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CATALYSIS BY COAL MINERALS - CHARACTERIZATION OF MINERAL MATTER IN COAL

I. Mineral Matter in Coal

The term "mineral matter" has been applied to all inorganic non-coal material occurring in coal and also to those elements usually considered to be inorganic, even if they are in organic combination. That is, all elements in coal except carbon, hydrogen, oxygen, nitrogen, and sulfur are considered to be part of the mineral matter, and four of these "organic" elements also occur in inorganic combination in coals. Carbon may be present in carbonates Ca(Fe, Mg)CO_3; hydrogen in free water and water of hydration; oxygen in water, oxides, carbonates, sulfates, and silicates; and sulfur in sulfides (primarily FeS_2) and sulfates.

Silicates, sulfides, sulfates, and carbonates are the most commonly occurring major minerals. The mineral matter in coal occurs predominantly as various mineral phases. The portion that exists in organic combination, although in some instances of great significance, is generally of less importance quantitatively.

Although there has been a great demand for data about the origin, distribution, and geologic significance of mineral matter in coal, the progress in this research has been hindered, mainly because of the physical inaccessibility of the mineral matter in coal. The techniques previously available for mineral separation from coals were based on some type of gravity separation and were unsatisfactory because of the large amount of inseparable mineral matter in coal.

Another difficulty, more insidious and less amenable to solution, is encountered in the study of mineral matter in coal: the system being investigated is very complicated. The complications result from the variety of physical and chemical conditions that existed in the environment in which the coal-forming materials were deposited and in which the coal formed. The system with which we are concerned, "mineral matter in coal," was a relatively low-temperature, low-pressure system with a large number of component phases. The system is an open one, and many of the components are mobile. There is also the further complication that the system has been active and may have been in the process of altering at any time since its genesis (approximately 300 million years for coals of the Pennsylvanian System).

Although the amount of mineral matter in coals is extremely variable, it is normally large enough to be significant in any method of utilizing the coal. In a study of 65 Illinois coals, Rao and Gluskoter (1973) found the mineral matter content to range from 9.39 percent to 22.34 percent (corresponding to an ash content of 7.34 percent and 15.8 percent, respectively). O'Gorman and Walker (1972) found an even larger range (9.05 percent to 32.26 percent) in mineral matter content in 16 "whole coal" samples from a wide distribution of locations in North America. Assuming that 15 percent mineral matter is a reasonable value for the mode of mineral matter content in North American coals, then that amount is mined with the coal and, unless partially removed by "cleaning," is introduced with the coal into each coal utilization process. Fifteen percent, additional and normally unwanted foreign material, is added to the boiler in the case of combustion or to the reactor in coal conversion processes. It is reasonable to assume that within this heterogeneous 15 percent there are deleterious components. There may also be beneficial components, but the first assumption (deleterious) is the more likely. The characterization of this component of coals therefore becomes important.

II. Mineralogical Analyses of Coal

1. Separation of Minerals from Coal

This section is concerned with minerals in the strict sense, "naturally occurring, inorganic, definite chemical composition and ordered atomic arrangement," and not with elemental analyses.

There have been many studies reported in the literature in which workers have analyzed the minerals which were picked by hand from the coal seams, from coal partings, or from cleat; or which were separated from the coal by a method based on differences in specific gravity between the coal and the minerals contained in the coal. As a first step, these were important contributions, but it quickly became apparent that the large amount of inseparable mineral matter in coals resulted in, to say the least, incomplete analytical data. The next stage in this research involved ashing coal at 300° C to 500° C, temperatures below that of normal combustion, or at room temperatures in an oxygen stream. This provided additional information, but the oxidation of many of the minerals in coals accompanied the oxidation of the organic fraction.

Within the past decade the technique of electronic (radio-frequency) low-temperature ashing has been applied to investigations of mineral matter in coal. In a low-temperature asher, oxygen is passed through a radio-frequency field and a discharge takes place. Activated oxygen passes over the coal sample, and oxidation of the organic matter takes place at relatively low temperatures (usually less than 150° C).

The effects of low-temperature ashing and of the oxidizing gas stream upon minerals in coal are minimal. No oxidation of mineral phases present has been reported, and the only phase changes observed were those to be expected at a temperature of 150° C and a pressure of 1 torr. Therefore, most of the major mineral constituents of coals, including pyrite, kaolinite, illite, quartz, and calcite, are unaffected by the radio-frequency ashing.

Recent studies of mineral matter in coal which have utilized radio-frequency low-temperature ashing include Gluskoter (1967), Estep et al. (1968), Wolfe (1969), O'Gorman and Walker (1972), and Rao and Gluskoter (1973).

2. Identification of Minerals in Coal

Once the low-temperature mineral matter residue has been obtained by radio-frequency ashing, a variety of techniques have been applied to the problem of identifying the minerals and then attempting to determine their concentrations.

The best developed, most inclusive, and probably the most reliable method used thus far is X-ray diffraction analyses. It has been used extensively by Gluskoter (1967), Wolfe (1969), O'Gorman and Walker (1972), and Rao and Gluskoter (1973), and has been somewhat successful in quantifying mineral analyses.

Estep et al. (1968) used infrared absorption bands in the region 650 to 200 cm^{-1} to analyze quantitatively as well as qualitatively for minerals in low-temperature ash. O'Gorman and Walker (1972) also applied this technique in their investigations.

Differential thermal analyses (D.T.A.) of minerals in a high-temperature coal ash has been reported by Warne (1965, 1970). The method was applied to the mineral matter fraction of four samples by O'Gorman and Walker (1972).

Electron microscopy, in spite of its rapid increase in popularity as a mineralogical research tool, has, as yet, found only limited application to the identification of minerals in coals. Dutcher et al. (1964) reported on a limited investigation which demonstrated the use of the electron probe in analyzing mineral matter in coal. Scanning electron microscopy with an energy dispersive X-ray system accessory has been used to a limited extent to study minerals obtained from the low-temperature ashing of coal (Gluskoter and Ruch, 1971; Gluskoter and Lindahl, 1973; and Ruch, Shimp, and Gluskoter, 1973).

A study of Fe^{57} Mössbauer spectra in coals was published by Lefelhocz et al. (1967). The study demonstrated the validity of the technique applied to coal and suggested the presence of high spin iron (II) in six-fold coordination in several of the samples studied.

Mass spectrometric investigations of isotopes in coal and coal minerals have also been very limited in scope. Rafter (1962) published the sulfur isotope data on 27 New Zealand coal samples but did so without drawing any conclusions from these data.

3. Investigation of Minerals in Coal In Situ

The coal petrographer uses the optical microscope, usually in reflected light mode, to characterize the organic fraction (macerals) in coals. This science has been developed to a high degree of precision particularly during the past quarter century. However, the same techniques have not been nearly as successful in the investigation of mineral matter in coal. Pyrite (FeS_2) because of its high reflectance and its abundance in coals is the most likely mineral to be studied microscopically. Several automated microscopes and image analyzing microscopes have been developed that could be used in such a study. McCartney and Ergin (1969) reported upon an automated reflectance scanning microscope system of their own design and included results of pyrite analyses.

X-radiography of slabs of coal or of sections of coal cores has been used to "map" the mineral matter in coals, although I am not aware of any such studies currently being done.

4. Determination of Quantity of Mineral Matter in Coal - From Chemical Analyses

There have been many attempts to calculate a "mineral matter" content of a coal from a chemical analyses of that coal. Parr (1928) suggested a method which only requires a total sulfur and ash analysis. Many workers have suggested refinements based on additional chemical parameters. The developments with regard to a calculated value for mineral matter are summarized by Given (1969). Frazer and Belcher (1973) have avoided the problem of calculating mineral matter from chemical analyses by using a radio-frequency low-temperature ashing method and determined mineral matter directly.

III. Chemical Analyses of Mineral Matter in Coal

The characterization of mineral matter in coal includes the determination of many chemical elements if the broad definition of mineral matter stated earlier is accepted.

Chemical analyses of geological materials in general has gone from the "wet" chemical methods to instrumental methods. The major elements (Si, Al, Ti, Ca, Mg, Fe, P, S, Na, K) are the same as in silicate rocks and are often done by X-ray fluorescence spectroscopy and perhaps flame photometry.

The minor and trace elements in coals have been determined by several techniques, the most popular of which are optical emission spectroscopy and atomic absorption spectroscopy. Neutron activation analyses is an excellent technique for many elements, but does require the use of a neutron source (atomic reactor). In addition, the techniques of X-ray fluorescence spectroscopy, ESCA (electron spectroscopy for chemical analyses) and spark source mass spectroscopy have been successfully applied to minor and trace elements in coal.

References to the many published values on major, minor, and trace elements have been omitted because of their great number. However, most of the published values must be evaluated, recognizing several limitations. The first of these is that, almost all, have analyzed a high-temperature ash and often the conditions of ashing are not stated. The volatility losses have not been determined in these cases. Another limitation which applies especially in regard to trace and minor elements is that there have not been any coal standards available until very recently.

Comprehensive investigations involving a large number of coal samples and the determination of many elements including trace elements have been undertaken recently by the U. S. Geological Survey (Swanson, 1972), the U. S. Bureau of Mines (Kessler et al., 1973), the Illinois State Geological Survey (Ruch et al., 1973), and Pennsylvania State University (O'Gorman and Walker, 1972).

IV. Possible Areas of Research Related to the Characterization of Mineral Matter in Coal

1. "Basic Research"

A - <u>Existing Techniques</u>. Sufficient work has been done during the past decade to demonstrate the complexity of the area of interest we are calling "mineral matter in coal." There is a definite paucity of information available on all but a few aspects of the broad topic. Any well planned and intelligently executed research project, involving techniques such as those discussed in the preceding sections will add knowledge concerning mineral matter in coal. Currently, the mineralogical analyses of less than 100 different coal seam samples have been published. This certainly can't represent a statistical sample of the more than 1.5×10^{12} tons of coal composing the reserves of the United States; and describing the mineralogy of the inorganic fraction of the coals is just the first step in the complete characterization of mineral matter in coal.

There are several additional techniques that are currently being developed that may be applicable to the study of mineral matter in coal. The ion probe, although an expensive piece of equipment to purchase and to operate, is one such potentially powerful analytical tool.

B - Size Analyses and Distribution. There has not yet been a study which has attempted to relate the size distribution of the total mineral matter residue in coal to other properties of the coal. The low-temperature mineral matter residue would be a reasonable starting material for such an investigation. One difficulty of the size analyses is that within the mineral matter are substantial quantities of fine-grained clay minerals and the method would have to identify particles below one micrometer in size. In order for this project to be carried out, the researcher would need a source of the low-temperature ash, a suitable technique for the size analyses, and very little else. Although this project would require a modest amount of equipment, it is sufficiently difficult to require appreciable talent to carry it out and could result in a significant contribution.

C - High-Temperature Phases of Mineral Matter in Coal. In coal conversion processes and in nearly all aspects of coal utilization, the first stages of the process include heating the coal. Once the mineral matter content of the coal has been determined, the heating characteristics of pure phases can be compared to the analyses of the minerals in coal. The success of those predictions will probably be poor, since the mineral systems in the coal are complex, heterogeneous, and open and are not correlative with pure phases. A closer approach to the actual conditions to be met in conversion processes would be to heat the mineral matter fractions obtained from the coals and observe the phases formed and the temperatures of the phase changes. Dr. Richard S. Mitchell, University of Virginia, has been working for several months on such a problem, using an X-ray diffraction heating furnace and low-temperature ash supplied to him by the Illinois State Geological Survey. The study has not yet been published.

The cost of this kind of a research project would not be extremely high, and might vary, depending upon the necessity of purchasing additional X-ray diffraction equipment (goniometer, recorder, programmer) and/or a high-temperature furnace. If all of the above mentioned items were to be purchased, they would probably cost under $25,000, assuming a basic X-ray diffraction unit was already in hand. If the full system was purchased the cost would be nearer $50,000.

2. "Applied" Research

Independent of the coal conversion process being investigated, a complete characterization of the starting material - the coal feed - would be desirable and, in the case of some characteristics, would be necessary. This would involve chemical analyses for major, minor, and trace elements; mineralogical analyses; petrographic analyses, and perhaps other analyses.

In more enlightened times, these analyses would probably not be research projects, but would be service work provided by commercial laboratories. Some parts of these analyses may be available from commercial laboratories, but most of these determinations have been made to date by researchers in universities and state and federal research establishments. In order to obtain complete analyses of the coals which are of interest to those investigating the many aspects of catalyses as it applies to coal conversion, it may be necessary to approach several of the laboratories and have each do determinations for which they have the best qualifications.

There are many organizations that can do chemical analyses and mineralogical analyses (fewer that can do petrographic analyses) but a much smaller number have demonstrated by their publications the ability to do those analyses on coal. There are four laboratories in the United States which, today, seem to rank above the rest with regards to the ability to conduct a broad-based mineral matter in coal program. This extremely subjective ranking is based on the availability of analytical equipment, the necessary scientific talent, and the proven ability to produce reasonable analytical results when investigating coals. These four laboratories, which have published their results, listed alphabetically, are the Illinois State Geological Survey, The Pennsylvania State University, the U. S. Bureau of Mines, and the U. S. Geological Survey.

The list given above is not given in an attempt to be exclusive, for there is certainly much scientific analytical ability in other universities and laboratories that could be applied to problems involving mineral matter in coal. However, these are the laboratories that have been doing research projects on mineral matter in coal and that have also been publishing their results.

It is very difficult to estimate the cost of a complete series of analyses of a coal sample. If chemical, mineralogical, and petrographic analyses comprised the minimum request, a cost of $1,000 to $2,000 a sample would not be out of line, and that assumes a series of at least 20 samples. Fewer samples would be individually more expensive. This dollar amount is only the roughest of estimates and would not be defended by its originator.

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