

The Determination of Mineral Distributions in Bituminous Coals
by Electron Microscopy*

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INTRODUCTION

The chemistry and concentration of mineral matter in coals are factors that play important roles in coal combustion. For example, fouling, slagging, corrosion, and erosion are all mineral dependent processes that occur in coal-fired steam plants. Of these processes, fouling and slagging are probably the most detrimental to steam plant efficiency. Attempts to predict the fouling and/or slagging potential of a given coal have led to the development of equations based upon the ratios of base to acid minerals multiplied by either the sulfur or sodium content. (1,2) Essentially, these ratios take into account the lowering of the ash fusion temperature as a function of increased alkali bearing minerals.

In addition to the impact of mineral matter on steam plant operations, mineral matter also contributes to atmospheric particulates via steam plant stack emissions. Methods for reducing and/or altering the effects of minerals in coal are limited by the size and distribution of the minerals which is in turn related to the origin of the minerals, namely, whether syngenetic or epigenetic. As reported by Mackowsky (3) epigenetic minerals can be more readily removed from the coal because they are not as intimately mixed with the organic constituents (macerals) as syngenetic minerals. Furthermore, the epigenetic minerals may be considerably different from the syngenetic minerals due to differences in environments at the time of deposition and/or growth.

Currently, a common procedure for identifying minerals in coals consists of firstly low temperature ashing (L.T.A.) the coal and secondly analyzing the inorganic residue by means of x-ray diffractometry. Added information about the mineral residue may be attained by utilizing a scanning electron microscope (SEM) with energy dispersive x-ray analysis (EDX) this procedure helps identify the minor minerals as well as locate trace elements. An advancement over the aforementioned SEM technique is one utilized by Finkelman (4) in which polished blocks were used so that not only the identity of minerals were obtained but also their relationship to the organic constituents could be determined.

In recent transmission electron microscopical studies of coals, (5,6) ultrafine minerals were observed ($<1 \mu\text{m}$). The observation and identity of these submicron minerals would have been difficult to achieve by use of the scanning electron microscope (SEM). However, the scanning transmission electron microscope (STEM) with energy dispersive x-ray analysis is an ideal analytical tool since it is capable of supplying elemental and diffraction data for particles as small as 30 nm in diameter. In this paper, we present observations and analyses of mineral matter in coals obtained through use of electron microscopes. These data significantly increase our knowledge of the mineral matter in coals as related to their affects on coal combustion.

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EXPERIMENTAL

Sample Selection and Preparation

The samples used in this study were obtained from several high volatile bituminous coals of Eastern United States - Illinois No. 6, Kentucky No. 9, Elkhorn No. 3, and Hazard No. 4. Specimens were prepared for the transmission electron microscope studies from the above coals using a technique previously reported.⁽⁷⁾ Optical thin sections approximately 10–15 μm thick were prepared. The thin sections were removed from the glass slides using acetone and subsequently mounted in an ion milling machine. Specimens were thinned (ion milled) using Argon gas and a liquid nitrogen cooled stage to insure against thermal damage to the specimen. Additional specimens consisting of polished blocks of coal were prepared for observation with the scanning electron microscope.

A high-voltage TEM (1MeV), a STEM (120Kv), and a SEM (JEM-U3) were used in this study. The STEM and SEM were fitted with energy dispersive x-ray analysis systems utilizing Si(Li) solid state detectors. Microchemical analyses of minerals for elements of atomic number 11 or greater could be attained for particles as small as 20 nm by using STEM with EDX.

RESULTS AND DISCUSSION

Submicron size minerals have been observed in all the high volatile bituminous coals that have been studied at this laboratory. A representative TEM micrograph of these coals (Fig. 1) reveals that these ultra-fine minerals are typically enclosed in a matrix consisting of vitrinite. These minerals are considered as syngenetic in origin; (i.e., contemporaneously deposited in the peat basin with the organic constituents). Limited selected area diffraction (SAD) and energy dispersive x-ray analyses (EDX) of several of these minerals, using the STEM, showed that kaolinite (clay) is the dominant mineral species. However it must be noted that this analysis is strictly qualitative.

Moza et al. (8), in a study of minerals in coal as related to coal combustion systems, suggested that mineral fragments less than 8 microns would not be expected to gain enough momentum to collide with heat transfer tubes and these minerals would escape in the gas stream. However, from our present study of submicron minerals one can conceive of these particles fusing together to become substantially larger fragments. For example, a cubic μm of vitrinite may contain as much as 300 minerals, many of which actually touch.

Additional ultrafine syngenetic minerals have been observed to be intimately mixed with exinite (usually sporinite) and fragments of inertinite and vitrinite. These durain-like bands were probably derived from sediments consisting of degraded organic materials and mineral detritus deposited together in the peat swamp. The mineral species comprising these deposits are much more varied than those found in the vitrinite. In fact, these minerals usually contain many of the minor and trace elements associated with the mineral matter in coal (5) such as tin, nickel, zirconium, titanium, and chromium. Typically, these minerals have a wider range of sizes varying from submicron particles to grains several microns long.

The TEM microstructure presented in Fig. 2 shows sporinite (Sp) segments bounded by regions consisting of granular maceral fragments and minerals (designated M-M). An aggregate of euhedral pyrite (Py) crystals located at one of the sporinite (Sp) boundaries is not an uncommon feature in many of the coals examined at this laboratory. The size of these pyrite crystals ($\sim 1 \mu\text{m}$) appears to be identical to the

pyrite crystals in framboids located in vitrinite bands. It is worth noting that these minerals should prove more easily removed from the coal than those within macerals.

In Fig. 3, another view of mineral matter in durain-like bands is shown. A section of sporinite (S_p) interfaces with the inertinite maceral semifusinite (S_F). The region between these two macerals contains fine granular material including minerals. Additional minerals and organic debris are located within the collapsed sporinite walls (C_C). A large quartz grain ($\sim 6 \mu m$) is located in a crushed cell in the semifusinite (S_F). Usually mineral inclusions within the vacant cell cavities of inertinite are considered as epigenetic. This point can be more clearly demonstrated by viewing an optical micrograph (Fig. 4) that shows epigenetic pyrite (Py) filling the crushed cell cavities in semifusinite (S_F).

Common structures found in bituminous coals are microfractures and/or joints that formed perpendicular to the bedding plane of the coal. These fractures (joints) are called cleat and originated in the coal after consolidation due to tectonic forces acting upon the earth's crust. In Fig. 5, a SEM micrograph of a polished block of coal, one can observe the appearance of cleat (CL). The epigenetic mineral filling the cleat (CL) was identified as calcite based upon EDX and x-ray diffraction analyses, the latter determination being performed on segments detached from the coal. The calcite forms a uniform mineral deposit approximately $10 \mu m$ thick and extends over several millimeters. A segment of the calcite sheet removed for analyses exposes one of the cleat walls (CLW). Typically, minerals in cleat can be readily separated from the organic constituents in coal, this is in contrast to the pyrite (Py) framboids (Fig. 5) enclosed in the vitrinite (V) band which would be extremely difficult to remove from the coal.

In addition to the presence of calcite in cleat, pyrite and kaolinite are also commonly found in cleat (9). The massiveness of the epigenetic mineral deposits in contrast to the syngenetic mineral distribution makes it apparent that the former mineral type constitute the major fraction of minerals in coal. The relative absence of calcite as a syngenetic mineral and its presence as a dominant cleat mineral in these coals suggests that calcite could readily be removed from the coal by current beneficiation methods. Indeed such cleaning of coals would also result in considerable reduction of pyrite and kaolinite. In general, the removal of calcite and pyrite should tend to increase the ash fusion temperature and consequently lead to a reduction in fouling and slagging.

CONCLUSIONS

1. Syngenetic and epigenetic minerals can be observed and identified by electron microscopy in conjunction with energy dispersive x-ray analysis.
2. Submicron micerals that are not readily identified or observed by scanning electron microscopy are easily viewed by use of transmission electron microscopy.
3. Calcite appears to be relatively scarce as a syngenetic mineral whereas calcite is an important epigenetic mineral usually occurring as cleat deposits.
4. Important minor syngenetic mineral assemblages appear to be associated with detritus. These minerals probably contain the major portion of minor and trace elements in coal.
5. Most of the epigenetic minerals should be readily removed from the coal resulting in a probable reduction in fouling and slagging.

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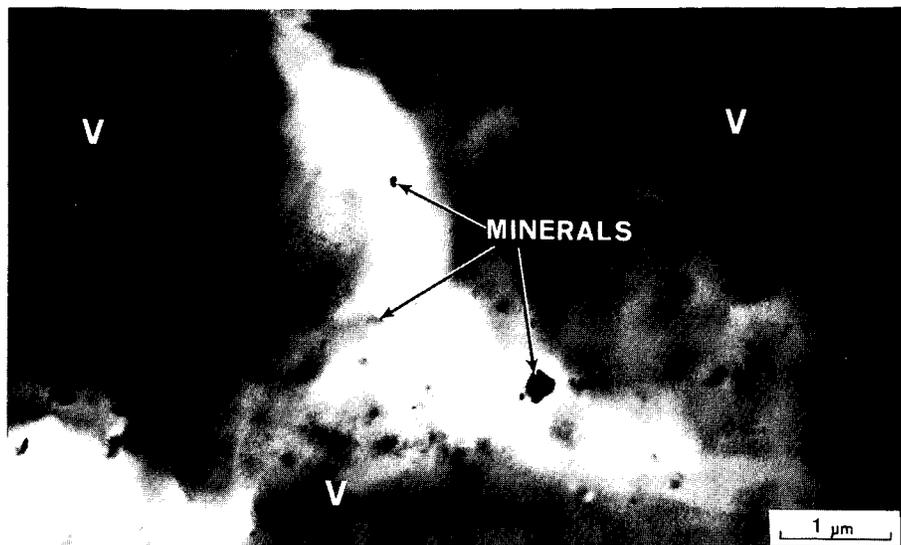


FIG. 1. TEM MICROGRAPH OF A HIGH VOLATILE BITUMINOUS COAL SHOWING THE DISTRIBUTION OF SUBMICRON MINERALS (See Arrows) IN VITRINITE (V).

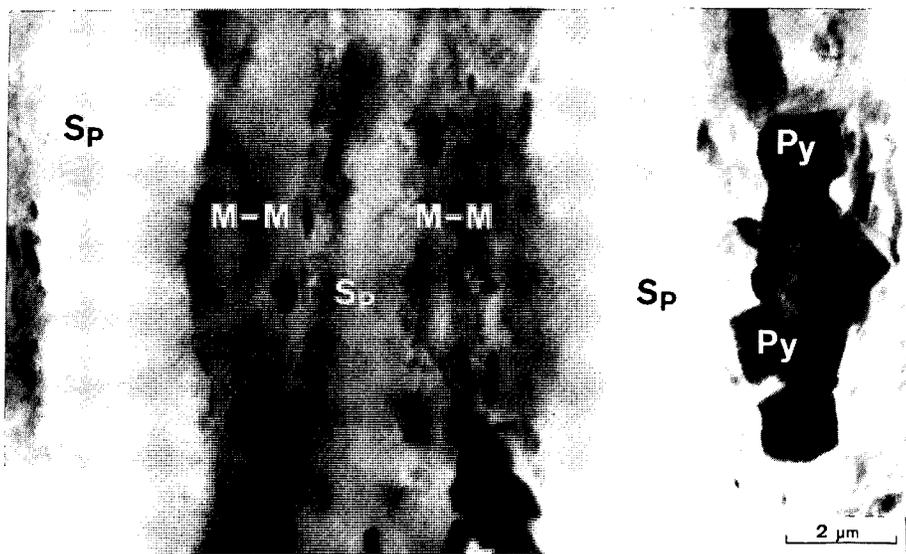


FIG. 2. TEM MICROGRAPH SHOWING THE RELATIONSHIP OF SPORINITE (Sp) WITH MINERAL BEARING BANDS (M-M). NOTE EUHEDRAL PYRITE (Py) CRYSTALS AT SPORINITE (Sp) BOUNDARY.



FIG. 3. TEM MICROGRAPH OF MICROSTRUCTURE CONTAINING SPORINITE (S_p) AND SEMIFUSINITE (S_f). A QUARTZ GRAIN (See Arrow) IS LODGED IN A CELL CAVITY IN THE SEMIFUSINITE (S_f).



FIG. 4. OPTICAL MICROGRAPH SHOWING EPIGENETIC PYRITE (P_y) FILLING THE CRUSHED CELL CAVITIES IN THE SEMIFUSINITE (S_f).

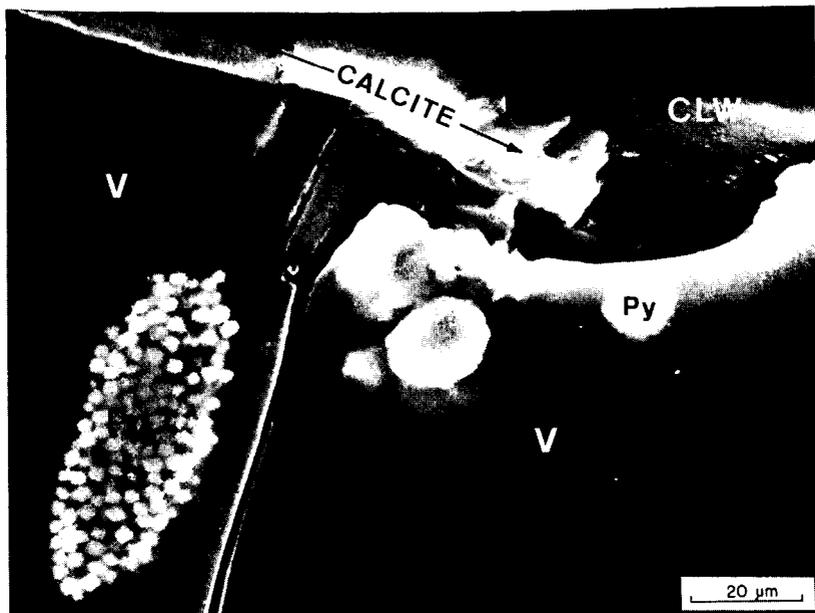


FIG. 5. SEM MICROGRAPH SHOWING CALCITE DEPOSIT (See Arrows) IN CLEAT. PYRITE (P_Y) FRAMBOIDS ENCLOSED IN VITRINITE (V) ALSO CAN BE SEEN.