CaSO_4 \quad \rightarrow \quad \text{Cysteine}$$

Sulfur is an important plant nutrient, as Chapter 11 explains, because sulfur is a vital component of several proteins. Sulfur shortage stunts the growth of plants and reduces crop yield.

Smelting of copper ore yields copper and fertilizer:

$$CuS + Air + NH_3 \rightarrow Cu + (NH_4)_2SO_4$$

In this reaction, sulfur is a byproduct. Depending on the chemical path chosen, sulfur acts as an air pollutant, as solid waste, or as sellable fertilizer.

Oil and gas refining produce fuel and elemental sulfur, as described in Chapter 8:

$$RSH \rightarrow RH + H_2S \rightarrow RH + S$$

Sulfur has to be removed from oil and gas. Originally, sulfur was considered a waste product; today it constitutes a valuable by-product which accounts for half of all sulfur sold.

Roasting of pyrite (Chapter 7) is used to produce elemental sulfur:

$$FeS \rightarrow Fe_2O_3 + S_x$$

At one time, pyrite was the most important source of sulfur worldwide. Today, pyrite is a major source of sulfur and acid in only Spain and Scandinavia.

Combustion of coal yields both energy and pollution:

$$100\ C + 1100\ Air \rightarrow 100\ CO_2 + 1\ SO_2 + 9500\ kcal/mole$$

On the average, coal contains only 1-4% sulfur, but this sulfur is nonetheless responsible for much of the present controversy concerning the use of coal for electricity generation.

Stack gases and urban air can yield smog (Chapter 6):

$$SO_2 + SO_3 + O_3 \rightarrow H_2SO_4$$

In certain areas, urban air contains ozone and hydrocarbons from automobile exhaust. These chemicals interact synergistically and form particulates which aggravate the detrimental effects of smog on health.

Combustion gases and acid rain destroy marble:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2$$

In many countries, and especially in Italy, invaluable outdoor art and architecture is made of marble which is vulnerable to acid. During just the last 50 years, coal emissions have inflicted more damage on some of these treasures than 2000 years of previous exposure to the elements.

Hydrogen sulfide corrodes hot iron:

$$Fe + H_2S \rightarrow Fe_2S$$

In Claus furnaces and coal gasifiers, sulfur can react with iron and form iron sulfides. Some of these sulfide phases form eutectics in which, at normal operating temperatures, one component can become liquid. Under these conditions corrosion is extremely rapid.

In each of the above examples, the impact of sulfur is the result of purely chemical reactions. Chemistry determines the products, the yields of products, the reaction paths, and the speed of the reactions. An understanding of basic chemistry is necessary to predict and influence whether the effect of sulfur will be beneficial or detrimental. It determines whether sulfur will form valuable products or merely waste. For example, in the case of copper smelting, by chemical manipulation of the original gases one can determine whether sulfur is obtained as elemental sulfur, a generally valuable commodity, as ammonium sulfate, which is a valuable fertilizer, or as sulfur dioxide gas, an air pollutant.

The basic chemical properties of sulfur remain the same regardless of the manner in which it is used. Thus, sulfur chemistry is the link between the various applications and uses of the element, and establishes the intrinsic limits of any process in which sulfur is involved. If the basic sulfur chemistry is resulting in undesirable products, or the thermodynamics or kinetics are unfavorable, all efforts, including legislation, political pressure, money or engineering are in vain. On the other hand, chemical inventions and innovation can induce basic changes in industry, superseding carefully planned management predictions or economic programs. Hence, this book will concern itself primarily with chemistry. Engineering constitutes another basic limitation, because it determines whether chemical opportunities can be fulfilled. However, even when engineering efforts fail, a process may become viable at a later time, when new techniques or materials become available.

*Sulfur, GNP and Living Standards*

In 1843, in his letters on chemistry quoted in Chapter 2, Justus Liebig concluded, "We can fairly judge of the commercial prosperity of a country from the amount of sulfuric acid it consumes." Table 1.3 shows the sulfur production in the U.S. since 1850. The growth is partly due to increasing population, and partly due to increase in the per capita