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PERCENTAGES OF ASH, TOTAL SULFUR AND SULFUR FORMS IN U.S.A. COALS

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ABSTRACT

The frequency distributions of ash and sulfur percentages for coals of the United States are presented graphically, including coals from the various coal producing counties and coal beds of 30 states plus Alaska. Coals of all ranks are included. The range of ash and sulfur percentages and their relative frequency are shown by the graphs.

The percentages of pyritic, organic and sulfate sulfur are shown versus total sulfur, for coals of Ohio and Illinois.

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This paper discusses the frequency distribution of ash and sulfur contents of coals of the United States. The coal reserves of America are so vast and diversified that the subject can be presented in only a general way in this short paper. However, the summarized technical information which follows should provide a useful statistical background for the study of particular phases of ash and sulfur in coal.

The publications of Federal and State agencies, and particularly the publications of the United States Bureau of Mines, contain the analyses of tens of thousands of samples of coal which have been collected and analyzed by carefully prescribed methods. Many of these were channel samples cut across the coal bed in the mine, or drill-core samples, both of which represent the natural coal as it lies in the ground.

However, a large proportion of the analyses, particularly those published in recent years, are of samples taken at mine tipples as the coal was being loaded into railroad cars or trucks, or of delivered coal. These tipple or delivered samples represent commercial shipments of coal which in most cases has been sized, cleaned or otherwise prepared for market.

Ash and Sulfur of Typical U. S. Coals

The number of published coal analyses is so great that the study of frequency distribution will be greatly facilitated by using a series of typical coal analyses. The most convenient reference is "Typical Analyses of Coals of the United States" (1) published in 1942 and reprinted in 1954. This contains 737 analyses which were carefully selected to exemplify the analysis of coal mined and shipped in each coal-producing county of the United States, and where feasible, coal from each bed in each county.

These analyses were selected to represent typical commercial shipments at that time, and some of the coal had been mechanically cleaned. When more than one size was being prepared, the average analysis of the total coal shipped was computed from the analysis of each size that was sampled. It is these typical composite analyses which are graphed in Figures 1 and 2. (The original reference, in about 25% of the cases, also shows the range in analysis which could be expected in coals from a given county.)

It is seen that the ash content on the "as-received" basis peaks at 9% ash, and that 90% of the analyses fall within the limits of 2.5% to 13% ash. The sulfur content peaks at 0.6% but is a very skewed curve, and only 57% of the analyses fall within the limits of 0.2% to 1.4% sulfur.

In considering the distribution and range of ash and sulfur analyses shown in Figures 1 and 2, it should be kept in mind that these analyses include coals of all ranks, that is lignites, subbituminous and bituminous coals, and anthracites, occurring in 30 states plus Alaska.

It must also be kept in mind that these analyses were published in 1942, and were originally assembled for use under the Bituminous Coal Act of 1937, so they are about twenty years old. During the past twenty years, there has been a fourfold increase in the percentage of coal production that is mechanically loaded and a similar increase in the percentage that is mechanically cleaned. Also, there have been some changes in the mines and coal beds worked. Thus it might be supposed that the data shown in Figures 1 and 2 are obsolete. However, some of these changes tend to compensate for each other.

Ash and Sulfur in Federal Coal Purchases - 1956

No new study of typical coals of the U. S. has been published in recent years, but it will be interesting to compare the analyses of tippie and delivered samples of coal purchased by the Federal Government in a recent year. The most recent publication in this series contains the analyses of samples collected for the fiscal year 1956⁽²⁾. This gives 1646 analyses of coals of all ranks, mined in 22 states plus Alaska. A large proportion of the samples represent screened sizes ranging from large lump to small slack, rather than the total coal from a mine. (The analyses of screened sizes from a given coal mine may vary substantially from each other.)

For most of the government coal purchases the bidders specify the analysis of the coal which they are offering, and the analysis guaranteed by the successful bidder becomes the standard of his contract. The deliveries are sampled and analyzed to determine whether the coal is of the quality guaranteed. The Federal Government purchased about 5 million tons of coal in fiscal year 1956, which was used chiefly for heating government buildings and installations. Such purchases represented about 1% of the total coal produced in the United States.

The analyses shown in Reference 2 and Figures 3 and 4 do not include coal purchased by the Tennessee Valley Authority, whose steam plants received 17,584,000 tons of coal during fiscal 1956.

The ash and sulfur contents on the dry basis of government purchases of various coal sizes in 1956 are shown in Figures 3 and 4. There is a striking similarity in the frequency distribution of ash and sulfur of these recent samples with the earlier analyses shown in Figure 1 and 2 (which represented the composites of coal sizes on an as-received basis).

The recent analyses peak at 6.5 to 9% ash, and 91% of the analyses fall within the range of 1-1/2% to 13% ash. As in the earlier analyses, the sulfur peaks at 0.6%, and has a very skewed curve, with 70% of the analyses falling within the limits of 0.2% to 1.4% sulfur. Thus the recent analyses show slightly cleaner coal, but are quite similar on the average to the earlier analyses.

It must be emphasized that none of the foregoing graphs are "weighted" with respect to the tonnage of coal represented. Thus in Figures 3 and 4, an analysis may represent anything from a single truck delivery of 1 to 5 tons, to the average of a year's receipts of a certain size coal from a certain mine, totalling more than 50,000 tons. Furthermore, Figures 3 and 4 do not include coal purchased for the two largest specific industrial uses, namely electric utilities and coke plants.

Figure 5 represents an attempt to compile sulfur percentage frequencies weighted for the tonnage of total bituminous coal produced in the eastern U. S. The data were obtained by multiplying the tonnage of coal produced in each bituminous-coal-producing county of the eastern half of the U. S. in 1953⁽³⁾ by the "typical" sulfur for that county⁽¹⁾. This method will give only an approximation and the results may not be close to the true figures in some individual cases. However, when

a number of such results are combined, as in Figure 5, the figures should be indicative in a general way. In any case, the writer does not know of any other attempt to present the sulfur contents of such a large proportion of U. S. coal shipments.

Figure 5 indicates two peaks for sulfur content, with one at about 0.8% and the other at 1.3% sulfur. If the estimates are valid, 213 million tons or 50% of the bituminous coal shipped in the eastern half of the U. S. in 1953 was in the range of 0.5% to 1.4% sulfur content. (In that year, 119 million tons of good purity U. S. coals were used for making oven coke in the United States and Canada, or were exported overseas mostly for metallurgical uses.) Figure 5 also shows that substantial tonnages were shipped of coal in the 3-4% sulfur range (e.g., for power generation.)

The data in Figure 5 are not closely comparable with Figures 2 and 4, since Figure 5 shows only bituminous coals in the eastern half of the United States (because the data were computed for a special survey.) Excluded are all lignite, sub-bituminous coal and anthracite wherever produced in the U. S., and all bituminous coals mined in the western half of the U. S. Such excluded coal, most of which was moderate to low in sulfur content, amounted to 65 million tons, or 13% of the total U. S. coal produced in that year. No attempt has been made to estimate weighted tonnages by ash content for 1953 shipments.

Ash and Sulfur in Metallurgical Coals

The following items are of interest in connection with the purity of coals used for coke manufacture.

Analysis of Oven Coke in the U. S., 1943-45 and 1951-53^(3, p. 226)

Year	Blast-Furnace Coke*		Foundry Coke	
	% Ash	% Sulfur	% Ash	% Sulfur
1943	9.7	0.8	8.1	0.6
1944	10.2	0.8	8.3	0.6
1945	10.5	0.8	8.6	0.6
1951	9.9	0.9	8.7	0.6
1952	9.9	0.9	8.7	0.6
1953	9.7	0.9	8.7	0.6

*1943-45 analyses include all coke other than foundry, and are presumed to be mostly blast-furnace coke.

When coal is coked, the average yield of coke plus coke breeze is about 75% of the weight of coal in the case of blast-furnace coke, and somewhat higher in the case of foundry coke. All of the ash remains in the coke and breeze, so that the ash content of coal used for making coke in 1953 evidently averaged slightly over 7%. The writer has found by graphic studies not presented here, that the sulfur percentage in oven coke is similar to but usually slightly lower than that in the coal used. Thus the coal mixtures coked in 1953 probably averaged slightly over 0.9% and 0.6% sulfur respectively for the two types of metallurgical coke.

In a series of reports investigating U. S. coals suitable for the production of metallurgical coke, either as mined or after beneficiation, the U. S. Bureau of Mines states⁽⁷⁾:

"According to present-day standards for metallurgical coal, many believe that, on the dry basis, the sulfur content of the coal should not exceed 1.25 percent and the ash 8 percent. Coal with more than this amount

of sulfur has been used for making metallurgical coke, especially when blended with coal containing less sulfur. In this series of reports, 1.25 percent sulfur is used as a gage to determine whether or not a coal can be used to produce metallurgical coke."

In any given industrial area, the maximum ash and sulfur percentages that will be acceptable in metallurgical coals will depend upon the purity and delivered cost of the available coking coals, the kind of iron ore used, etc.

Sulfur Forms in U. S. Coals

Three forms of sulfur are recognized in coal: (a) sulfur combined with iron (FeS_2) as pyrite or marcasite and known as pyritic sulfur, (b) sulfur combined with the coal substance as organic sulfur, and (c) small quantities of sulfate sulfur in the form of calcium sulfate or iron sulfate. Freshly mined unoxidized coal usually contains only a very small amount of sulfate sulfur⁽³⁾.

Figures 6 and 7 show for Ohio and Illinois coals, the distribution of organic, pyritic and sulfate sulfur percentages versus total sulfur. It will be seen that organic sulfur amounts to 20 to 60% of the total in most coals from these states, that pyritic sulfur ranges from 40 to 80% in most cases, and that the sulfate sulfur is a very small part of the total. The writer has made similar graphs which are not presented here, of sulfur forms from certain other states including Iowa, Kentucky and Tennessee. In all of the cases studied, the sulfur in coals containing 0.5% sulfur or less was almost entirely organic, with pyritic sulfur beginning to show up at about 0.5 or 0.6% total sulfur.

The writer has prepared numerous other graphs for special purposes which show the frequency distribution of various coal constituents and physical properties by rank of coal, coal bed, geographical area, etc. However, no additional graphs will be presented here since readers will usually be interested in special cases which they can best select and graph for themselves.

Trends in Ash and Sulfur Contents

Not much systematic information has been published on broad trends in the ash and sulfur contents of commercial coal shipments. Since there are more than 8,000 coal mines operating in 27 states, and since most of these mines ship several sizes of coal differing in ash and sulfur contents, the collection and statistical treatment of such information would be very costly, and probably not worth the effort.

Leading coal producers intensively study the characteristics of their coal reserves, including washability by available methods, and they regularly test the quality of coal shipped. Large coal users study the characteristics of coals available to them and they may analyze shipments of coal received. Thus there is much information on coal ash and sulfur percentages in company files, which applies to specific cases.

The factors which will affect ash and sulfur specifications for particular uses in the future, and the future availability of coals to meet such specifications, are much too complex for discussion here. Sound decisions will have to be worked out for each specific case, depending on the technical and regional economic factors that are involved.

The United States has enormous coal reserves -- nearly one trillion tons of recoverable coal according to the latest estimate of the U. S. Geological Survey. This is equivalent to about 1900 years supply at the present rate of U. S. coal consumption. These reserves include huge tonnages of both low sulfur and high sulfur coals, of low ash and high ash coals, of coking and non-coking coals -- in fact, coals of all ranks.

However, the many grades and ranks of coal do not all occur in the same region, and freight costs limit the distance to which a given coal will be shipped. Purity specifications for coal for a particular use are not absolute values, but are instead strongly influenced by the nature of the coals that are economically available in the area, and the current status of the user's technology.

About 60% of the bituminous coal produced in the U. S. is mechanically cleaned, and the percentage is increasing. There is great activity in coal preparation research both in the U. S. and many foreign countries. The writer is confident that in the decades ahead, U. S. coal reserves will prove adequate in quantity and quality to meet the expected need for increasing tonnages of specification coal. Continued technological progress in the mining, preparation and use of coal will solve problems which may arise.

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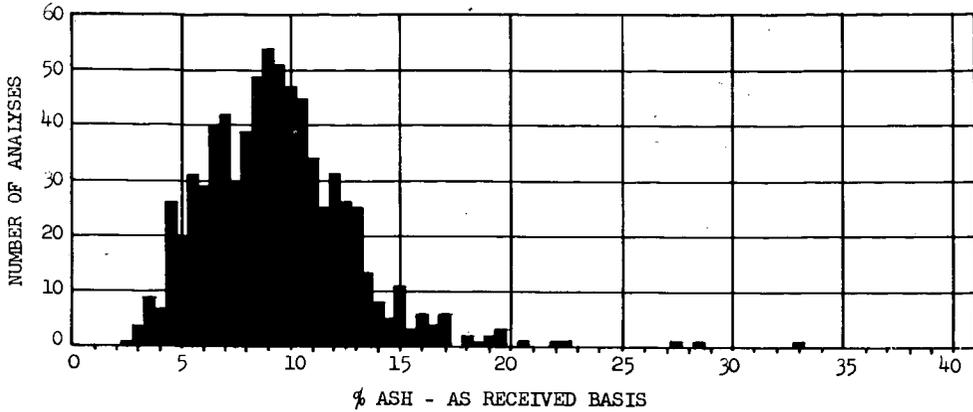


Fig. 1 - Ash Contents of Typical Coals of the United States, Including All Ranks. Analyses from Ref. 1 (1942)

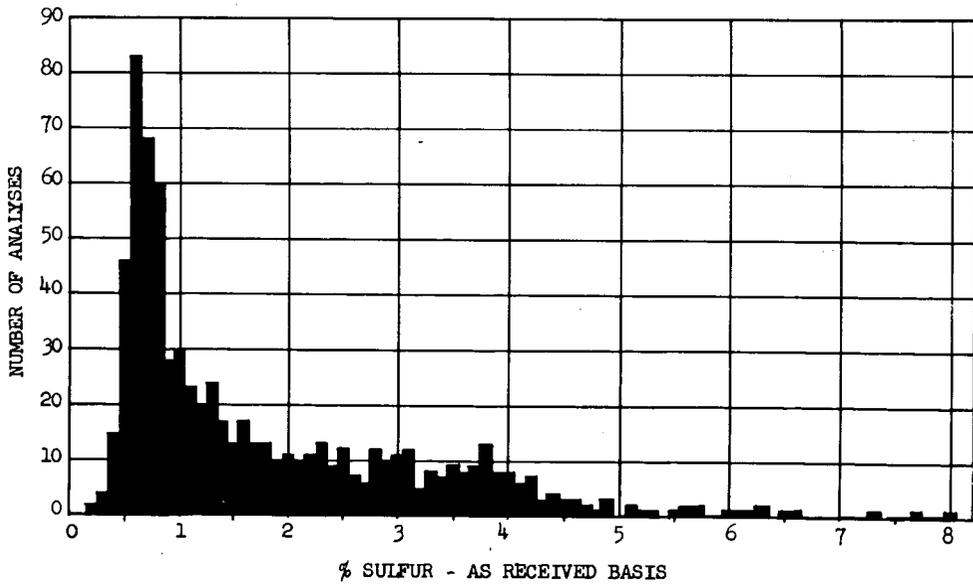


Fig. 2 - Sulfur Contents of Typical Coals of the United States, Including All Ranks. Analyses from Ref. 1 (1942)

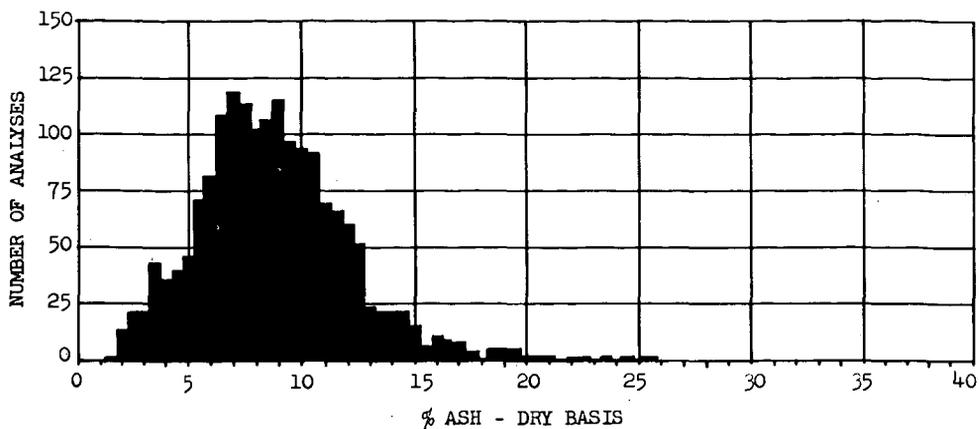


Fig. 3 - Ash Contents of Coals of All Ranks Purchased for Federal Government Use - 1956. Analyses from Ref. 2 (1957)

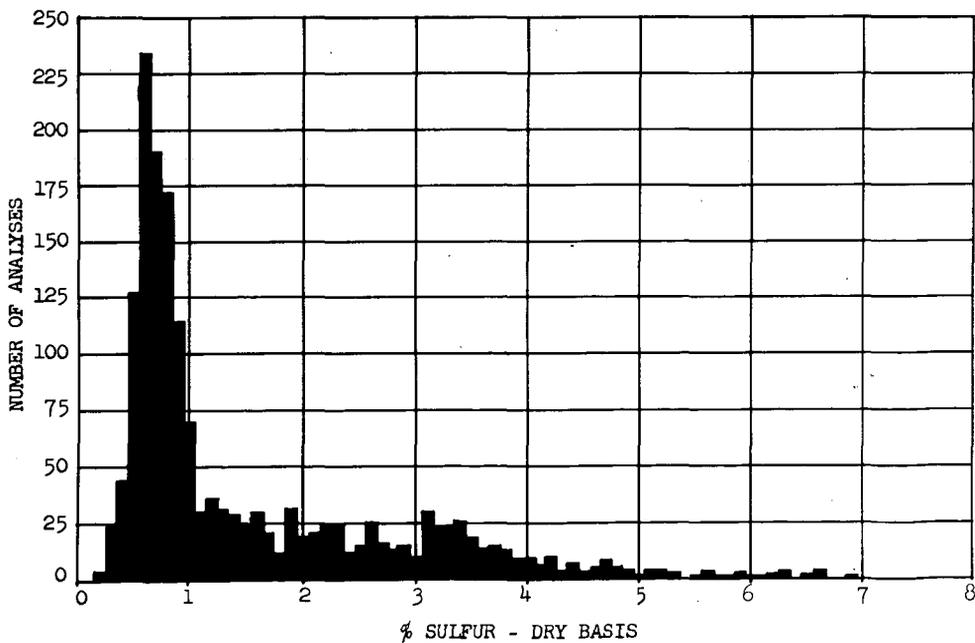


Fig. 4 - Sulfur Contents of Coals of All Ranks Purchased for Federal Government Use - 1956. Analyses from Ref. 2 (1957)

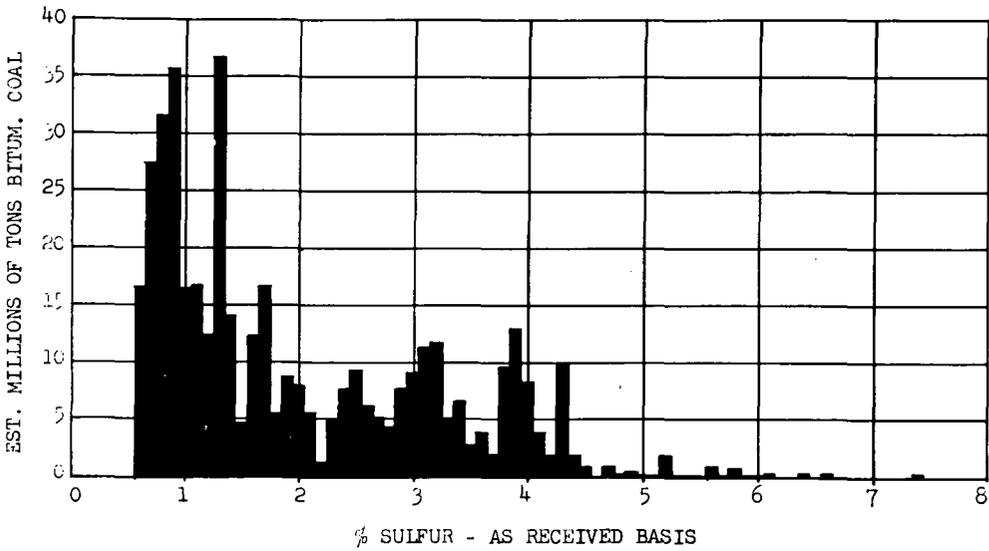


Fig. 5 - Estimated Tonnage of Bituminous Coals of Various Sulfur Contents Produced in the Eastern Half of the United States - 1953. Data estimated from Refs. 1 and 3

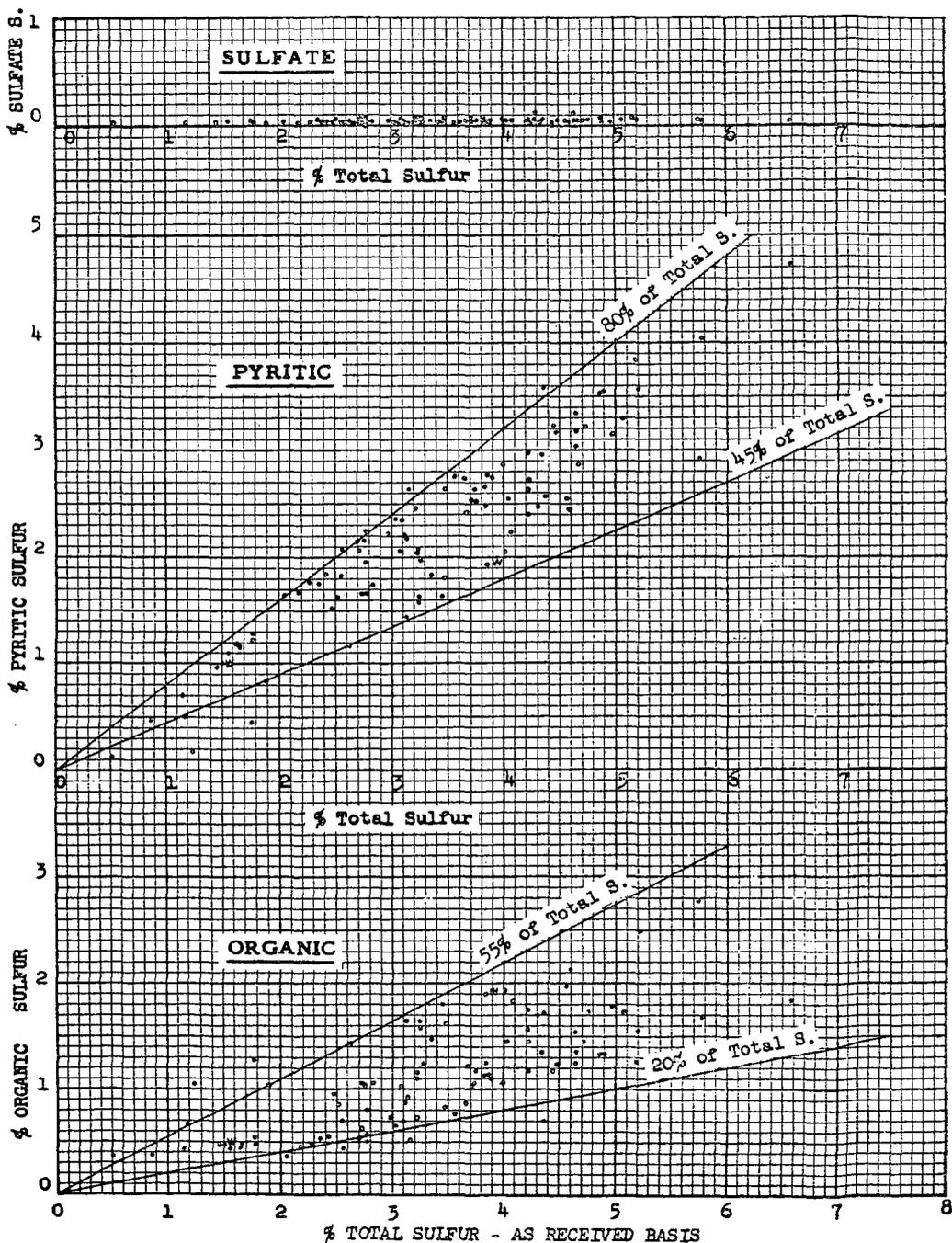


Fig. 6 - Sulfur Forms in OHIO Coals--Range in Organic, Pyritic and Sulfate Sulfur at Various Total Sulfur Percentages. Represents tittle samples from 16 counties and 9 coal beds. Analyses from Ref. 4

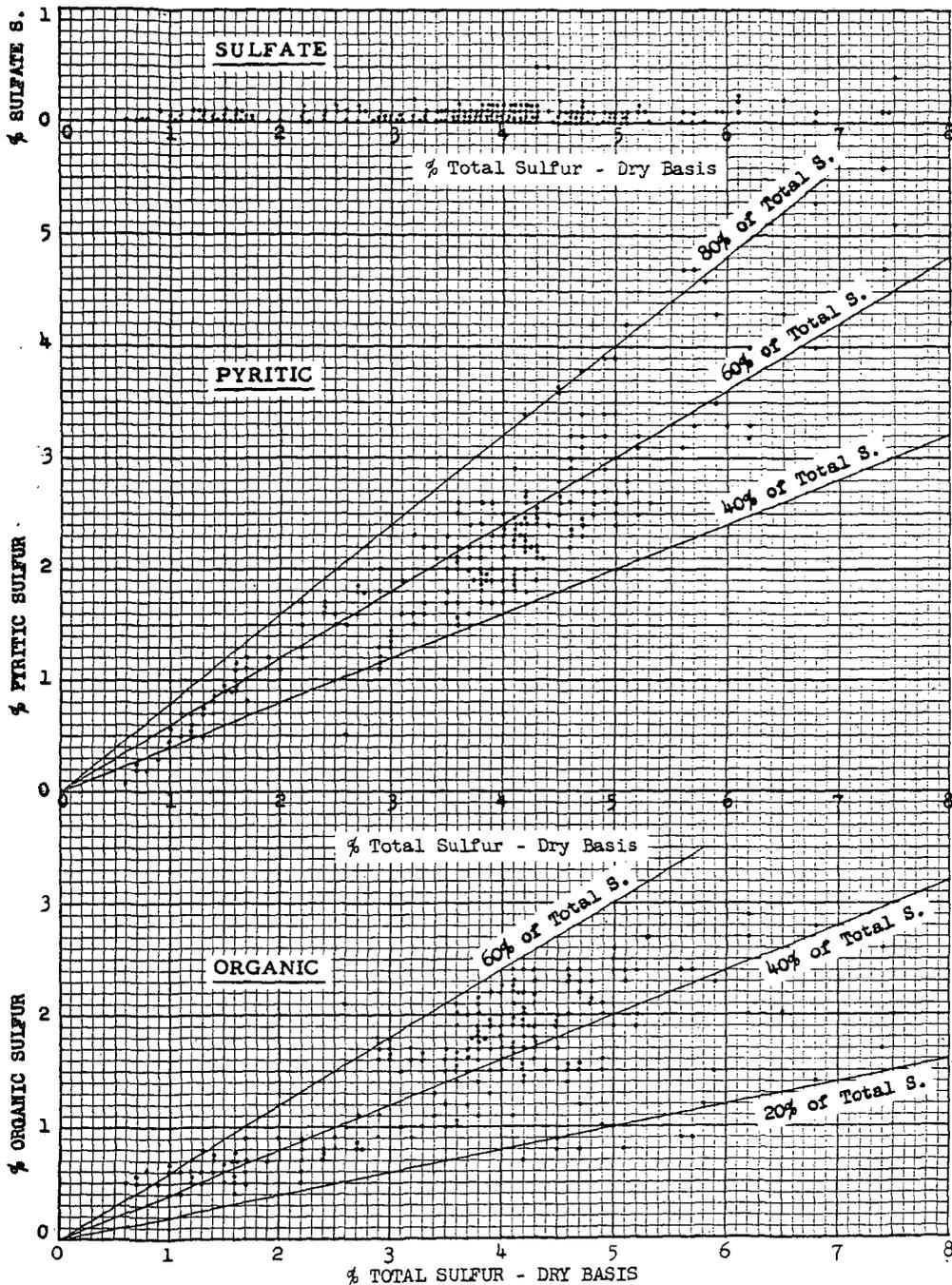


Fig. 7 - Sulfur Forms in ILLINOIS Coals--Range in Organic, Pyritic and Sulfate Sulfur at Various Total Sulfur Percentages. Represents face samples (some from inactive mines) from 36 counties and all commercially important beds. Analyses from Refs. 5 and 6

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BIOCHEMICAL AND GEOCHEMICAL ORIGINS OF ASH-FORMING INGREDIENTS IN COAL

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ABSTRACT

Coal is a product of geological as well as biological agencies; as such, the ash forming ingredients in the coal have had a complex history. The origins of ash forming ingredients in the coal are traced through the entire cycle of coalification--from the living plant, through the peat stage during burial and compaction, and finally to the weathering stage. Special emphasis is placed upon minor elements, not normally concentrated in the separable minerals, but more likely concentrated by living plants, and by chemical combinations with degradation products of coal flora in the peat stage. Analyses of ash of original peat, and of ash of peat extracts such as humic acids, humins, holocellulose, and alpha cellulose yield significant data relative to the function of degradative products as concentrating agents for heavy transition elements such as Co, Ni, Cu, Zn, Nb, Mo, Sn, Au, Pb, and Bi. Germanium, not detected in any plant ashes, nor in any peat ashes, is found in the ash of humic acid extracts from the same peats. The alkaline and alkaline earth elements are generally lower in the ash of coals and peats than in the ash of plants and the reasons for this are discussed in the light of the life cycle of plants. The low manganese content of plant degradative products and of coal is compared to the high iron content of coal and of plant degradative products.

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INTRODUCTION

Coal is a product of geological as well as biological agencies. All too often the geological aspect of coal is ignored. In general coal technologists and fuel chemists dealing with the whole coal as a substance consider ash-free or mineral matter-free coal as a starting point for processing or for calculation. This is a snare and a delusion unless one always keeps in mind the fact that mineral-matter free or ash-free coal is only a concept and is ideally approached on rare occasions only by careful separation of selected vitrain.

It is entirely improper and quite inaccurate to consider minerals deposited with plant materials in a coal swamp as adventitious matter. Every naturally occurring body of water, from a droplet on the end of a stalactite to an ocean basin, is a suitable environment for mineral deposition. The very existence of coal is dependent upon a rare sequence of geologic events. Each stage contributing to the transformation of living plant material into coal also effects some transfer to what are commonly termed mineral elements.

This paper is concerned with the biochemical as well as the geochemical origins of the ash forming ingredients in coal, and is intended to serve as a guide to the appreciation of the many factors involved in adding and removing elements from an open system throughout the coalification cycle.

Samples and Analysis:--Sixty-nine samples of ash of coal flora, of peat, and of peat extracts have been analyzed spectrographically by the semi-quantitative method of Waring and Ansell. (1)

Twenty of these samples were from the herbarium of the Smithsonian Institution and an additional plant sample was collected from near the museum grounds in Washington, D.C. These samples were ashed at 600°C in a muffle furnace before being analyzed spectrographically.

Thirteen peat samples were from Rice Lake Bog near Duluth, Minnesota; these samples represented one-foot intervals of a 13-foot core. These samples were ashed at 800°C in a muffle furnace.

Thirty-five samples of ash from seven composite peat samples from Rice Lake Bog, from extracts of humic acids, humins, holocellulose, and alpha cellulose from each of these peat samples were supplied by Professor M. Passer of the University of Minnesota at Duluth. These samples were ashed at 600°C in a muffle furnace.

General Considerations of Ash-Forming Ingredients:--Total mineral matter in coal is taken to be the summation of all elements present which are not constituents of the coal substance--the organic matter itself, which consists of carbon, hydrogen, oxygen, nitrogen, and sulfur.

There is a difference between "minerals" in coal and "mineral matter" in coal. The distinction is an actual one and is not only theoretical. Minerals, in the geological sense, have distinct properties and can, in large part, be physically separated from the organic coal substance, the limitation of separation being physical distribution. Mineral matter in coal includes the minerals in coal, and, in addition, should include those chemically bound elements other than C, H, O, N, and S. Some of these elements, like fluorine and chlorine, are largely removed during combustion or ashing. Other elements like boron and beryllium, make a large contribution to the total ash content because of the oxygen combined with them. In contrast, some carbon may be present as carbonates in minerals; certainly hydrogen and oxygen are present as water or hydroxide in clays; additional oxygen is present in the silica and alumina and other oxides in minerals; nitrogen is rare in minerals in coal. Sulfur as pyrite and as sulfates usually exceeds organic sulfur.

An ultimate analysis for carbon, hydrogen, sulfur, nitrogen, and oxygen accurately represents the composition of the organic matter in coal only when corrections are applied to account for those elements present in the minerals in the coal. Unless a complete mineral analysis is made to determine the composition and the amounts of minerals present in the coal, the corrections can only be made from formulas applied to the ash content of the coal. In the crudest of estimations the percent ash is equated to mineral matter. Parr, among others, recognized this as only a gross approximation and made refinements by applying corrections based on the sulfur content of the coal and sulfate in the ash together with other factors.

King, Maries, and Crossley (2) added factors which were varied depending upon experience with specific British coals. Millot (3) has further modified the King, Maries, and Crossley formula to specifically compensate for mineral matter in carbonaceous shales associated with British coals. These corrections have been given much attention by the fuel scientist and fuel engineer concerned with the inherent fuel value of coal as well as by the research chemist concerned with an accurate analysis of the reactive organic materials.

A thorough investigation of the nature of ash-forming ingredients in coal must consider the fact that the environment of deposition of plant debris--the coal swamp or peat bog--is in essence a medium in which chemical reactions are occurring. Materials are being dissolved and removed from the system; other substances are being added. Some of the materials added are relatively inert while others are highly reactive. The reaction vessel is large--for a small peat bog, the order of acres in area, and for a Carboniferous coal swamp, tens of thousands of square miles. Not all the reactions are proceeding simultaneously, nor will all of the reactions necessarily take place within a given limited area in the coal swamp, but the summation of these reactions should yield a picture which can be logically interpreted.

Thus the possible origins of ash-forming ingredients in coal are:

- A. From elements originally present in coal forming plants and not lost during degradation and coalification.

- B. From elements combined with organic matter during the peat stage.
- C. From elements combined with organic matter during compaction and burial.
- D. From elements combined with organic matter during weathering and oxidation.
- E. From finely divided minerals deposited in the coal swamp.
- F. From minerals formed in the coal during the peat stage and during subsequent geologic history.

The products of these six sources of ash-forming ingredients can be related to terms commonly used by coal technologists. It has previously been suggested by Deul⁽⁴⁾ that the ash-forming ingredients consist of mechanically separable minerals, inseparable minerals, and non-volatile elements organically combined, complexed, or base-exchanged. The use of such terms is better than use of terms like "inherent ash" or "fixed ash", which to many persons implies that the ash is that derived from the original plant substance.

Separable ash and inseparable ash are terms essentially incorrect. One does not separate ash from unburned coal--one only can separate ash-forming ingredients. Anyone who has worked with high-ash coals and attempted to make appropriate corrections in an ultimate analysis will readily understand the inherent inaccuracy in using such a concept.

All ash-forming ingredients are not necessarily minerals--a certain percentage of them are bound with the organic matter as compounds or as complexes. The rest of this paper is a genetic treatment of the origin of ash-forming ingredients in coal.

ELEMENTS IN PLANTS

Before discussing the kinds of mineral matter that are deposited in a coal swamp or in a peat bog, it is necessary to consider the nature of the so-called inorganic elements that were present in the living plants that died, were in part degraded, and later buried under sediments and preserved as coal. The very plants that are now coal cannot be studied but some of the Carboniferous plants and almost all of the Tertiary plants have living relatives. Even though these younger relatives may differ in size and in range of occurrence, they still provide a living link with the past in that their life processes and their nutritive demands are similar to those of their ancestors.

Certain elements are known to be essential to life processes. Although authorities differ in minute details there is a remarkable concurrence of opinion, especially insofar as the plants are concerned. Dean⁽⁵⁾ in a discussion of plant nutrition and soil fertility lists 16 elements considered necessary for the growth of green plants. These are identical to those listed by Miller⁽⁶⁾. Goldschmidt⁽⁷⁾ lists the biophil elements and, though not differentiating between plant and animal life, he includes all 16 elements mentioned by Dean and by Miller. These elements are P, K, Ca, Mg, Fe, Cu, Cl, Mn, Zn, B and Mo, in addition to C, H, O, N, and S. A wide variety of other elements could have been included in this list as growth-promoting or otherwise beneficial elements, but they are not universally beneficial or else they have such a complex metabolic

function that much doubt exists as to the validity of including them as essential elements. However, this doubt in no way prevents consideration of the function of some plants as concentrators of certain elements, irrespective of the nutritional need for the elements so concentrated. Sodium, iodine, and cobalt are known to be present in most green plants, these are essential to animals but have not been proven essential to green plants. Dean (5) recognizes that although silicon and aluminum occur almost universally in plants they perform no recognized function.

Unlike many animals plants have little selectivity of plant nutrients. If plants become rooted in a toxic environment the plant continues to accumulate the toxic element along with the nutrient elements and as a result the organism may perish. Dean (5) states that:

"The rate of nutrient accumulation is not independent of the concentration in the soil solution, and (except for instances of high concentrations) this rate of absorption is proportional to the concentration of a specific ion species. Ion accumulation or absorption thus is regulated by both external and internal factors."

and that:

"In the case of boron (to a lesser degree the other microconstituents) if the soil contains excessive amounts, toxic quantities are absorbed by plants and growth is restricted."

For this investigation, the ash of 21 samples of coal flora have been analyzed spectrographically and examined in an attempt to determine the range of concentrations for the inorganic elements. Sixteen of the twenty-one plants are typical of Carboniferous coal plants and among these 16 specimens eight genera are represented. The Tertiary flora represented five specimens representing five different genera. These 21 samples are the largest collection of such plants known to have been analyzed; and, though there may be some questions as to the selection of materials, the data are by far better than the available analyses of cereal plants and certain crop plants. Use of herbarium samples has considerable merit in that they are plants selected by botanists as representative specimens, and which presumably show no abnormalities. There are many analyses of the ash of wood used for lumber, but there are invariably of low ash heartwood and include none of the bark, stems and leaves.

The semiquantitative spectrographic analyses of ashes of the 21 plants detected 32 elements. Seventeen of these elements were detected in every plant ash 23 were found in more than half, and only nine were detected in less than half of the plant ashes. No plant ash showed fewer than 19 elements; two plant ashes showed 29 of the 32 elements detected. If we add to these elements C, H, O, N, S, and Cl, which are not detectable by the spectrographic technique used, and Zn which was below the limit of detection in all the plant ashes, then 39 elements in all must be present among these plant ashes. A minimum of from 26 to 36 elements is present in each of these plants.

The data from the analyses are tabulated in Figure 1 as a frequency distribution of the elements within the concentration ranges detected. Because of some uncertainty in the exact percentage present the ranges are separated by broken lines, indicating that elements may be present in higher or lower concentrations. Furthermore, elements not detected in certain samples are not assumed to be present in the next lower range, nor are they presumed

to be totally absent, hence, the tapered boundary pointing downward. No doubt lithium is present in all the plant ashes, but the relative insensitivity of this particular analytical method to lithium explains why it was not found in four samples. Cerium, which is much more abundant than lanthanum and neodymium was not detected--probably not because of its lower concentration but rather because its spectral sensitivity is only one-tenth that of lanthanum and neodymium. On the other hand, beryllium is so sensitive to spectral detection, like silver, that its absence in 20 plant ashes is indeed a good indication that it is present in concentrations far below one part per million in the ash.

Variation in the ash contents is large, from as low as 2.9 percent to a high of 59 percent of dry weight--a factor of 20. Within a single genus the ash content does not appear to vary by more than a factor or two. Too few samples were studied to permit more than the grossest generalizations but it does appear that the ash content of various species of a single genus collected from the same locality may show variations as great as specimens of the same genus collected from different localities. The ash content of individual specimens is of no great significance when taken alone, but when compared to that of a group of plant ashes some sensible pattern is discernable.

Median concentrations of the elements estimated by inspection of the data in Figure 1 are compared in Figure 2 to the abundance of elements in the earth's crust (8). Generalizations can be made which, if they have no other purpose, demonstrate the wide range of elemental concentrations exhibited by typical coal flora as shown in Figure 1. In some instances these concentrations may vary by a factor greater than 1000 as for aluminum and titanium, and by a factor of greater than several hundred for manganese, lead, and zirconium, and by factors of from 50 to 100 for many other elements. Even where the median concentration in plant ash is below that of the crustal abundance, the percentage of that element in one or more of the 21 plant ashes exceed the crustal average for the elements titanium, aluminum, and vanadium. For other elements, which are notably enriched in plant ashes, each of the 21 specimens shows concentrations which exceed the crustal abundance; these are Ag, P, Sr, B, Cu, Ba and Pb. These data indicate that a variation by a factor of ten, contrary to the opinion of Horton and Aubrey (9), may well be expected from similar plants collected at the same site.

ELEMENTS IN PEAT

Knowing that elements both essential and nonessential to plant nutrition may be present in the ash of plants in varying concentration the next logical step is to determine the range of elemental concentrations in peat ash of these and other elements not detected in the plant ash.

Spectrographic analyses of peat have been made by Mitchell (10) and by Salmi (11) but there is no treatment of analyses in the literature to show a genetic sequence as is presented in this paper.

The analyses of the ash of 13 one-foot samples of the peat are given in Figure 3. The differences in the composition of the peat ash are great, not only from consideration of the percentage of elements present, but from the relatively narrow range of concentration for some of the elements. For ease in comparing the range of concentration of elements in ash of peat to ash of coal flora as shown in Figure 1 the peat ash analyses are presented in the same order in a frequency distribution diagram in Figure 3.

The alkali and alkaline earth elements K, Ca, Mg, Na, Li, Ba and Sr, which are concentrated in plant ashes, are notably depleted in peat ashes. These elements are relatively soluble and are almost immediately lost from plant fluids during the early peat stage.

Manganese and iron, both essential to plant life, show striking differences in geochemical behavior. Compared to their relative concentration in plant ashes, iron is greatly enriched in peat while manganese is depleted. Under the reducing conditions prevalent in a peat swamp manganese is removed while iron is fixed as sulfides.

Zinc, another essential element, present in plant ashes well below the limit of detection by this analytical method, is highly concentrated in peat. Reclaimed peat soils in New York state⁽¹²⁾ have been found to contain concentration of zinc that are toxic for some crops. Probably zinc is lost from plant fluids in the early degradative stages and is fixed by humic acids. Zinc in solution in ground and surface waters would also be fixed in the peat in the same manner.

ELEMENTS PRESENT IN ASHES OF HUMIC ACID EXTRACTS FROM PEAT

The elements Fe, Cu, Mo, Zn, Pb, Cr, Ni, Co, and Sn are more highly concentrated in the humic acid fraction separated from peat than in the peat or any other fraction. The analyses of the ash of humic acid extracts are shown in Figure 4.

Niobium, bismuth, germanium and gold are found in the ash of humic acid fractions. These elements were not detected in plant ashes, in the whole peat ash nor in any other fraction separated from the peat. Tannic acid, a plant extract closely related to and probably included among these humic acids, has long been used to precipitate heavy metals in quantitative analysis. Niobium specifically is subject to precipitation by tannic acid, and, if found at all in an organic environment it is not unexpected that it be in the humic acid fraction.

Of perhaps more interest is the occurrence of germanium in the humic acid fraction. The electronic age has stimulated investigation of coal and flue dusts as possible commercial sources of germanium, but to this time no large readily concentrated sources have been found. It seems most likely that germanium can be concentrated in coal from solution so long as the humic acids have not been condensed or polymerized to the level that they are no longer reactive.

The geological environment of peat deposits is not to be ignored. The data in Figures 3 and 4 are not typical for boron. Boron is highly enriched in plants with respect to the crustal abundance. But the highly mafic rocks underlying these Duluth peats are probably deficient in boron--hence, the plants which formed this particular peat were also boron deficient. Reclaimed peat soils in Minnesota will not support good crop growth unless 50 pounds of borax per acre is added to the soil.

ELEMENTS IN MINERALS FOUND IN COAL

The contribution of detrital minerals to the trace element assemblage in the ash of whole coal is difficult to evaluate. The elements added are most likely the lithophile elements--Si, Al, Fe, Ti, Mg, K, Na, Mn, Ba, Sr and Zr. These elements are also present in large percentages in plant ash and in peat ash. As far as known no unweathered American coals have been fractionated to

separate and concentrate minerals with subsequent analysis of the mineral concentrate and the organic concentrate and then compared with the original coal to determine a mass balance. However, if such a mineral separation from coal were made and the relative concentration of the lithophile elements in the minerals compared to the coal substance, a better appreciation could be had of the importance of detrital minerals to the elemental distribution of ash of whole coal.

Pyrite, iron disulfide, is an important contributor of iron to coal ash. Some weathered lignites with little or no pyrite present, show high concentrations of "organic" iron--probably iron held in combination with reactive humic material.

Sodium chloride, or halite, is now recognized to be a not uncommon mineral in coals, especially in some English and American deposits. Coals, including some in which marine fossils are occasionally found, probably owe some of their sodium chloride content to catastrophic marine invasions, but not all the sodium chloride was necessarily derived from ocean water.

ELEMENTS COMBINED WITH ORGANIC MATTER DURING WEATHERING AND OXIDATION

Coal beds near the surface are subject to oxidation and weathering, especially in fractured strata. Alteration of pyrite is a first indication of this. Near surface coals are rarely free of gypsum formed by interaction of calcium ions in ground water with sulfate ions derived from oxidized sulfide. Oxides of iron will stain coal or may combine with sulfates to form jarosite, a yellow potassium iron sulfate or other sulfates. A simple calculation will show why the ash content rises in weathered coal.

Percolating surface and ground waters may carry elements in solution which will react with the coal substance to form unusual deposits of some trace elements. Recent studies^(13, 14) have shown that uranium and molybdenum are combined with organic matter in low rank coals during weathering and that iron and germanium may be added to coals during this stage as well.

Too few data are at hand for elements other than uranium but it is most likely that chemical reactivity of coal components is an important factor in controlling the amount of an element that can be held by coal. Schopf and Gray⁽¹⁵⁾ have shown that uranium in Dakota lignites is concentrated in those zones which are highest in translucent humic degradation matter--a highly reactive component.

Unless the geological and geochemical history of a coal is well known the elements combined with organic matter during the weathering stage will be difficult to detect because the changes during this stage may well be masked by reactions that proceeded in all previous stages. This fact notwithstanding, the addition of ash-forming elements during weathering and oxidation is always possible in near surface or fractured coals.

SUMMARY

The origins of ash-forming ingredients in coal have been traced from the living plant through to the weathering and oxidation of coal. Elements, rich in plant ashes and leached during degradation are K, Ca, Mg, Na, Li, Ba, and Sr. Elements concentrated in peat and derived in large part from original plants are zinc and boron. Manganese is lost from plants and rarely enriched in coal. The humic acids extracted from peat are enriched in Fe, Cu, Mo, Pb, Cr, Ni, Co, Sn and Zn. The elements Nb, Bi, Ge, and Au were not detected in plant ashes and in peat ashes but are found in the ash of humic acid fractions. Uranium, molybdenum, and perhaps iron and germanium are combined with organic matter in coal during weathering.

Minerals added to coal in the peat stage are the common sedimentary detrital clays. Pyrite is formed in the peat bog and during diagenesis. During weathering, pyrite oxidation forms abundant sulfates with a concomitant increase in ash content.

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PERCENTAGE RANGE OF ELEMENT IN ASH	%	K	Ca	Mg	P	Fe	Mn	B	Cu	Mo	Zn	Si	Al	Na	Ti	Ba	Sr	Pb	Li
> 10		17	9	3								11	4						
5-10		2	6	6								5	3	2					
1-5		2	6	10	8	2	2					4	5	16	1	1			
.5-1				2	8	3	3	7				1	1	3	3	8	2	2	
.1-5					5	15	4	7	2				6		3	8	17	3	
.05-1						1	4	7	15						9	4	2	8	17
.01-05							8		4				2		2			1	4
.005-.01										2					2			7	
.001-.005										8									
.0005-.001										2	21								
.0001-.0005										9									

Fig. 1a -- Concentration of elements in ash of 21 coal flora shown as a frequency distribution within percentage ranges.

PERCENTAGE RANGE OF ELEMENT IN ASH	%	As	Cr	Zr	V	Ni	Co	Sn	La	Nd	Ga	Y	Yb	Sc	Ag	Be
> 10																
5-10																
1-5																
.5-1																
.1-5		1														
.05-1		20	3	1	3	4		1	2	1						
.01-05			6	3		16		4	1	1	2					
.005-.01			12	7		1	12	7	15	19	7	7		3		
.001-.005				8	9		9	13			13	12	1	2	8	
.0005-.001				2	9								7	16	13	1
													13			20

Fig. 1b -- Concentration of elements in ash of 21 coal flora shown as a frequency distribution within percentage ranges.

Element	Crustal Abundance % or ppm	Median Concentration in Plant Ash % or ppm	Enriched or Depleted in plant ash compared to Crustal Abundance	
			<u>E</u>	<u>D</u>
K	2.6%	+10%	E	
Ca	3.6%	+ 5%	-	-
Mg	2.09%	5%	E	
P	0.12%	.5-1%	E	
Fe	5.0%	.1-.5%		D
Mn	0.1%	.1%	-	-
B	1 ppm	1000-5000 ppm	E	
Cu	70 ppm	500-1000 ppm	E	
Mo	1 ppm	10 ppm	E	
Zn	132 ppm	<80 ppm		D
Si	27.7%	10%		D
Al	8.1%	1%		D
Na	2.8%	3%	-	-
Ti	.44%	.05-.1%		D
Ba	250 ppm	5000 ppm	E	
Sr	300 ppm	1000-5000 ppm	E	
Pb	16 ppm	500 ppm	E	
Li	65 ppm	500-1000 ppm	E	
Cr	200 ppm	10-50 ppm		D
Zr	220 ppm	10 ppm		D
V	150 ppm	50 ppm		D
Ni	80 ppm	50-100 ppm	-	-
Co	23 ppm	10 ppm		D
Ag	0.1 ppm	1-5 ppm	E	

Figure 2. Crustal Abundance and Median Concentration of Some Elements Detected in Ash of Coal Flora and Relative Enrichment or Depletion of Elements Detected Compared to Crustal Abundance

%	K	Ca	Mg	P	Fe	Mn	B	Cu	Mo	Zn	Si	Al	Na	Ti	Ba	Sr	Pb	Li
> 10											10	13						
5-10		3			2						3							
1-5	13	8			6													
.5-1		2	4	4	5								6					
.1-5			8	6									7	13				
.05-1			1	3						2					11			
.01-05						2	11	7		8					2	13	1	13
.005-.01						11	2	6										
.001-.005									2	3								9
.0005-.001									9									3
.0001-.0005									2									

Fig. 3a -- Concentration of elements in ash of 13 peat samples shown as a frequency distribution within percentage ranges.

%	As	Cr	Zr	V	Ni	Co	Sn	La	Nd	Ga	Y	Yb	Sc	Ag	Be
> 10															
5-10															
1-5															
.5-1															
.1-5															
.05-1															
.01-05	13														
.005-.01		1	13	13			1			13					
.001-.005		12			13	3	2	4			13				
.0005-.001						7	3	9	13				13		
.0001-.0005						3	7					13			
.00005-.0001														1	
.00001-.00005														12	13

Fig. 3b -- Concentration of elements in ash of 13 peat samples shown as a frequency distribution within percentage ranges.

PERCENTAGE RANGE OF ELEMENT IN ASH	%																	
	K	Ca	Mg	P	Fe	Mn	B	Cu	Mo	Zn	Si	Al	Na	Ti	Ba	Sr	Pb	Li
>10											7	7	1					
5-10	1			1									1					
1-5	6			6	2								4					
.5-1				1	4								1	4				
.1-5		6	7					1		1				3			1	2
.05-1		1						6							4		1	
.01-05						4	5		1	1				3	1	2	2	5
.005-.01						3	2		6	4						6	2	
.001-.005										1								1

Fig. 4a -- Concentration of elements in ash of humic acid extracts from 7 peat samples shown as a frequency distribution within percentage ranges.

PERCENTAGE RANGE OF ELEMENT IN ASH	%																		
	As	Cr	Zr	V	Ni	Co	Sn	La	Nd	Ga	Y	Yb	Sc	Ag	Ba	Nb	Bi	Au	Ge
>10																			
5-10																			
1-5																			
.5-1																			
.1-5							5												
.05-1			3				1												
.01-05	3	6	4	2	3														
.005-.01	4	1		5	4	1	1	1		7	1					4			
.001-.005						5		5			6		7	2		1	2	1	6
.0005-.001						1		1	7			1		4		2	5	6	1
.0001-.0005											6			1					
.00005-.0001															2				
																5			

Fig. 4b -- Concentration of elements in ash of humic acid extracts from 7 peat samples shown as a frequency distribution within percentage ranges.

THE SEPARABILITY OF PYRITES PARTICLES IN
SOME PULVERIZED COALS

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Abstract

The manner of dispersion of pyrites particles in pulverized coal, and their separability from the carbonaceous matter was studied.

The pyrites content was determined in forty-one pulverized coal samples, and in the heavy fractions of these samples obtained in a density separation in a liquid medium. Two of these samples were segregated into sieving fractions. These fractions were also subjected to pyrites determinations and density separations.

More than one half of this group of samples was chosen from among high-sulfur-content coals.

Values for the removal in the heavy fraction of pyrites, ash and combustible matter, are tabulated.

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The Separability of Pyrites Particles in
Some Pulverized Coals

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Introduction

This work was undertaken as a part of a program to study the mineral matter in commercially pulverized coal. Reasons for gathering information about the minerals in coal are questions concerning corrosion in boilers, the formation and manner of deposition of slag in boilers, the combustion properties of coal particles, the composition and properties of fly ash, and related problems.

A commonly occurring coal mineral of considerable interest is pyrites.* This mineral is usually present in lump coal in the form of discreet particles or thin bands, as inspection of polished faces will reveal^{1) 5)}. Occasionally, the pyrites will be found in forms that exceed millimeter or even centimeter size.

The purpose of this investigation was to gather data from which conclusions could be drawn about the manner of dispersion of pyrites in pulverized coal, and about the limiting values for the physical separability of pyrites from the carbonaceous matter. Literature search did not yield such information.

Two pulverized coals were studied in detail. In sieving fractions, as well as in the whole coal powder, pyrites content was determined. The pulverized coals and their sieving fractions were also subjected to density separations in a liquid medium. Subsequently, a group of coals consisting of thirty-nine samples, including twenty-two high-sulfur-content coals from several states, was studied. Density separations and pyrites determinations were made in order to obtain data for the calculation of the percentage of the pyrites removed from each sample in the heavy fraction. In many cases ash determinations were made as well. This led to the calculation of the percentages of ash and combustible matter that were removed in the heavy fraction during the density separation.

Experimental

Method D 197-30, of the American Society for Testing Materials²⁾, was used to obtain sieving fractions from the pulverized coals. Fractions <325 mesh, not mentioned in this procedure, were also prepared.

All density separations were done with a mixture of carbon tetrachloride and xylene, having a density of 1.450 g/ml. This density was chosen after it was found that at lower densities appreciable quantities of light organic particles will fail to be separated from the heavy, partly or wholly inorganic particles that are removed in the sink fraction. Somewhat higher densities did not influence to a great extent the percentage of a powdered coal sample that would sink.

* The word "pyrites" in this work is intended as a term of reference meaning iron disulfide in the form of pyrite or marcasite.

The fluid mixture used was chosen because sharp separations were more readily obtainable in it than in other mixtures that were tried.

The separations were made with samples of 5 grams of pulverized coal, in 500 ml stoppered conical separating funnels. These pyrex funnels had a generating angle of nearly 17°. After introducing the powder into the funnel, 250 ml of density fluid were added, the funnel stoppered and well shaken, and finally clamped in a vertical position. After one hour the contents were carefully shaken in such a manner that the upper part of the vessel would be well wetted, the floating fraction thoroughly disturbed, but the heavy fraction left essentially undisturbed. After one more hour, this procedure was repeated; the funnel was then left untouched until a clear separation had come about. The first 50 ml of fluid and sediment were drawn off at the bottom and filtered; the weight of the sediment was obtained after drying to constant weight at 100°C. The float fractions were similarly reclaimed quantitatively.

Pyrites determinations were made according to a modification⁶⁾ of a method described by Mott⁴⁾. Ash was determined by the method of ASTM D 271-48³⁾. Pyrites and ash were determined in samples before a density separation had been made, and in the float fraction after such a separation. The pyrites content and ash content of the sink fractions could then be calculated. (Recovery of the sink fractions from the filter paper for direct determination of these quantities, would have been unsatisfactory because of the small amounts involved.)

In the tabulation of data, "sink loss" represents the percentage of the dry powdered coal that sinks in the density fluid. "Pyrites removal", "ash removal" and "combustible loss" express the percentages of the original pyrites, ash and combustible contents respectively, that are found in the heavy fraction of the density separation.

Description of Samples

Samples from a number of different mines were used. They may be arranged in two groups. The first group, tabulated below, consists of bituminous coals from Pennsylvania and West Virginia. If more than one sample from a mine was used, this is indicated by the number following the name of the mine.

TABLE I
First Group of Coal Samples Examined

No.	Name of Mine	State of Origin	General Classification
1	Williams (2)	West Virginia	Fairmont
2	Rich Hill (2)	Pennsylvania	District No. 1
3	Arkwright	West Virginia	Fairmont
4	Purseglove	West Virginia	Fairmont
5	Rosedale	West Virginia	Fairmont
6	Indian Creek (2)	Pennsylvania	District No. 1
7	Kano	West Virginia	Fairmont
8	Badger	West Virginia	Fairmont
9	Compass	West Virginia	Fairmont
10	Lynn	West Virginia	Fairmont
11	Diamond	Pennsylvania	District No. 1
12	Clymer	Pennsylvania	District No. 1
13	Ebensburg	Pennsylvania	District No. 1
14-16	Composite Samples (3)	-	Run of Mill

The samples of this group were all ground in the same commercial mill. It is probably impossible to obtain powders with the same particle size distribution from different coals, even if the factors that influence the operation of the mill, insofar as they do not stem from the coal, could be kept constant. Furthermore, the properties of the various coals differ widely (grindability, hardness).

Of this group, an average of about 90% of a sample passes a 100-mesh sieve, and nearly 60% passes a 200-mesh sieve.

The second group of samples, identified in Table VI by their states of origin, was a selection of high-sulfur-content coal samples supplied by the U. S. Bureau of Mines.* This group of samples was ground in a laboratory type mill. An average of about 88% of a sample passes a 100-mesh sieve, and about 82% passes a 200-mesh sieve.

Data and Discussion

All experimental data presented are averages of at least two replicate determinations; derived data are based on these averages.

TABLE II

Particle Size Distribution, Percent of Whole Coal Powder

Fraction	Williams	Rich Hill
<325 mesh	36.45	44.30
325-200 "	23.65	24.70
200-100 "	27.95	22.90
100-50 "	11.00	7.13
50-30 "	1.50	.86
30-16 "	.12	.03

TABLE III

Pyrites Percentage in Whole Coal, Sieving Fractions and in Float and Sink Fractions of These Sieving Fractions

Sieving Fraction	Williams Whole Coal: 1.65			Rich Hill Whole Coal: 1.78		
	Whole Fraction	Floats	Sinks	Whole Fraction	Floats	Sinks
<325 mesh	.88	.39	25.2	1.59	.52	24.7
200-325 "	1.80	.29	27.0	1.95	.14	15.5
100-200 "	2.26	.31	27.7	2.60	.13	14.6
50-100 "	2.38	.31	46.6	3.37	.22	40.5

Pyrites content of the sink fractions of the sieving fractions varied from 14.6% to 46.6% (Table III). With the exception of the finest fraction, at least 84.8% of the pyrites of each fraction was found in the corresponding sink fraction (Table IV).

* Through the courtesy of Mr. R. F. Abernathy and Mr. J. J. Barnes, Central Experiment Station, Region V, U. S. Bureau of Mines, Pittsburgh, Pa.

TABLE IV

Heavy Fractions Data

Fraction	Heavy fraction as % of corresponding sieving fraction.		Percentage of pyrites in a sieving fraction removed in sink fraction.	
	Williams	Rich Hill	Williams	Rich Hill
< 325 mesh	1.96	4.47	56.5	68.5
200-325 "	5.67	11.30	84.3	93.7
100-200 "	7.00	16.35	87.3	94.2
50-100 "	7.50	20.70	87.9	94.8

This suggests that a large part of the pyrites in these two powdered coals was present in a comparatively unencumbered state, and that a relatively small part of the total weight of the pyrites was located inside of coal particles or attached to relatively large coal particles. This was borne out by a microscopic inspection of the sink fractions. To this purpose samples of these heavy fractions were embedded in blocks of lucite, which were then ground and polished. Few pyrites particles, >325 mesh, were attached to carbonaceous particles. None were found attached to other inorganic materials.

Computation shows that the sum of the amounts of pyrites that settle in the heavy fractions is in excess of 80% of the pyrites content of the original sample. A density separation removes 86.9% of the pyrites from Williams whole powder, and 90.8% of the pyrites from Rich Hill whole powder.

No reason was found to extend this detailed work to other pulverized coals. However, the separability of the pyrites from other whole coal samples was determined by the density separation method mentioned. The data obtained in these separations, as well as the results of pyrites and ash determinations, and derived data, are given in Tables V and VI. The range of the different removal and loss percentages achieved with these forty-one coal samples at a density level of 1.450, is apparent from the data presented in these tables. Pyrites and ash are in part removed in the sink fraction; this heavy fraction varies from 3.85% to 21.63% of the weight of the original sample. Thirty-two samples had a sink loss of less than 10%.

The percentage of the pyrites that is removed, expressed on the basis of the original pyritic sulfur content, varies from 47% to 91%.

Ash removal percentages vary from 27% to 46%.

Combustible losses in the sink fraction range from 2.6% to 17.4%.

Hardgrove grindability numbers have been tabulated when available. These values, and information of geographic nature have only been given for the better identification of the coals.

The various loss and removal data stem from one separation operation. If the sink fraction is subjected to an additional density separation in a fluid of the same density as previously used, a part of the combustible matter can be reclaimed. This was not systematically investigated. In two cases (samples 1 and 2) the combustible loss could thus be decreased by .7%, however. In these two cases, the limit of separability by physical means, had been approached in one density separation.

It is not likely that many of the samples studied are truly representative

for a coal seam or a mine. The varying conditions under which coal has been formed have caused an infinite number of different results. This makes it difficult wholly to represent the coal of even one bed by a group of samples as limited in number as the group that was studied. In view of the great variety in origin and type of coal in this group of samples, a discussion of averages of results and of correlation data is therefore omitted.

Conclusions

1) Pyrites particles in commercially pulverized coal are largely present as free particles, or as particles that are relatively unencumbered by carbonaceous or other inorganic matter. This is also true for coal pulverized to a somewhat greater degree in a laboratory type mill.

2) Part of the pyrites can be segregated from the pulverized coal by a density fluid. Forty-one samples were studied. At a density level of 1.450, the percentage of pyrites removed varied from 47% to 91%. At the same time, the ash content of the powder was decreased by an amount varying from 27% to 46%. This was accompanied by a loss of combustible matter, ranging from 2.6% to 17.4%.

TABLE V
Results of Density Separations, Ash and Pyrites Determinations; Removal Values and Grindability Data
(First Group of Coals)

Sample Number	Sinks, % of Coal	Pyrites in Whole Coal, %	Pyrites in Floats, %	Pyrites Removal, %	Ash in Whole Coal, %	Ash in Floats, %	Ash Removal, %	Combustible loss, %	Hardgrove grindability
1	5.74	1.65	.22	87	-	-	-	-	61
1a	5.99	3.20	.52	85	8.54	4.97	42	2.6	65
2	9.98	1.78	.17	91	-	-	-	-	98
2a	10.18	1.98	.22	87	10.33	6.85	34	7.5	98
3	7.24	1.59	.45	72	-	-	-	-	67
4	7.07	1.50	.60	61	-	-	-	-	70
5	7.49	1.95	.47	76	-	-	-	-	75
6	11.88	2.56	.21	93	-	-	-	-	97
6a	10.54	2.08	.24	87	9.43	5.71	40	7.5	100
7	4.23	1.03	.30	70	-	-	-	-	67
8	5.45	1.20	.39	70	-	-	-	-	-
9	4.98	2.55	.51	80	6.68	4.38	34	2.9	63
10	5.81	2.51	.49	80	7.07	4.85	31	3.9	77
11	8.45	3.73	.84	77	8.66	5.10	41	5.4	115
12	9.72	2.32	.64	73	11.08	6.69	40	6.0	104
13	6.35	1.70	.43	75	6.05	4.66	23	5.3	112
14	6.10	2.58	.43	85	7.30	4.99	32	4.1	-
15	5.84	2.40	.47	80	7.48	5.03	33	3.7	-
16	6.93	3.01	.49	84	8.20	4.90	41	4.0	-
Column Averages	7.36	2.20	.43	80	8.26	5.28	35	4.0	-

TABLE VI
Results of Density Separations, Ash and Pyrites Determinations; Removal Values
(High-sulfur-content Coals)

Sample Number	State of Origin	Sinks, % of Coal	Pyrites in Whole Coal, %	Pyrites in Floats, %	Pyrites Removal, %	Ash in Whole Coal, %	Ash in Floats, %	Ash Removal, %	Combustible loss, %
20	Illinois	8.15	2.32	1.10	52	7.98	4.89	29	5.8
21	"	8.05	2.04	.67	67	7.57	5.17	28	6.4
22	"	9.98	3.26	1.05	68	8.93	5.88	31	7.7
23	"	9.91	2.68	.97	64	9.86	6.23	37	7.0
24	"	8.90	2.51	.97	61	9.32	6.23	33	6.4
25	"	9.24	2.51	.90	64	9.74	6.73	31	6.9
26	Kentucky	5.15	2.02	.22	55	6.53	4.48	31	2.6
27	"	7.44	2.23	.22	59	8.00	4.49	16	4.3
28	"	3.85	2.04	.99	51	5.26	3.03	27	2.6
29	"	7.73	2.36	1.05	56	7.87	5.07	36	5.4
30	Ohio	6.92	2.56	1.35	47	7.82	5.27	32	4.6
31	"	7.80	3.03	1.01	67	7.88	5.63	29	4.9
32	"	21.68	9.62	3.24	66	12.07	5.69	53	17.4
33	"	17.27	7.82	3.00	61	9.71	5.91	39	14.5
34	"	12.35	5.20	2.15	59	7.56	4.58	39	10.3
35	"	11.53	6.40	2.36	63	9.09	5.00	15	10.4
36	W. Virginia	7.88	3.11	.67	80	9.08	5.91	35	5.2
37	"	6.94	3.18	.62	81	8.51	5.44	36	4.3
38	"	12.40	4.83	.79	72	12.28	6.79	15	7.9
39	"	10.36	2.36	.60	75	10.73	7.49	30	8.0
40	Kansas	8.24	3.28	1.46	55	10.49	6.08	42	4.2
41	"	7.59	3.07	1.39	55	9.56	5.66	41	4.1
Column Averages		9.53	3.58	.96	63	8.90	5.58	37	6.9

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A MODIFICATION OF MOTT'S METHOD
FOR THE DETERMINATION OF PYRITIC SULFUR IN COAL

by

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Abstract

Mott's method, involving two simultaneous acid extractions of powdered coal samples, has been simplified to a labor saving non-simultaneous extraction procedure, applicable in cases where only pyritic sulfur has to be determined.

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Introduction

Mott⁽²⁾ developed a procedure for the determination of sulfate and pyritic sulfur in coal, that is referred to in the literature as the British Coke Research Association method. It differs from the Powell and Parr⁽⁴⁾ method in that the extractions take place with dilute boiling acids during one half hour, instead of at room temperature, or at 60°C, for periods up to forty hours. Mott's method is recommended by Edwards, Daybell and Pringle⁽¹⁾ when the highest accuracy is required. A short description follows.

Five grams of coal, ground to pass a No. 70 sieve, are boiled for one half hour with 50 ml of 5 N HCl in a 500 ml conical flask provided with a reflux condenser. The coal residue is then filtered off and washed. In the combined filtrate and washings, iron and, if desired, the sulfate sulfur are determined.

One gram of the same coal powder is boiled for one half hour with 50 ml of 2 N HNO₃ in the manner indicated above. After filtering and washing the residue, iron is determined in the combined filtrate and washings. The percentage iron found by hydrochloric acid extraction (Fe') is subtracted from the percentage found by nitric acid digestion (Fe''). The former is non-pyritic in origin, while the latter is pyritic as well as non-pyritic. The concentration of pyritic sulfur is calculated from the proportion, $S = 1.148(Fe'' - Fe')$.

In case it is not necessary or essential to determine sulfate, but only pyritic sulfur, a simplification resulting in the saving of work, can be applied.

It is proposed that, in contrast to the B.C.R.A. or "simultaneous" method, a "non-simultaneous" procedure be followed. The coal is extracted with HCl, filtered and washed. The extract is discarded. The residue is quantitatively transferred to the nitric acid, extracted, filtered and washed. The iron in the combined filtrate and washings is determined; it is solely of pyritic origin. The pyritic sulfur is then calculated from the proportion, $S = 1.148 Fe$.

Both methods were applied to a series of samples of bituminous coals from Pennsylvania and West Virginia.

Experimental

Determinations of pyritic sulfur were made in all samples by the B.C.R.A. method. These were followed by determinations made by the modified method according to the following detailed description.

One gram of coal, powdered to pass a No. 70 sieve (American Society for Testing Materials, E 11-39) is boiled for one half hour in a 500 ml conical flask with 50 ml of 5 N HCl. The flask is provided with a reflux condenser.*

The coal is filtered off and washed with dilute HCl (1:20) until the filtrate is free of iron (test with KONS), then a few times with distilled water. The filtrate is discarded.** Filter paper and residue are then transferred to a 500 ml conical flask and boiled for one half hour with 50 ml of 2 N HNO₃ in the manner indicated above. The contents of the flask are filtered and repeatedly washed with 2 N HNO₃. The iron in the combined filtrate and washings is determined in one of the usual ways. The procedure used in this work, a titration of Fe⁺⁺ with Ce⁺⁺⁺, is given in detail in standard texts(2,5).

Table I gives data obtained with Mott's method (Column A), and with the proposed modification (Column B), for the pyritic sulfur contents, for twelve samples of pulverized coal.

TABLE I

Pyritic Sulfur Content, Percent of Coal

Coal	A	B
	E.C.R.A. Method	Modified Method
1	.94	.97
2	1.22	1.22
3	.81	.81
4	.95	1.02
5	.65	.63
6	2.23	2.33
7	.86	.87
8	.26	.27
9	.91	.93
10	1.53	1.46
11	.94	.94
12	.88	.87

Discussion of Results

It was found that it was difficult in some cases (particularly in the case of coals with a high pyritic sulfur content) to prepare duplicate samples. Very careful mixing of the samples of powdered coals resulted in the values tabulated. It is likely that the cause of erroneous results was in the inhomogeneous distribution of the larger pyrite particles in the ground coal. It has been shown that these particles are present associated with only a small amount of organic matter(6). Since they are considerably denser than the organic material in coal, it seems quite possible that pyrite particles may become locally concentrated in the grinding process and during transport and subsequent handling. The often considerable inhomogeneity of coal in its natural state is an additional potential source of sampling difficulties.

* The use of rubber stoppers (a potential source of sulfur) in acid extraction apparatus is permissible, because only iron is determined.

** No attempt to determine sulfate in this filtrate should be made since only one gram of coal was used. A five gram sample, as recommended by Mott(2) for sulphate sulfur determinations, is advisable.

The tabulated results are averages of duplicate determinations. An additional ninety-six pairs of duplicate determinations of pyritic sulfur were made by the modified method, using samples of coal from as many different sources. These data are not presented, however, they were used in the statistical calculations.

The standard deviation of the differences between duplicate pairs of determinations was found to be equal to $\pm .087\%$ pyr. S for Mott's method (based on twelve sets of data), and equal to $\pm .054\%$ pyr. S for the modified method (based on ninety-six sets of data).

In the case of Mott's method, the expected uncertainty in the mean of a pair of duplicate determinations, will not exceed $\pm .192\%$ pyr. S in 95% of all cases. At the same confidence level, the expected uncertainty in the mean of a pair of duplicate determinations will not exceed $\pm .106\%$ pyr. S for the modified method. On the basis of these calculated values, it may be concluded that the modified method affords greater precision than Mott's method. The modified method is simpler (readings and observations are reduced to 50% of the number necessary for Mott's method). This may in part account for the greater precision of the modified method.

Application of Student's t test to the data in Table I shows that there is no significant difference between the mean values obtained for the series of twelve samples by the two methods. Therefore, it may be concluded that there is no significant systematic difference between the two methods.

Conclusion

A modification of Mott's method for the determination of pyritic sulfur in coal was developed. This modification is labor saving. Statistical treatment of data obtained on a series of coal samples, using both methods, shows that the modified method compares favorably with the existing method.

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EFFECT OF HYDROGEN SULFIDE ON THE SULFUR CONTENT OF BITUMINOUS COKE
AT 800 TO 1000°C.

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ABSTRACT

Three samples of coke were reacted with two different concentrations of hydrogen sulfide at 800, 900 and 1000°C. for two hours each. The samples represented a bulk sample prepared from a High Volatile A coal in a small laboratory oven at 1100°C. wall temperature. Reduction of the bulk coke to minus 10 mesh and screening gave sample A, 10 x 60 mesh, and sample C, minus 60 mesh. An aliquot of sample A ground to minus 60 mesh produced sample B. Based on the grinding properties and color, coke C was assumed to be less carbonized than coke A.

Increases in sulfur content reached a maximum at about 900°C. with each sample. Organic sulfur is chiefly responsible for the increase. Coke C was most reactive and coke A least. These differences indicate that the reaction begins below 800°C. and that the degree of reactivity is influenced by the nature of the carbon and its ultrafine structure.

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INTRODUCTION

Hydrogen sulfide is the predominating sulfur-bearing component of bituminous coal gas in the byproduct coke oven process. It usually amounts to over 95% of the sulfur in the crude gas at a concentration range of 0.3 to 3.0 volume per cent, which depends largely on the amount of sulfur in the coal. However, most commercial coal gas contains about 0.6 volume per cent (1). From coke oven and gas retort operations, analyses show that 25 to 30% of the coal sulfur is liberated as hydrogen sulfide (2). The analyses also show that 50 to 60% and sometimes higher, of the coal sulfur is retained in the coke.

The evolution of hydrogen sulfide and other sulfur compounds from coal begins at about 250°C. The reactions which produce these volatiles are largely completed in the range of 500 to 800°C (3). Both the organic and inorganic, mostly pyritic, forms of sulfur, which constitute over 90% of the sulfur in most coking coals, form hydrogen sulfide (4). The sulfate form, which exists only in small quantities, is reduced to the sulfide form in the coking process. The amount of hydrogen sulfide liberated ranges from about 25 to 50% of the organic sulfur in the coal. Pyrite decomposes completely at 600°C. in coal to produce hydrogen sulfide, ferrous sulfide, and pyrrhotite (4). Its decomposition is favored at the temperatures existing in coke ovens, wherein hydrogen and methane are the main components of the coal gas (5).

The reactions occurring in coke ovens are complex, since the primary products evolved from the plastic zone suffer secondary decomposition during their travel of contact with incandescent coke and hot oven walls. Secondary reactions appear to be the most important factor influencing the total amount and concentration of the sulfurous volatiles regardless of the parent sulfur forms in the coal. Moreover, the nature of mineral matter in coal may also be an important factor in affecting the amount and types of sulfurous volatiles liberated (6).

The most marked change determined directly by chemical means occurs with pyrite. The organic form in both coal and coke is obtained by difference. Its form in coke is in stable complex combination with carbon atoms originating partly from the organic form of the parent coal and partly from the sulfur liberated by the decomposition of pyrite and adsorbed during carbonization (4,7). The nature of the stable complex formed by reaction of sulfur produced from decomposition of pyrite with coke was described as analogous to the carbon-surface oxide complex of coal (8).

The constitution of this complex is unknown (7). The organic sulfur in coal partly forms complexes with carbon in the range of 400° to 500°C. which do not exhibit the properties of the original form in coal (4). In coke, the complex was described as a solid solution of carbon and sulfur which includes adsorbed free sulfur (9). X-ray analyses indicated that the solution characterizes a

mixed crystal system in which it is believed a sulfur atom replaces a carbon atom within the graphite-like crystal lattice (10,11,12). The organic sulfur in coke was also considered to exist partly as a solution or as physically held by adsorption and the remainder as chemical combination which compounds were impossible to isolate (13).

Conclusive evidence of the existence of similar complexes has been established in sulfurous carbons formed by interaction of carbons with hydrogen sulfide, sulfur dioxide, sulfur and other sulfurous gases (7,8). Among these the effect of coal ash constituents, iron oxide and silica, on the fixation of sulfur in filter paper char interacted with hydrogen sulfide at 700°C. was investigated (8). Upon heating of the chars to 1200°C, the presence of iron has apparently caused a marked retention of sulfur while silica exhibited very little or no retention. Above this temperature the carbon-sulfur complex interacts with both the iron sulfide formed at lower temperatures and the silica with a consequent loss of sulfur. Similar retention of sulfur in coke was also observed when pyrite, ferrous oxide, metallic iron and other chemicals, which produce stable sulfides, were added to the coal before carbonization (4,14,15). The retention appears attributable to the fact that the affinity of iron for sulfur is greater than that of hydrogen for sulfur at the temperature existing in the coke oven (7). Ferrous sulfide is the chief stable sulfurous compound of coke, and any iron formed by its reduction in the coke oven will generally tend to revert to the sulfide in the presence of hydrogen sulfide (7).

Although no quantitative data are recorded, hydrogen sulfide is recognized to react with hot coke to form the carbon-sulfur complex (7,15,16). When heated alone, hydrogen sulfide decomposes into hydrogen and diatomic sulfur above 650°C. (17). Based on this, it appears that elemental sulfur is very likely an intermediate in the formation of the carbon-sulfur complex in coke. This complex together with the residual organic sulfur of the raw coal and that from reduction of ferrous sulfide constitute the total organic sulfur in coke. In the by-product coke oven process, hydrogen sulfide comes into contact with hot coke during its escape from the plastic state of the coal. Consequently, its reaction with coke may take place at various temperatures.

This investigation is concerned with the interaction of hydrogen sulfide and high-temperature coke in the temperature range of 800° to 1000°C. The purpose is to determine its effect on the sulfur content and on the distribution of sulfur forms of coke at these temperatures.

PREPARATION AND ANALYSES OF COKE SAMPLES

Carbonization of the Coal. The bituminous coal employed to prepare the coke samples was of High Volatile A Rank from the Elkhorn No. 3 seam in Letcher County, Kentucky. It was ground to minus 10 mesh (U.S. Standard) for carbonization. Its proximate analysis was 1.0% moisture, 36.2% volatile matter, 2.6% ash, and 60.2% fixed carbon.

The coal was coked in a small laboratory movable-wall oven equipped with a calibrated ring dynamometer and Baldwin-Lima strain gauge analyzer for measuring carbonization pressure (18). A seven-pound sample of bulk density 40.4 lbs./cu.ft. was coked in 80 minutes with the oven walls heated electrically at 1100°C. The maximum force obtained was 58 lbs. which is equivalent to about 1 lb./sq.in. of the Russell oven (19). A yield of 4.4 pounds of coke was obtained.

Samples of Coke Prepared. The coke was reduced to minus 10-mesh (U.S. Standard) by successively passing it through a jaw crusher and Braun pulverizer. A 200-g. riffled sample was then further reduced to minus 60 mesh (U.S. Standard) in a Mikro-Mill pulverizer for analysis. Screening of the remaining minus 10-mesh sample produced 47% of minus 60-mesh size. This procedure allowed the separation of coke into different fractions based on their grindability characteristics. It was assumed that these fines contained more of the coke that was produced in the central portion of the coke oven charge. The fines appeared blacker in color, softer to the touch and less carbonized than the 10 x 60 portion adjacent to the coke oven walls.

The remaining 53% (10 x 60 mesh) was divided and about half was ground to minus 60 mesh. This gave two samples of the harder fraction of different mean particle size. Table I indicates the degree of carbonization of the coke according to the

dry, ash-free volatile matter content. Coke C, the softer minus 60-mesh fraction, contained 2.8% volatile matter whereas cokes A and B, representing the harder fraction of the original minus-10 sample, contained 2.0% volatile matter.

Chemical Analyses. A.S.T.M. Standard procedures for proximate analysis and total sulfur by the Eschka method were employed for the coal and coke samples (20). In the Eschka method, the sulfur is oxidized to the sulfate form and the amount of sulfur is finally calculated from the quantity of barium sulfate determined.

The pyritic form of sulfur was determined by oxidation during extraction to the sulfate form with dilute nitric acid (4). The sulfate in the final purified solution, free of iron, is converted to barium sulfate from which the pyritic sulfur is calculated. The determination of the sulfate form was made by using dilute hydrochloric acid and barium chloride to precipitate the sulfate (4). It is to be noted that the coal under study did not contain any sulfate sulfur.

Acid-volatilized inorganic sulfur was determined because hydrogen sulfide was detected during analysis of a number of cokes for pyrite (4). Previous workers also observed this and attributed this reaction to the presence of sulfides of calcium, et cetera (4,15,22). Its determination was carried out in a closed system by treating 2 g. of coal or coke with 100 ml. of dilute nitric acid, 1.3, from a dropping funnel. The hydrogen sulfide liberated was swept by air for an hour into an ammoniacal solution of cadmium chloride contained in two flasks. The solution was prepared by dissolving 3.2 g. of anhydrous cadmium chloride in 100 ml. of distilled water and adding 60 ml. of concentrated ammonium hydroxide to this solution. The yield of cadmium sulfide is determined and the percentage sulfur is accordingly calculated. The organic form of sulfur was determined by difference between the sum of the inorganic forms and the total sulfur content. The analyses of the coal and coke samples are presented in Table I.

Screen Analysis of Coke Samples. The size distribution data for cokes A, B and C are shown in Table 2. The data confirm the viewpoint on the grindability characteristics of the bulk coke sample in its reduction to minus 10 mesh. The harder and the softer coke data were calculated using the method of Hatch and Choate (23), and these data are shown on log-probability paper in Figure 1 for convenience.

The slope of the straight line portion of this curve is an indication of the ease of grinding. That is, the greater the slope, the harder it is to grind the sample. The departure from the straight line in the upper portion of the curve is caused by the limitation of the data and the deviation from the theory. This is obtained by omitting the upper limit of 10 mesh in the theory. Because of fluidization by air during grinding and sieving, the data deviate from the straight line in the lower portion of the curve in the fine particle size region. This is illustrated by the dotted line marked "theoretical" in Figure 1. The lower deviation cannot be caused by a build up of mineral matter in the fines, since there may be a slight reverse tendency as indicated by the ash values on Table 1. This might mean that the coke-mineral matter combination is slightly harder than the coke which contains less firmly bonded mineral matter.

The properties of coke vary principally because of the temperature gradient that exists during carbonization. Its non-uniformity in color and strength has been recognized (24,25). The strength of coke on grinding was found to increase with the temperature of formation of coke as opposed to a decrease in shatter index of the same coal (26). Flotation of ground coke into various fractions has shown that the black part of coke (sink fraction) contained more volatile matter and ash than the more carbonized part (float fraction) (27). The analysis of the coke samples in Table 1 and the different slopes of the straight line portion of the sieve analysis data in Figure 1 show evidence of the unhomogenous nature of coke.

APPARATUS AND PROCEDURE

The apparatus is schematically represented in Figure 2. The numbers refer to the corresponding numbers in Table 3 which includes a detailed design and specifications of the apparatus. The purity of the gases is also shown in Table 3. The simple design allowed a metered stream of hydrogen sulfide diluted with nitrogen. The gas

mixture was preheated before it made contact with a vertical fixed bed of coke which was maintained at the temperature of the run.

A 45-g. coke sample was introduced into the reactor through a funnel at the top and allowed to drop on to the support screen. The delivery and condenser system was then connected to the reactor. Nitrogen gas at a constant rate of 0.3 cu. ft./hr. purged the entrapped air. The reactor and the preheater were regulated to the run temperature. This required about 20 minutes. The hydrogen sulfide supply was adjusted to the desired rate, and the reaction with the hot coke proceeded for two hours. At the end of the run, after cutting off the supply of hydrogen sulfide, cold nitrogen was used to return the coke to room temperature.

The reactions were carried out with two different concentrations of hydrogen sulfide, 0.013 cu. ft./hr or mol concentration of 4.2% and 0.029 cu.ft./hr or mol concentration of 8.8% using nitrogen as carrier gas. The results of the reactions with cokes A, B and C at 800, 900, and 1000°C. are shown in Table 4.

DISCUSSION OF RESULTS

The analyses of the coal given in Tables 1 and 2 show 0.70% sulfur and 2.6% ash. The sulfur is 91.4% organic and 8.6% pyritic in nature. The relatively small amounts of sulfur, mineral matter and pyrite permitted the study of the reaction of hydrogen sulfide and coke, which factors would have less effect on the reactions contributing to the sulfur content of the coke. The bulk coke data indicate that almost 50% of the coal sulfur was liberated during carbonization. This agrees with in the range of values reported by other workers (2). Assuming that up to half of the pyritic sulfur contributed to the organic sulfur of coke, calculations show that the percentage of the organic sulfur liberated ranges from about 49.5 to 50. It has been reported that the amount of organic sulfur released ranges from 25 to 50% (4). No distinction in the organic sulfur content was found between the cokes A, B, and C, but these differ with the bulk sample, probably due to experimental errors.

The percentages of inorganic forms of sulfur in the cokes given in Table 1 indicate that sulfides of calcium and of other cations have been formed as based on evolution of hydrogen sulfide under acid conditions. The formation of sulfides has been reported by other workers (4,15,22). The differences in the inorganic forms in cokes A, B, and C indicate that acid volatile sulfur and pyrite decomposition are favored at more severe carbonizing conditions. However, these differences are very close to the limits of the experimental error inherent in the analysis.

The effect of the reaction of hydrogen sulfide on the sulfur content of the coke samples is shown in Figure 3. In each case the sulfur increased, but the increase varied with the concentration of hydrogen sulfide, the reaction temperature and the nature of the coke. Greater increases in sulfur occurred with the higher concentration of hydrogen sulfide, which amount reached a maximum at about 900°C. At the lower concentration optimum reactivity appeared slightly below this temperature, indicating the probable effect of concentration on the equilibrium conditions. The results indicate that the carbon-sulfur complex becomes less stable above this temperature. Ferrous sulfide and other sulfides are more stable at these temperatures (4,7).

Coke C, being the softer portion of the bulk sample, was more reactive than the harder cokes A and B. Coke A, 10 x 60 mesh, was less reactive than its counterpart Coke B, minus 60 mesh, indicating that surface area probably influences the reaction. The greater reactivity of Coke C, minus 60 mesh, over that of Coke B shows the possible effect of carbonizing conditions in the oven. These differences suggest that the reaction begins and proceeds more effectively with coke produced at some lower temperatures than that at the coke oven walls. The nature and the stability of the carbon-sulfur complex, the porosity, size and the nature of the coke as well as the mineral matter may influence the degree of the reaction and the amount of sulfur retained. These could account for the variations indicated in Figure 2.

The influence of hydrogen sulfide on the sulfur forms is given in Figures 4 and 5. In view of the scattering of the data and of the limits of experimental

error, it is apparent that concentration of hydrogen sulfide and temperature had no marked influence on the quantity of inorganic sulfur. For the most part, the amount of this sulfur was greater than that in the original coke samples because the total sulfur was higher in the reacted samples. Pyrite, being the only inorganic sulfur constituent in the coal, was probably decomposed to form ferrous sulfide under the conditions studied. The increased amount of inorganic sulfur, determined as acid extracted and volatile sulfur, points to the formation of sulfides with calcium and other cations.

Again coke C was more reactive than the harder cokes A and B as indicated by their difference in extracted sulfur content given in Table 4. Its content in coke C was highest at all reaction temperatures and concentration of hydrogen sulfide. The results suggest that the reaction is favored at lower carbonization temperatures. Under such conditions the mineral matter is probably less firmly bonded to the more porous coke which would account for the higher reactivity of coke C. Coke A was least reactive which implies that particle size and porosity are factors affecting the reactions.

The increase in total sulfur is chiefly paralleled by the increase of organic sulfur as illustrated in Figures 3 and 5. Optimum reactivity appeared around 900°C. whereat the higher concentration of hydrogen sulfide was more reactive. Table 4 shows that maximum increase of organic sulfur was about 3.4-fold while that of total sulfur was around 3.6-fold. This experimental evidence supports the view of various workers that hydrogen sulfide contributes to the organic sulfur of coke during the carbonization process (4,7,15,16,25).

The reaction of hydrogen sulfide with hot coke was deemed to involve the formation of a carbon-sulfur complex on the surface of the carbon (1). After the complex reached a sufficient concentration, the sulfur was evolved as carbon disulfide. It is generally recognized that carbon disulfide is produced at higher temperatures of carbonization (28). The decrease in organic sulfur of the coke samples at 1000°C. in this study is explained on this basis.

Hydrogen sulfide has been found to decompose homogeneously to give hydrogen and sulfur (S_2) at 650°C. (17). Although its decomposition temperature during carbonization is unknown, it no doubt decomposes at temperatures below that at the coke oven walls. Sulfur is known to exist as polyatomic molecules at relatively low temperatures, but with increasing temperatures from the plastic state of the coal to the coke oven walls, any such molecules if formed, would tend to dissociate into smaller units. Its ability to form carbon-sulfur complexes is well known. The nature of the complex was considered to be similar to Rhead and Wheeler's carbon surface oxide complex C_2O (8). Based on this and on the fact that the outer orbital electronic configurations of sulfur and oxygen are similar, sulfur and oxygen atoms might react with carbon in an analogous manner. The initial formation of the carbon-sulfur complex via hydrogen sulfide appears to depend upon the nature of the reactive sites on carbon and upon the environment. The availability of the sites would probably be governed by the extent of the competing dehydrogenation reactions involved with free sulfur. Because of these factors and because of the secondary decomposition nature of the reaction, it is probable that the formation of the complex commences somewhere above 500°C.

The nature of the carbon appears to be important in the formation of the complex. It was suggested that only amorphous carbon forms the complex and that this is due to the high degree of unsaturation of the surface atoms of such carbon (8). From a physical point of view, the magnitude of specific surface areas of (powdered) cokes was considered to be connected with the formation of carbon sulfur complexes (7). The evidence in this study tends to support these views.

The higher reactivity of coke C over carbonized cokes A and B suggests that the reaction takes place more effectively with coke produced at temperatures below that at the coke oven walls. Such coke presumably contains more reactive sites upon which the sulfur is probably adsorbed and reacts more easily with the carbon. Although the retention of sulfur as a complex is known to depend on the temperature and the atmosphere prevailing during carbonization, it may also depend on the nature

of the complex. Figure 5 shows that the organic sulfur of coke C is considerably less stable than that of cokes A and B at 1000° under the condition studied. The temperature gradient in a byproduct oven suggests that a portion of the complex formed by reaction with hydrogen sulfide would tend to survive the carbonization process.

Physically, the formation of coke from the semicoke stage is a progressive contraction process. Recent studies show that with increased carbonization temperature a continuous decrease occurs in the diameters of the capillary constrictions associated with the internal structure of coke (29). Evidence of this was based on the decreased size of gaseous molecules necessary to penetrate into the internal structure. This implies that the diffusion of hydrogen sulfide into the capillaries would be greater with coke produced at lower temperatures. The differences in the reactivity of the coke samples tend to support this concept.

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TABLE I

PROXIMATE ANALYSIS AND SULFUR FORMS OF COAL AND COKES

Sample Basis (1)	Proximate Analysis, %					Sulfur Analyses, %			
	Moisture	V.M.	F.C.	Ash	Total	Inorganic Extract.	Vol.	Organic	
Coal	1	1.0	36.2	60.2	2.6	0.69	0.06	0.00	0.63
	2	-	36.6	60.8	2.6	.70	.06	-	.64
	3	-	37.6	62.4	-	-	-	-	.65
Coke (Bulk)	1	0.7	2.2	92.0	5.1	0.56	0.02	0.06	0.48
	2	-	2.2	92.7	5.1	.56	.02	.06	.48
	3	-	2.3	97.7	-	-	-	-	.51
Coke A (2)	1	0.6	1.9	93.1	4.4	0.56	0.01	0.05	0.50
	2	-	1.9	93.7	4.4	.56	.01	.05	.50
	3	-	2.0	98.0	-	-	-	-	.53
Coke B (2)	1	0.9	1.9	92.1	5.1	0.56	0.01	0.05	0.50
	2	-	1.9	92.9	5.2	.56	.01	.05	.50
	3	-	2.0	98.0	-	-	-	-	.53
Coke C (2)	1	1.2	2.6	90.7	5.5	0.56	0.02	0.03	0.51
	2	-	2.6	91.8	5.6	.57	.02	.03	.52
	3	-	2.8	97.2	-	-	-	-	.55

(1) 1, as received; 2, dry; 3, dry, ash-free

(2) Coke A, 10 x 60 mesh of original -10 mesh; Coke B, coke A ground to -60 mesh; Coke C, -60 mesh of original -10 mesh

TABLE 2

SCREEN ANALYSIS OF COKE SAMPLES

U.S. Standard Mesh	Screen Opening Microns	Log ₁₀ of Geometric Mean Opening Microns	Determined Wt., %			Calculated Wt., %	
			Coke A	Coke B	Coke C	Cokes A & B Cumulative	Coke C Cumulative
200	74	1.946	39.1	45.7	18.4	18.4	45.7
140 x 200	105	2.098	13.0	14.8	6.1	24.5	60.5
100 x 140	149	2.286	18.9	18.5	8.9	33.4	79.0
60 x 100	250	2.511	29.0	21.0	13.6	47.0	100.0
40 x 60	420	2.775	20.9		11.0	58.0	
20 x 45	840	3.114	39.9		21.2	79.2	
10 x 20	2000		39.2		20.8	100.0	

(1) Example: $(74 \times 105)^{1/2} = 88$; $\log_{10} 88 = 1.946$

TABLE 3

APPARATUS SPECIFICATIONS; ITEM NUMBER
REFER TO FIGURE 2

ITEM NO:	DESCRIPTION
1	Cylinder (nitrogen gas; Matheson Co. Inc., water-pumped, standard purity)
2	Brooks rotameter, size 1-15-3, maximum capacity 0.40 cu.ft. per hr. at 25°C., 1 atm.
3	"Drierite" drying towel and copper wool deoxygenifier with furnace at 450°C.
4	Cylinder (hydrogen sulfide; Matheson Co. Inc., 99.9% pure)
5	Fischer rotameter, No. 08-150 D.W.G.-S-21654-3, maximum capacity 0.05 cu.ft. per hour at 25°C., 1 atm.
6	Mixing tee
7	Preheater, Hevi Duty furnace, type 70, 1-inch ID and preheater tube packed with porcelain rods; temperature maintained at 500°C. with variac type 116
8	Mullite Coors reactor tube, 24" long and 1-inch ID, 29/42 ♀ female joints at ends, with preheater zone packed with silica rods 1/4 inch OD and 12 inches long, support screen, nickel-iron alloy, 60-mesh and 1-inch dia. as shown in the enlarged view in Figure 2. Chromel-Alumel thermocouple, encased in Vycor glass well at base of reactor tube, and attached to Hoskins thermoelectric pyrometer type AH
9	Reactor furnace, Hoskins, type FH 303A equipped with a 15-volt 37-ampere output transformer controlled by variac type 116
10	Liebeg condenser, 20 inches long, with 150-ml condensate trap and fines trap; 24/40 ♀ joints
11	Hydrogen sulfide absorption trap with fritted glass filter, corning extra course, absorption medium 10% aqueous monoethanolamine
12	Sargent Wet Test Meter, maximum capacity 100 cu.ft.

TABLE 4

EFFECT OF HYDROGEN SULFIDE ON THE SULFUR CONTENT OF COKE FOR TWO-HOUR RUNS AT 800, 900, and 1000°C.

Analyses Before Reaction, % Sulfur

<u>Sample</u>	<u>Inorganic Sulfur Extracted</u>	<u>Sulfur Volatile</u>	<u>Organic⁽¹⁾ Sulfur</u>	<u>Total Sulfur</u>
Original Coal	.06	.00	.63	.69
Bulk Coke	.02	.06	.48	.56
Coke A, Hard, 10x60 mesh	.01	.05	.50	.56
Coke B, Hard, minus 60 mesh	.01	.05	.50	.56
Coke C, Soft, minus 60 mesh	.02	.03	.51	.56

Analyses After Reaction, % Sulfur

Flow rate of Hydrogen Sulfide: 0.013 cu.ft./hr.(0.015 mols/hr.)(Mol conc.4.2%)

Temp., °C.

800 Coke A, Hard, 10x60 mesh	.08	.00	.72	.80
Coke B, Hard, minus 60 mesh	.14	.04	1.06	1.24
Coke C, Soft, minus 60 mesh	.34	.02	1.36	1.72
900 Coke A, Hard, 10x60 mesh	.01	.01	.66	.68
Coke B, Hard, minus 60 mesh	.04	.02	.72	.78
Coke C, Soft, minus 60 mesh	.22	.02	1.39	1.63
1000 Coke A, Hard, 10x60 mesh	.02	.00	.66	.68
Coke B, Hard, minus 60 mesh	.07	.03	.78	.88
Coke C, Soft, minus 60 mesh	.24	.04	.54	.82

Flow rate of Hydrogen Sulfide: 0.029 cu.ft./hr.(0.034 mols/hr)(Mol conc.8.8%)

800 Coke A, Hard, 10x60 mesh	.07	.01	.81	.89
Coke B, Hard, minus 60 mesh	.12	.05	.96	1.13
Coke C, Soft, minus 60 mesh	.28	.00	1.68	1.96
900 Coke A, Hard, 10x60 mesh	.04	.03	.98	1.05
Coke B, Hard, minus 60 mesh	.12	.03	1.08	1.23
Coke C, Soft, minus 60 mesh	.27	.01	1.74	2.02
1000 Coke A, Hard, 10x60 mesh	.01	.01	.79	.81
Coke B, Hard, minus 60 mesh	.13	.02	1.10	1.25
Coke C, Soft, minus 60 mesh	.32	.52(2)	1.20	2.04

(1) Organic sulfur is all sulfur other than inorganic (extracted and volatile)

(2) Believed to be in error

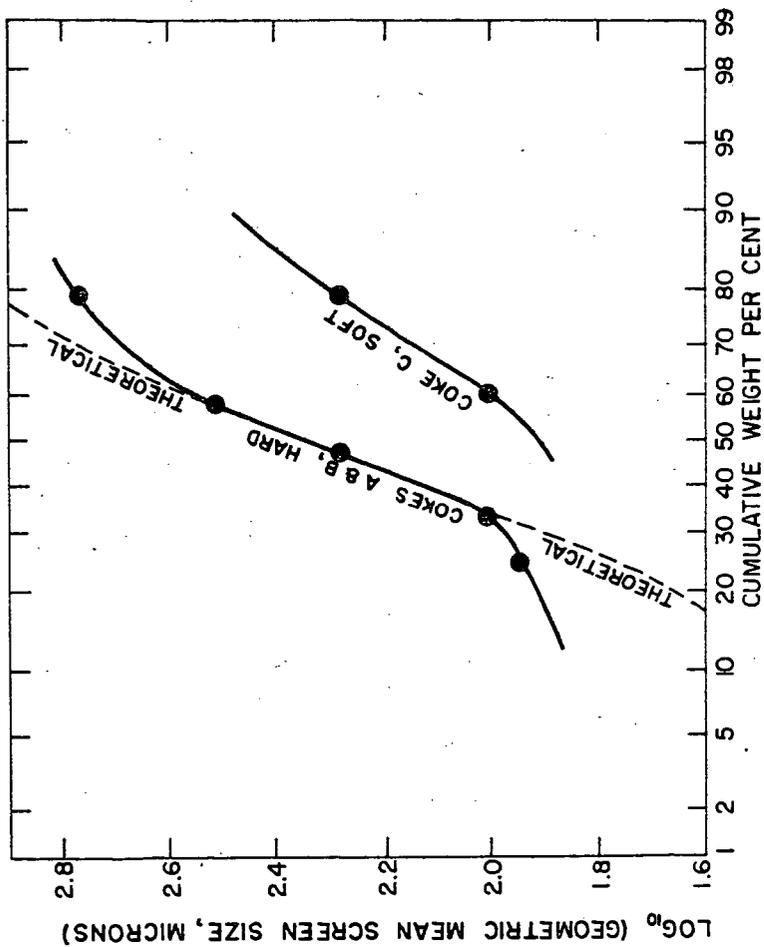


FIGURE 1 - GRINDABILITY PROPERTIES OF COKE SAMPLES

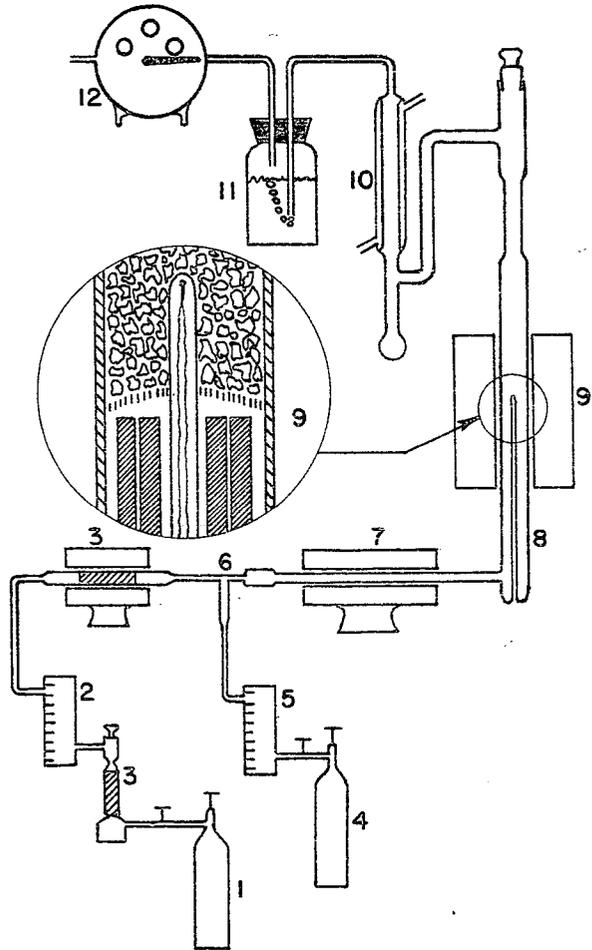


FIGURE 2 - EXPERIMENTAL APPARATUS
(REFER TO TABLE 3 FOR
SPECIFICATIONS)

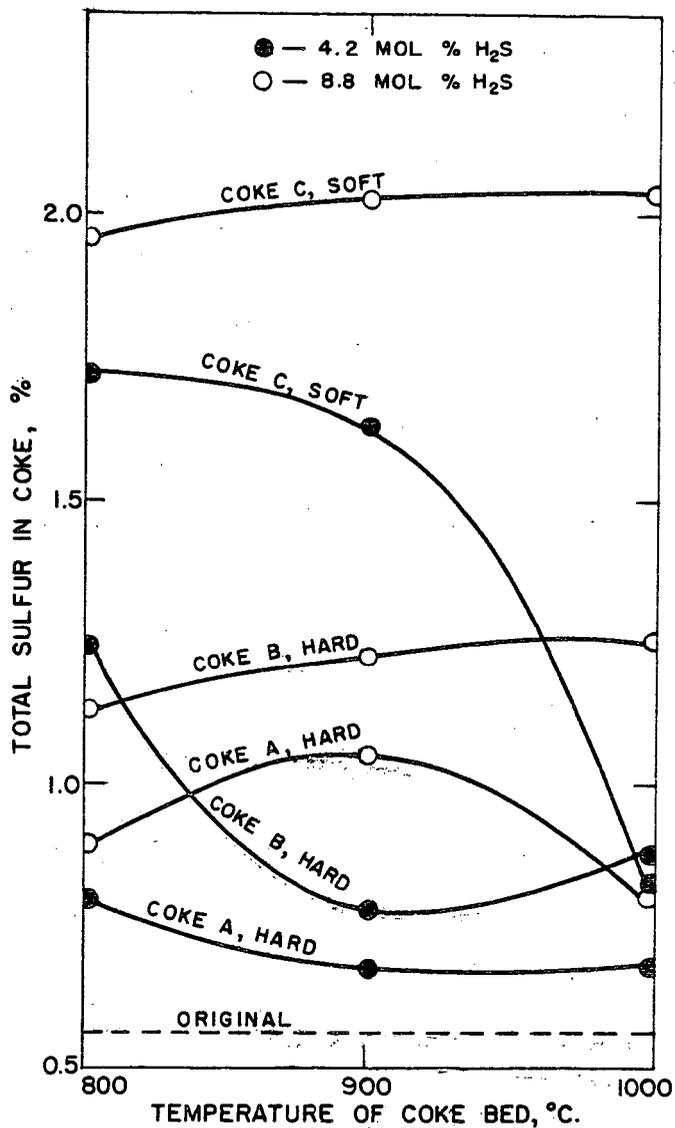


FIGURE 3 - EFFECT OF HYDROGEN SULFIDE ON TOTAL SULFUR CONTENT OF COKE

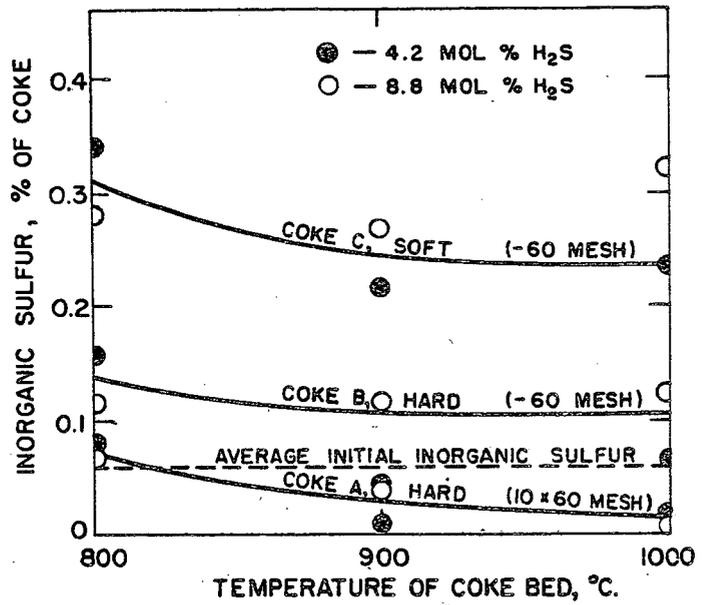


FIGURE 4 - EFFECT OF HYDROGEN SULFIDE ON THE INORGANIC SULFUR CONTENT OF COKE

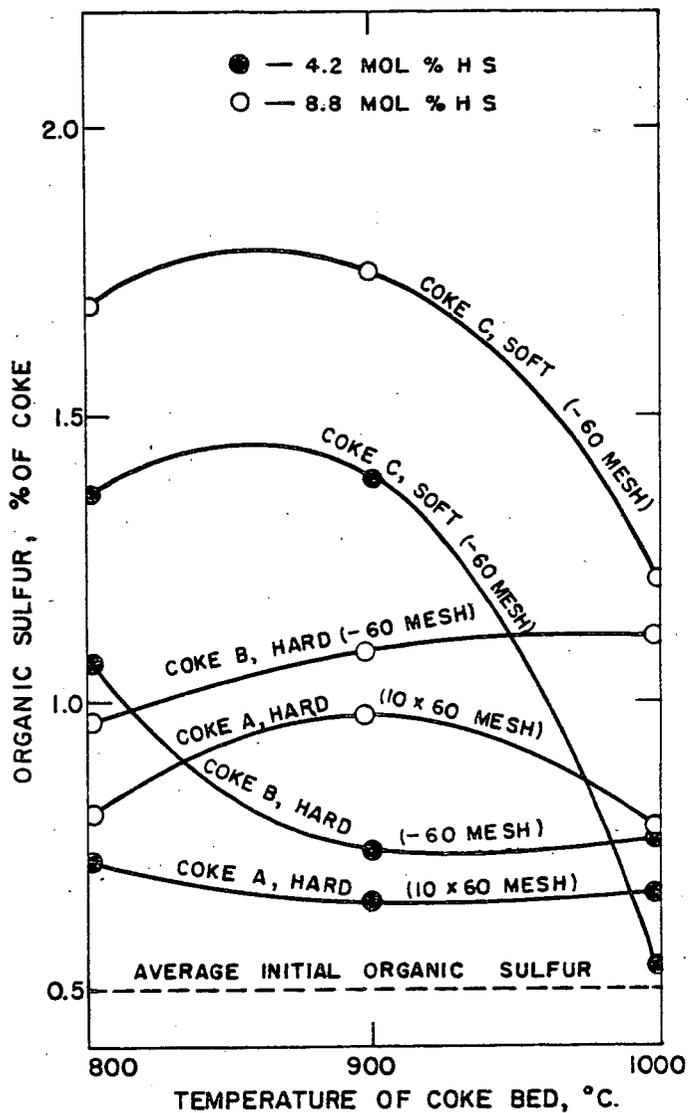


FIGURE 5 - EFFECT OF HYDROGEN SULFIDE ON THE ORGANIC SULFUR CONTENT OF COKE