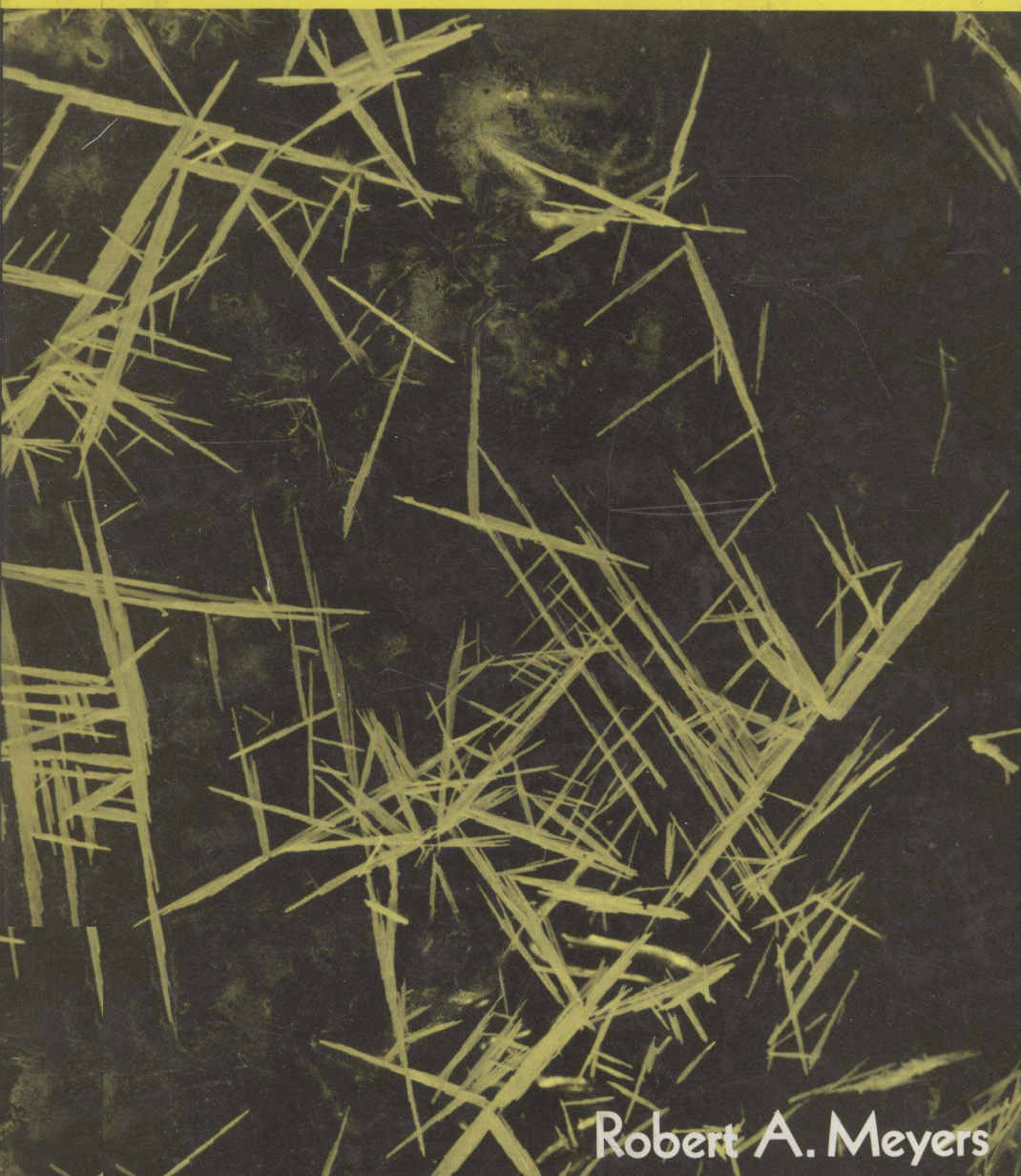


COAL

DESULFURIZATION



Robert A. Meyers

COAL DESULFURIZATION

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with a Foreword by Edward Teller

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COAL DESULFURIZATION

FOREWORD

In the 18th century England ran out of firewood. The British turned to a dirty substitute, coal.

The environmentalists of those days protested but coal was an economic necessity and won out. It probably became the main driving force behind the Industrial Revolution.

Actually, coal has been used in various forms in the production of iron and steel. Indeed, it was needed for this purpose because it gave a hotter flame than wood. The fact that coal was brought into general usage in England more than 200 years ago produced a most important side effect. For the first time in history a truly cheap metal, iron, was available. This is one of the main reasons why the Industrial Revolution could occur.

For a long time coal was king. But in the last few decades it has been more successfully attacked by the environmentalists and dethroned by petroleum. But, in turn, the reign of oil is drawing to a close; one of the main reasons is that the supply appears to be limited. Coal, on the other hand, is plentiful, particularly in the United States. Almost one-third of the world's known coal reserves are located in the United States.

At the same time, the environmental objections are being voiced more strongly than ever and these objections have some justification. In the case of coal, the worst offender is probably sulfur and much of the coal in the United States has a high sulfur content. For this reason, a book on coal desulfurization is of great and obvious importance.

The story is, and should be, long. The foreword, on the other hand, ought to be short. The relevant fact, in a few short words, is that sulfur is present in two different forms; organic sulfur, bound in the organic coal matrix itself, and inorganic, mostly pyritic sulfur dispersed in both the inorganic and organic portion of coal. Part of the pyrite can be separated along with inorganic coal rock and a portion of the organic coal matrix by simple physical means. In some coal deposits, the physically separable sulfur is a big fraction, indeed more than one-half of the sulfur present. In other deposits, the pyrite is not as amenable to physical separation so that a chemical method would be desirable.

It is of the greatest possible importance to understand in a thorough fashion how we can get rid of sulfur in an economic manner. This book addresses this question. A thorough understanding of the problem will make a truly important contribution to the solution of our energy problem.

EDWARD TELLER
Lawrence Livermore Laboratory

PREFACE

Coal is second only to petroleum and natural gas as a source of energy and is slated to surpass the other fossil fuels in production and usage within the near future. Sulfur, contained as inorganic and organic compounds in the coal matrix, provides a serious drawback to the increased utilization of coal. It is my belief that it is technically feasible to remove sulfur from coal by chemical reaction.

This book provides a thorough review of methods for the removal of the sulfur content of coal by chemical means. The review is not simply a summation and correlation of the literature, but rather is highly critical in its treatment. Constant attention is given to process engineering and economic viability. In many cases, published data is recalculated and reinterpreted, giving rise to conclusions differing significantly from those cited in the source literature. In addition, hitherto unpublished work, from our laboratories, is presented for appropriate elucidation of various points.

An attempt is made to systematically categorize methods which can theoretically be used to desulfurize coal. The categorization is based on mechanistic considerations and physical-chemical correlations such as oxidation-reduction potentials, reaction rate constants, solubilities, etc. This has resulted in the definition of a number of potentially rewarding research areas which could lead to new methods for the desulfurization of coal.

To date, one method for chemical desulfurization of coal, ferric sulfate leaching, has been extensively tested. This method is described in detail, starting with the basic chemistry and proceeding through process development and engineering design and cost estimation results. Where applicable, other desulfurization methods reported in the literature are similarly treated. Thus, it is an objective of this book to present the entire spectrum of chemical desulfurization technology — from basic research through engineering for practical application.

A description of the sulfur content distribution of world and U.S. coal and the need for the removal of sulfur from coal are discussed in Chapter 1. The physical and chemical structure of coal as related to coal desulfurization is presented in Chapter 2. The basic chemistry associated with the various possible methods for desulfurization of coal is presented systematically in Chapter 3, while economic considerations are introduced in Chapter 4. Chapter 5 presents a detailed description of ferric sulfate leaching for desulfurization of coal. A number of additional methods are presented in Chapters 6 through 9 for removal of pyritic sulfur, while processes for the removal of organic sulfur from coal are discussed in Chapter 10.

R.A.M.

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I am very much indebted to Mr. L.J. Van Nice, the brightest scientist with whom it has ever been my pleasure to work, for providing a stimulating technical atmosphere for the preparation of this book, and to his colleagues E.P. Koutsoukos, M.J. Santy, J.W. Hamersma, C.F. Murray, and R.A. Orsini, for providing much of Chapter 5.

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CHAPTER 1

INTRODUCTION

- I. World Coal Reserves and Sulfur Content
 - A. Coal Reserves and Type
 - B. Sulfur Distribution
- II. Why Remove Sulfur?
 - A. Air Pollution Control
 - B. Coking Coal
- III. Why Chemical Desulfurization?

Coal is unquestionably the fossil fuel of the future for generation of electrical energy, but its utilization gives rise to a number of ecological problems. These range from acid mine drainage, subsidence and destruction of land surface as a consequence of mining operations, to ash waste problems and air pollution from particulate and sulfur dioxide emissions resulting from combustion in utility boilers. It is estimated that worldwide sulfur dioxide emissions from coal combustion in 1965 amounted to 102×10^6 tons, a two-fold increase since 1940 (1).

The following sections describe the sulfur content and sulfur type distribution of coals on both a worldwide and U.S. basis, as well as the necessity for sulfur removal from coal, and the potential advantages of chemical desulfurization.

I. WORLD COAL RESERVES AND SULFUR CONTENT

A. Coal Reserves and Type

Table 1-1 lists the remaining "producible" coal reserves of the world. As indicated in Table 1-1, three super-powers (the United States, the People's Republic of China and the USSR) have 80% of the remaining coal reserves of the world; underdeveloped regions, such as Africa and South and Central America, are underendowed with this form of fuel.

TABLE 1-1
Remaining Coal Reserves of the World by Region and Principal
Coal-Producing Countries (3)

Region and country	Producible coal 10 ⁹ metric tons	Percent of regional total	Percent of world total
Asia			
U.S.S.R.	600	52.3	25.8
China	506	44.1	21.8
India	32	2.8	1.4
Japan	5	0.4	0.2
Others	4	0.4	0.2
Total	1,147	100.0	49.4
North America			
United States	753	94.4	32.5
Canada	43	5.4	1.8
Mexico	2	0.2	0.1
Total	798	100.0	34.4
Europe			
Germany	143	47.5	6.2
United Kingdom	85	28.2	3.7
Poland	40	13.3	1.7
Czechoslovakia	10	3.3	0.4
France	6	2.0	0.3
Belgium	3	1.0	0.1
Netherlands	2	0.7	0.1
Others	12	4.0	0.5
Total	301	100.0	13.0
Africa	35	—	1.5
Australia	29	—	1.3
South and Central America	10	—	0.4
World Total	2,320		100.0

It should be pointed out that lower estimates of coal reserves are obtained by limiting the estimation to coal which can be economically mined using current technology. For example, U.S. coal reserves are estimated at only 150×10^9 tons of "hypothetical" reserves (2). Thus, the "producible" type estimates may be on the high side.

Current production is also dominated by the super-powers (Table 1-2), with West and East Europe completing the list of major producers. Combined production from these countries accounted for nearly 60% of the total world output in 1973.

TABLE 1-2
Major Coal Producing Countries in 1973 (4)

Region and country	Production (10 ⁶ short tons)
Asia	
USSR	736
China (Mainland)	450
North America	
U.S.	592
Europe	
Germany (West)	231
Germany (East)	272
United Kingdom	140
Poland	216

The potential future importance of coal as a fossil fuel is shown by considering the life of producible coal reserves at a 0% production growth rate. The U.S.A. has approximately 1300 years of reserves, the People's Republic of China 1100 years, the USSR 800 years, the two Germanys 240 years, the United Kingdom 600 years and Poland 190 years of reserve.

B. Sulfur Distribution

Although many thousands of coal samples have been taken from operating coal mines, core samples, outcroppings, etc. and are reported in the literature, the sulfur content of the coal reserves of the world is not known with great accuracy. To obtain this data, it would be necessary to obtain an additional order of magnitude of coal samples for analysis, using a statistically valid sampling procedure, or more rigorously (and facetiously) to dig up, sample and analyze all the coal reserves of the world. Nevertheless, it is instructive to consider available data for both total sulfur content and the two major sulfur forms in coal (pyritic and organic sulfur) obtained for some selected coals from each major producing region (Table 1-3). The coals shown in the table are not meant as representative of any particular region or country, but are representative of worldwide distributions of sulfur.

It can be seen that the total sulfur content of these coal samples varies from 0.38% to a high of 5.32%. This is essentially the range of sulfur content which is normally found among coal samples on either a worldwide or regional basis. The pyritic sulfur content of these selected coals varies from a low of 0.09% to a high of 3.97%, while the organic sulfur content varies from a low of

TABLE 1-3
Sulfur Forms in Selected Bituminous Coal – Worldwide

Region and country	Location or mine	Sulfur, percent w/w ^a			Ratio Pyritic to Organic Sulfur
		Total	Pyritic	Organic	
Asia					
USSR	Shakhtersky (5)	0.38	0.09	0.29	0.031
China (Mainland)	Taitung (5)	1.19	0.87	0.32	2.7
India	Tipong (5)	3.63	1.59	2.04	0.78
Japan	Miike (5)	2.61	0.81	1.80	0.45
Malaysia	Sarawak (5)	5.32	3.97	1.35	2.9
North America					
U.S.	Eagle No. 2 (6)	4.29	2.68	1.61	1.7
Canada	Fernie (5)	0.60	0.03	0.57	0.053
Europe					
Germany	---- (7)	1.78	0.92	0.76	1.2
United Kingdom	Derbyshire (8)	2.61	1.55	0.87	1.8
Poland	--- (5)	0.81	0.30	0.51	0.59
Africa					
So. Africa	Transvaal (9)	1.39	0.59	0.70	0.84
Australia					
	Lower Newcastle (10)	0.94	0.15	0.79	0.19
South America					
Brazil	Santa Caterina (11)	1.32	0.80	0.53	1.5

^aMoisture-free basis, pyrite + sulfate reported as pyrite

0.29% to a high of 2.04%. Generally speaking, organic sulfur levels much greater than 2% or much less than 0.3% are almost never encountered, and pyritic sulfur levels greater than 4% are also uncommon. However, the pyrite content of a few coals can approach zero when there is both little inherent pyrite and when careful mining operations (such as manual labor) prevent the mining of pyrite-containing formations adjacent to the coal seam. The ratio of pyritic to organic sulfur can vary over 2-3 orders of magnitude.

The sulfur content and sulfur forms distribution of U.S. coals have been more extensively reported than those of other countries (12, 13, 14, 15). Still,

no set of data is available which fully and statistically describes both the sulfur content and sulfur distribution for U.S. coals.

Some sulfur analyses of run-of-mine coal recently obtained from major operating mines representative of the three most important U.S. coal regions are shown in Figure 1-1. Emphasis is placed on Appalachian coal samples, since the Appalachian region supplies more than 60% of current U.S. coal production. It can be seen that the overall sulfur content of western coals is low, generally below 1.0%, and the major sulfur form is organic. Run-of-mine Interior Basin coals generally have a sulfur content of about 4.0%, with about 30-50% of the sulfur being organic. Appalachian coals cover a larger range of sulfur content and ratio of sulfur forms, but tend to have organic sulfur content lower than either the pyritic sulfur or the organic sulfur levels of Interior Basin coals. Thus, the geographical trend in sulfur content from east to west is high sulfur to low sulfur and a preponderance of pyritic sulfur to a preponderance of organic sulfur.

As noted above, a majority of current U.S. coal production comes from the Appalachian region, i.e., the states of Virginia, Tennessee, Pennsylvania, Kentucky (east) and West Virginia. The sulfur content of Pennsylvania coal is typical of the region (Figure 1-2). The organic sulfur levels tend to center around 0.5-1.0% and pyritic sulfur level varies from nearly zero to more than 3.0%, giving rise to total sulfur content mainly at the 1.0-4.0% level. Here it becomes apparent that the removal of one type of sulfur alone, the pyritic sulfur, can reduce a large number of these coal samples to less than 1.0% total sulfur, a value consistent with many air pollution control standards.

II. WHY REMOVE SULFUR?

Sulfur, in the form of its element or combined with other elements, is a nutrient for both plant and animal life. However, in recycling sulfur (as in other nutrients) back to nature, ecological soundness requires that there must be no excess at any given point in the cycle. In general, the fate of sulfur dioxide emissions involves photo-oxidation in the atmosphere to form sulfur trioxide which, under humidifying conditions, becomes sulfuric acid or sulfate aerosol. Residual sulfur dioxide and sulfuric acid or sulfates are scavenged from the atmosphere by vegetation, eventually being discharged into the sea by the world's rivers, along with sulfur accumulated from weathering rocks and sulfur applied as fertilizer. Some of the sulfate is directly deposited into the ocean via rain or dust. When an excess occurs, the atmosphere-to-land portion of the sulfur cycle is unsound.

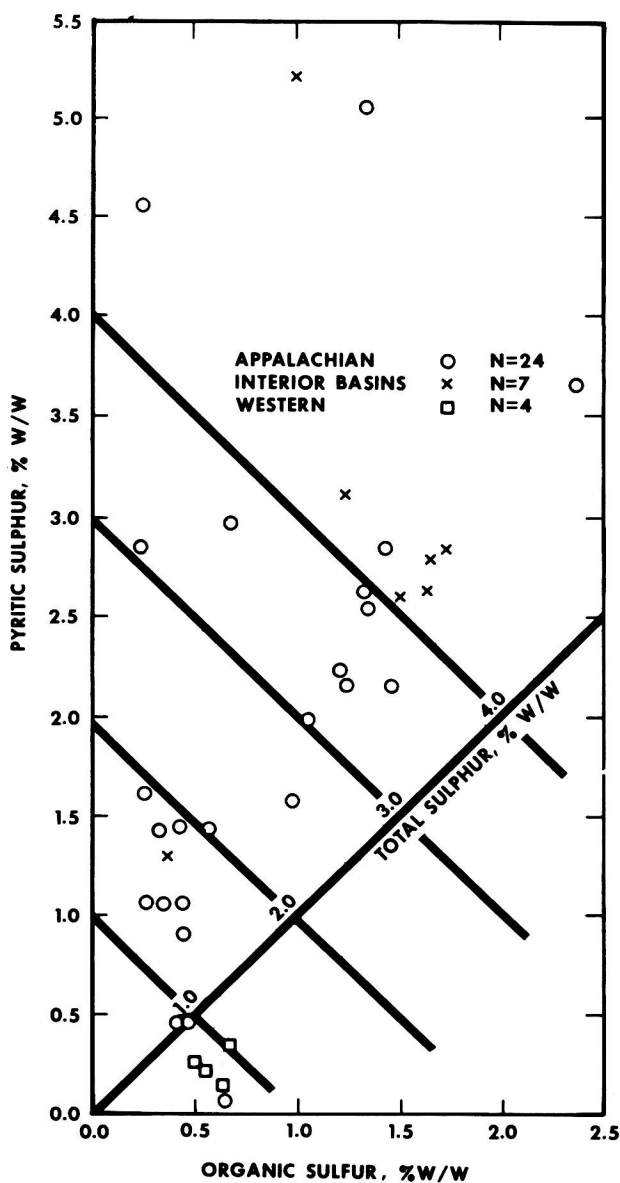


Figure 1-1. Distribution of sulfur forms (dry moisture free basis) in run-of-mine U.S. coals (6)