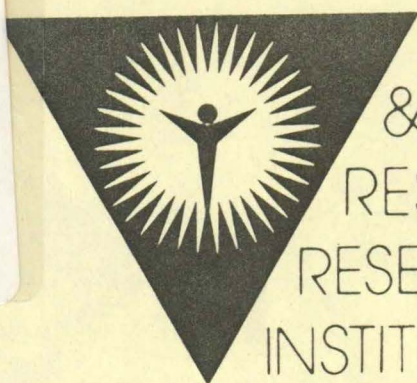


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COAL MICROSTRUCTURE AND THE SIGNIFICANCE OF  
PYRITE INCLUSIONS


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COAL MICROSTRUCTURE AND THE SIGNIFICANCE OF PYRITE INCLUSIONS

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Abstract

Initial new findings show significant features of coal microstructure and are related to understanding the process of coal formation and consolidation. These can be exploited to offer improvements in sulfur removal. As pyrite ( $\text{FeS}_2$ ) constitutes the major source of sulfur in coal, a description of the occurrence of pyrite in the coal in terms of size, morphology, and distribution is developed utilizing information from combined SEM-ED X-ray analysis. The interrelation of macerals (coal constituents) and inorganic phases is characterized, and on the basis of the identification of useful features of the ultrafine structure of the various coal constituents, these may be related to the development and application of innovative comminution and beneficiation techniques.

Chemical breakup of the coal is related to coal constituent microstructural control. Insight into the distribution of microscopic pyrite leads to the recognition of the presence of colloidal size pyrite as being a primary constituent of various sized pyrite concretions found in coal samples. This relates directly to providing significant fundamental information concerning the reliability of chemical determinations of sulfur which is difficult to obtain through other analytical techniques.

The porous nature of certain coal constituents and the specification of inorganic phase infillings of pores is examined in detail. Recommendations are offered for preparing surfaces for analysis including certain electrochemical etching techniques. Features of coal constitution developed by these techniques bear on the functional behavior of separable constituents.

Key Words: Coal, Pyrite, Sulfur, Coal Microstructure, Coal Chemistry, Scanning Electron Microscopy

Introduction

Most of the inorganic sulfur in coal is present as pyrite,  $\text{FeS}_2$ . Microstructural and microchemical characteristics of coal relate to choices and improvements of processing and purification procedures to remove sulfur in an attempt to meet environmental and air pollution level requirements. This work centers on providing needed microstructural-microchemical information. By means of scanning electron microscopy (SEM) and associated chemical analytical techniques, distribution data for pyrite in coal is being obtained. In addition to general surveys of complete coal mine channel samples, very detailed results have been obtained on a micrometer size basis. This is very time consuming; however, the findings delineate the presence and distribution of pyrite for a significant size range generally omitted in applying conventional petrographic characterization techniques, as well as suggest the application of appropriate techniques to remove this material prior to combustion of the coal at a power plant.

Also experiments have been performed to contribute to assessing the confidence in applying current ASTM sulfur determination techniques to identify the organic sulfur component in coal analyses. The other primary source of sulfur in coal (in addition to pyrite) is attributed to organic sulfur. Usually organic sulfur in coal is determined simply as a numerical difference between total sulfur and the sum of pyritic and sulfate (gypsum; usually <0.5 wt. %) sulfur. Large uncertainties may arise. If a significant amount of pyrite is undissolved, this would not appear in the pyritic sulfur determinations and consequently would be characterized as organic sulfur.

The amount of sulfur in coal is directly related to costs of removal. The relative amount of sulfur in coal as pyrite or as organic sulfur relates to processing and purification procedures. Therefore, the microstructural-microchemical information is of practical interest as the United



States moves toward greater utilization of its coal reserves.

The objective of the following discussion is to provide reasonable insight into three areas of concern:

- (1) the nature and distribution of pyrite,
- (2) aspects of chemical comminution and beneficiation, and
- (3) the reliability of chemical determinations of sulfur, especially of organic sulfur.

#### The Nature and Distribution of Pyrite

Optical microscope investigations have been useful in classification and characterization of coal constituents.<sup>1-3</sup> Complementary transmission electron microscope (TEM) and SEM studies<sup>4-8</sup> have been useful in understanding the microporosity of coal. In addition to the macerals (coal constituents) that make up coal, mineral inclusions such as pyrite are encountered. A significant portion of pyrite in coal may occur either as individual micron size crystallites, or as assemblies of these crystallites forming framboids (a word coined by Rust in 1935 meaning berry-like)<sup>9</sup> generally 10 to 30 microns in width, or as assemblies of these framboids interconnected by additional pyrite occurring over a large size range up to centimeters in width or greater. Both pyrite ( $\text{FeS}_2$ , cubic) and marcasite ( $\text{FeS}_2$ , orthorhombic) are observed as well crystallized inclusions in coal samples, the cubic form being the most abundant of the sulfide minerals. Other inorganic forms of sulfur such as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) are relatively low in abundance or rapidly appear as weathering products from the pyrite.

One of the earliest studies of the occurrence of sulfur in coals was done by Thiessen.<sup>10</sup> He emphasized the irregularity of distribution as well as discussed the organic sulfur which was in coal "in an amicroscopic form (not visible with an ordinary microscope), probably combined with the organic matter that exists in the coal". His general comments include:

- (1) "all the coals that have been examined microscopically contain microscopic grains of pyrite disseminated in them",
- (2) "these are distributed very irregularly and usually occur in colonies",
- (3) "different coal seams vary in the total content of this form of pyrite",
- (4) "different horizons differ in the total content", and
- (5) "different parts of a section may differ widely in the number of globules present".

Other studies than that of Thiessen<sup>10</sup> offer somewhat different findings (e.g., fine pyrite is much more uniformly distributed than coarse pyrite, and organic sulfur is quite uniformly distributed, especially in low-sulfur coals<sup>11</sup>; extent of pyrite

removal can be predicted from microscopic analysis<sup>12</sup>); however, these comments are appropriate with minor modification to the findings for most coals. Work in sections to follow will detail new specific information concerning occurrence, distribution factors, and interrelations with coal microstructure which are of interest in planning sulfur removal schemes.

#### Experimental Procedure

Microscale characterization of sulfide phases is performed utilizing combined SEM - energy dispersive X-ray analysis techniques for obtaining the microstructural and the microchemical information, respectively. This provides accurate and precise fundamental information, which is obtainable by no other technique, concerning size, shape, orientation, and distribution of phases within the coal.

Complete channel samples were obtained. From these, subsamples for SEM studies were mounted for analysis. The orientation in the face and vertical position in the bed were maintained. On fresh fracture surfaces, normal to the stratification, a traverse was made across a specimen and for the sequential specimens. All channel subsamples received a vacuum deposited coating of approximately 200 Å of gold (in some cases, a pre-coating of graphite was required, as well) to minimize charging problems. Surfaces were examined both as received and as treated by an ultrasonic cleaning process (in distilled water) to remove fine dust particles. Under the least favorable conditions, about 2 1/2mm of a specimen could be satisfactorily characterized by the SEM observations together with the energy dispersive X-ray analyses per beam hour.

Subsamples were also chosen for comminution experiments, etching studies, etc., where other types of analyses (such as wavelength dispersive analyses using an electron microprobe for carbon, sulfur, iron, calcium, and so on) were performed. This was necessary as pyrite and other phases (such as calcite) can occur as intimate infillings of the maceral microstructure or as complex nodules. Certain experiments, such as  $\text{HNO}_3$  penetration studies, required highly polished surfaces for analysis. Other experiments required matching specimen halves to develop comparisons.

Electrochemical etching experiments used a mixture of 47cc perchloric acid, 600cc methanol, 360cc butyl cellosolve, and 13cc distilled water (70 volts D.C. for 180 seconds).

The effect of various solvents (cutting fluids, etc.) must be closely monitored. New phases can easily be formed on surfaces.

#### Microstructural Features

In developing an understanding of the interrelation of pyrite to the coal, it is useful to



Detail microstructural features of the coal. Figure 1a-b presents several schematic drawings of commonly observed features, and relates these to the actual material (Star mine, Iowa, in this case). The textural features shown in Figure 1c and d are for a specimen comminuted in anhydrous liquid ammonia where portions of the coal layers have separated and are viewed at high magnifications. These views are related directly to Figure 5 which follows in another section.

Figure 2 is a top view of the coal seam for a sample which was the matching untreated half of a specimen, the other half of which was subjected to the chemical comminution (Figures 1c, 1d, and 5). Two regions are indicated in Figure 2. Region 1 is shown at higher magnification in Figure 3, and region 2 is shown at higher magnification in Figure 4.

Taking Figures 1-4 together, a three dimensional structural assembly of the coalified wood cells can be visualized. Details of cellular compression, microstructure, and interrelation of macerals and constituents such as pyrite, and repeat layers of highly consolidated coal are apparent. These enter into sulfur removal schemes and explanations of the pyrite distribution variations seen for coals.

#### Aspects of Chemical Comminution and Beneficiation

It is useful to develop a bridge between some of the pyrite distribution factors and ways to remove the pyrite as well as possibly upgrade the coal. What sulfur is removable? There are at least two aspects of this question to consider: 1. most of the sulfur is pyrite, and 2. some portion of the so-called "organic" sulfur can be colloidal pyrite crystallites, each generally of the order of a micrometer in diameter, or as small (10-40 micrometers in diameter) framboids. This second aspect will be discussed in another section. A considerable amount of the pyrite in coal can occur as units or groupings less than 50 micrometers in diameter. The more efficient use of coal relies on considerable improvement in rational methods of preparation and in preparation control. Differences in fracturing characteristics can aid in constituent separation. Crushing the coal to 200 mesh (<76 $\mu$ m diameter) can be very productive. It is apparent from Figures 1c, 1d, and 4 (and others to follow) that breakup to a size as small as the size of the component coalified plant cells would improve the potential for sulfur removal even further. A particle size of 6 to 10  $\mu$ m would be excellent, and a particle size of the order of 1 or 2  $\mu$ m would probably be optimum. Improvements can be made by choosing an effective comminuting agent to reduce coal particle size further, while in addition, a solvent can be chosen to dissolve the pyrite and not affect the organic material (scanning electron microscope work on the "organic" sulfur problem has shown that nitric acid is

quite effective in dissolving the pyrite that it comes in contact with, but does not appear to attack the coal). Of course, additional considerations must also be taken into account, as for example, will the comminuting agent alter combustion characteristics, economic and pollution considerations, or feedstock possibilities for gasification in a favorable way.

#### Chemical Comminution

Matching halves of coal samples from the Star mine were prepared. One of a set was subjected to treatment with anhydrous liquid ammonia (Fig. 5), and an untreated half of a set was kept for comparison (Fig. 2).

The treated material, such as that shown in Figure 5, fragmented. These fragments were maintained in their original orientations for close examination utilizing SEM. This material received a thin (200Å) vacuum deposited gold coating prior to SEM examination. Figure 5 represents a secondary electron photomicrograph of the Star coal sample when viewed edgewise to the bedding (i.e., a side view of the coal seam sample). Relatively light, closely spaced (0.016mm), horizontal lines that can be seen to run across the sample are saw blade marks. The material has fragmented into blocks approximately 1mm in width and 1/4 to 1/2mm in thickness as seen in this view perpendicular to the original deposition of layers of the plant material. Closer examination reveals fragmentation patterns associated with maceral control as well as other coal constituents such as pyrite. In Figure 5, two cracked regions are labeled to identify specific areas to demonstrate this.

The crack labeled number 1 in Figure 5 is shown at higher magnification in Figure 6. This higher magnification view clearly shows the crack proceeding through a roughly linear deposit of pyrite crystallites. Again the common pyrite crystallite size of approximately a micrometer in diameter is observed. This pyrite filling and the subsequent crack which has formed in association with the chemical treatment is approximately horizontal and parallel to the bedding planes.

Figures 1c and 1d show the fragmentation due to the chemical treatment to be also strongly controlled by the macerals and maceral boundaries. Both figures represent high magnification views of one of the well defined fragments which is at the tip of a wedge-shaped fragment which ends near the point of arrow 2 in Figure 5. The sample has been tilted away from the viewer in comparison with the sample orientation in Figure 2, so that both side and bottom features of the coalified material can be seen. The fibers are of the order of 10 $\mu$ m in diameter.

Other comminution agents were also investigated. Scanning electron microscope studies of pyrite extracted by the Meyers process (hot solution of ferric sulfate oxidizes pyrite) show that



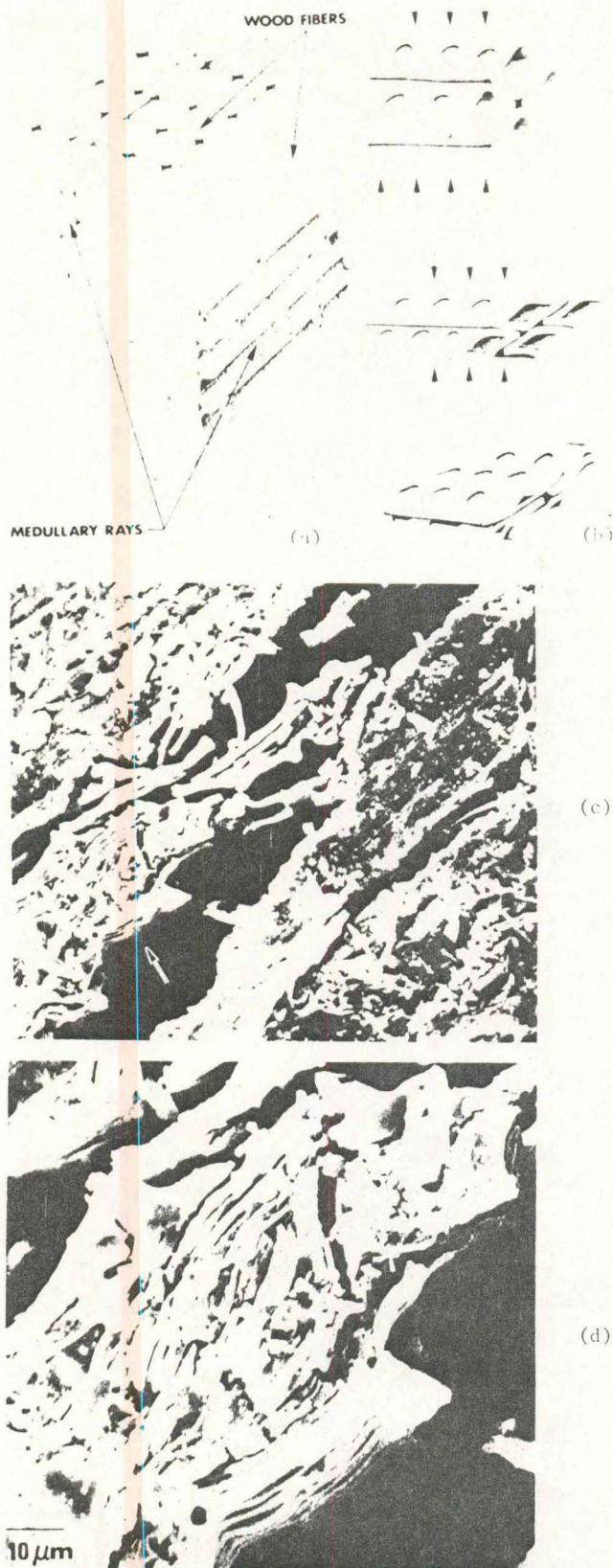


Figure 1. An insight into the relative organization of the microstructural constituents of coal as well as the effect of chemical treatment on their separation and fragmentation is derived from Figs. 1a-d.

(a) A schematic of longitudinal pitted wood fibers shown in relation to the radial medullary rays of a stem (or branch, etc.). In this view hollow elongated longitudinal wood fibers (with spherical openings found along the length of these fibers) are shown running vertically. The radial medullary rays are shown in this diagram running at an angle from lower left to upper right of this cross sectional view.

(b) The plant material comprising coal is compressed and subsequently coalified. Various degrees of compression in these three schematics are related to an actual specimen in Fig. c and d. In this case, the schematic is of a group of four longitudinal pitted wood fibers which have fallen over (corresponding to bedding features) and shows the direction of compression of the four hollow cells which have circular pits forming horizontal rows on the cell surfaces. The middle schematic indicates an intermediate stage in the compression of the above cells. The lower schematic shows a final compression stage where the cells have been crushed and somewhat distorted. This stage is seen for features of an actual sample in Fig. c and d.

(c) Wedge shaped fragment (inertinite) of region 2 located within Fig. 2. Notice the fragmentation due to the chemical comminution treatment (anhydrous liquid ammonia) is strongly controlled by the macerals and maceral boundaries. The Star mine sample has been tilted so that both side and bottom features of the coalified plants can be seen. The portion of the features closest to the arrow corresponds to the bottom of a layer of pitted wood fibers, whereas most of the field of view of this micrograph corresponds to an end-on view of the longitudinal pitted wood fibers (coal bedding features). The arrow corresponds to the magnified region seen in Fig. d.

(d) Magnified view of the region indicated by the arrow in Fig. c. This is a side view of the compressed longitudinal pitted coalified wood fibers, and this can be seen as the physical manifestation of the lower schematic of Fig. b. The lower right quarter of the micrograph corresponds to the flattened elliptical features, viewed at a steep angle, which were originally the pits on the wood fibers. Refer to Fig. 2 for details of the pits.

the coal reacts. Pyrite alteration products are very distinct from untreated pyrite. Studies on Star mine coal comminuted with a solution of sodium hydroxide in methanol showed similar results, and the coal fragments were about 1/50cm in diameter.

Microstructural studies of Star coal treated with acetone showed fragmentation into submillimeter particles and clear separation from such



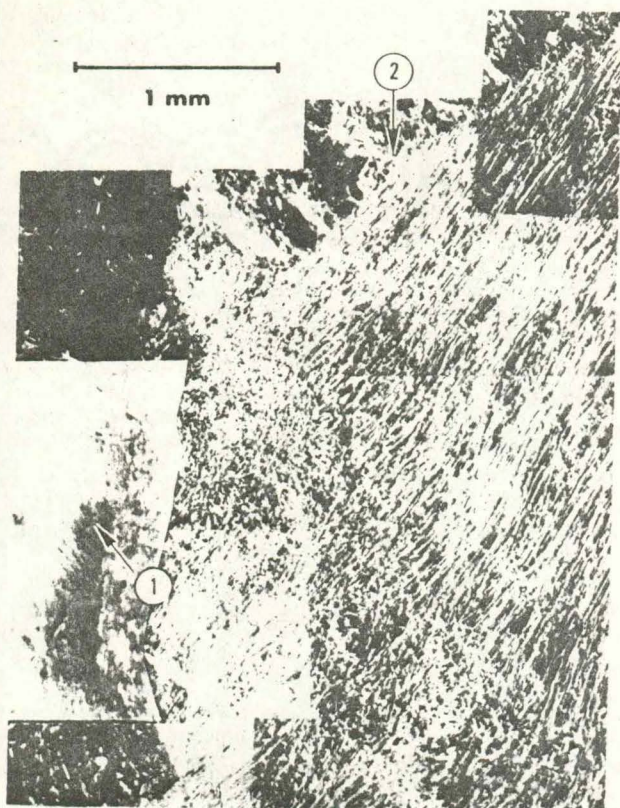


Figure 2. Top of fresh fracture surface of untreated coal sample (Star mine) corresponding to a high magnification view of the top of the coal seam. Two regions are identified on this micrograph. Region 1 is a surface which is relatively lower than that for most of the field of view. Region 1 corresponds to the longitudinal pitted coalified wood fibers (trending from the point of the arrow up toward the left) and is shown at higher magnification in Fig. 3, whereas region 2 ties in features seen in the higher magnification micrograph of Fig. 4. Most of what is seen in this view (representative region 2) corresponds to radial medullary rays seen trending from lower left to upper right in this photograph. An edge corresponding to highly compressed fibers between the pitted fibers and the medullary rays is seen, for example, in the region near the "1" on this figure.

material as gypsum. A solution of acetone to which solid carbon dioxide was added was relatively ineffective in breaking up coal specimens until the  $\text{CO}_2$  in solution had vaporized at which point results similar to those for acetone alone were obtained. Liquid nitrogen treatment of coal showed no major changes.

Reliability of Chemical Determinations of Sulfur, Especially of Organic Sulfur

It is well-known that sulfur is present in a variety of inorganic combinations such as iron

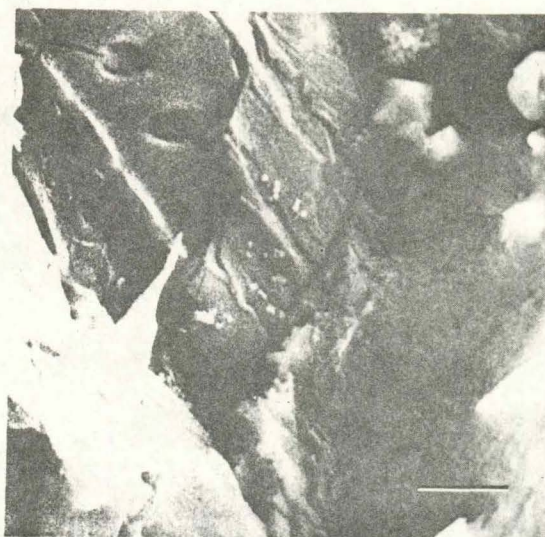


Figure 3. This figure provides information on maceral constitution. Shown are longitudinal pitted fibers (left half of photo) and highly compressed material for which microstructural detail is absent (right half of photo). Notice the correspondence with the schematic of Fig. 1a. Also compare the distinct features of this region with those of region 2 of Fig. 2. Rows of pits on cell wall surfaces are seen. The pits on the walls of the cells are approximately  $6 \mu\text{m}$  in diameter. Scale bar is  $10 \mu\text{m}$ .



Figure 4. This is a higher magnification view of region 2 of Fig. 2, and shows detail of the radial medullary rays (primarily as a side view of the rays). Compare the relative smoothness of these cell features with the pitted features of Fig. 3. The uppermost left corner is near the tip of arrow 2 in Fig. 2. Note the deposit of micrometer size pyrite crystals. Scale bar is  $10 \mu\text{m}$ .



pyrites and gypsum, but there is little exact knowledge of the forms in which it exists in organic combination. Organic sulfur is present in all coal; it is that part of the total sulfur which is neither chemically determined sulfate sulfur (generally attributed to gypsum) nor chemically determined pyritic sulfur.<sup>13-31</sup> There appears to be no clear relationship between pyritic and organic sulfur contents on the basis of published literature on this topic; however, findings in this report contribute some insight into this problem.

Sulfur in coal exhibits an importance out of proportion to its concentration, which is usually low. Its importance is related principally to corrosion problems in combustion equipment, to slagging of combustion or boiler equipment, and to pollution. Thus, sulfur data have a high priority in the evaluation of coals, and are used as guides to successful commercial processing of coal. The total sulfur value is commonly specified in coal contracts. Three other types of sulfur values may be reported: pyritic sulfur, sulfate sulfur, and organic sulfur. A general rough rule of thumb for coal is that the sulfur in coals is distributed approximately equally between inorganic and organic forms, regardless of the total sulfur content; however, this generalization is of little value for describing Iowa coals where the pyritic content is greater than the organic sulfur content. It will be shown that a good portion of the "organic" sulfur may be the micrometer size pyrite and small frambooids (10-40 $\mu$ m). The quoted pyritic sulfur content of coals refers mainly to the finely disseminated small crystals and frambooids. Sulfate sulfur is generally very low. Organic sulfur is computed (not chemically determined) simply by subtracting the sum of the pyrite and sulfate sulfur from the total sulfur concentration. Uncertainties in the chemical analyses for any of the sulfur factors take on great importance as they relate to standards which may actually vary throughout the U.S. depending on the coal burned and the way that the sulfur is distributed in the fuel.

There is little direct evidence (most of it questionable and derived from certain high sulfur coals) to establish how the organic sulfur is combined. There are inconsistencies in having to account for the distribution of the sulfur in coal between the inorganic and organic types.<sup>27</sup> Sufficient contradictions and large uncertainties exist in published organic sulfur values to suggest implementation of new analytical techniques, as well as to question just what most of the organic sulfur is.

The reliability and confidence levels obtained in microscopic analyses have been well documented.<sup>12,32-35</sup> Accuracy of microscopic maceral analysis of coal depends on the regularity of the occurring organic component (e.g., a coefficient of variation of the mean of several

percent); for pyrite - of the order of the pyrite content<sup>33</sup>, 15% average error for pyrite.<sup>12</sup> Accuracy will be low. Scanning electron microscopy offers an improvement in discrimination, size evaluation, and assessment of the extent of frambooids.

Consider the following information obtained for a channel sample from the Lovilia mine ("deep" mine) and for a channel sample from the Star mine ("surface" mine). First, compare the distribution of pyrite between three forms in the mines (colloidal size single crystals, frambooids ... various size agglomerations of single crystals, and larger pyrite masses) given in the following table:

Table 1. Distribution of Pyrite Between Forms

|                                | Lovilia mine,<br>Iowa | Star mine,<br>Iowa |
|--------------------------------|-----------------------|--------------------|
| Single crystal                 | 7.5%                  | 21.1%              |
| Frambooids                     | 6.1%                  | 10.9%              |
| Other larger,<br>massive forms | 86.4%                 | 68.0%              |
|                                | 100.0%                | 100.0%             |

This, coupled with how the various forms are distributed with depth in a particular mine, provides an interesting basis for some general comments. On the basis of chemical analyses and SEM analyses, most of the sulfur seems to be accounted for by the various forms of pyrite. For the Lovilia mine, the pyrite is highly concentrated at the top of the seam and this rapidly tapers off with depth in a seam (the bottom 50% exhibits almost no pyrite). In strong contrast, the Star mine pyrite is more widely distributed. A significant fraction of the pyrite is present as colloidal crystals and as frambooids (generally <40 micrometers in diameter).

Second, the proportion of pyrite in various size ranges offers an insight into difficulties in pyrite removal by conventional techniques as well as considerations for establishing the degree of confidence in precision and accuracy of sulfur determinations in coal by conventional chemical analytical techniques. Some of this information is presented in Table 2.

Table 2. Proportion of Pyrite in Certain Size Ranges

| <u>Lovilia mine</u> |                               |
|---------------------|-------------------------------|
| 50%                 | <300 $\mu$ m                  |
| 30%                 | < 76 $\mu$ m (i.e., 200 mesh) |
| <u>Star mine</u>    |                               |
| 50%                 | <45 $\mu$ m                   |
| 57%                 | <76 $\mu$ m (i.e., 200 mesh)  |



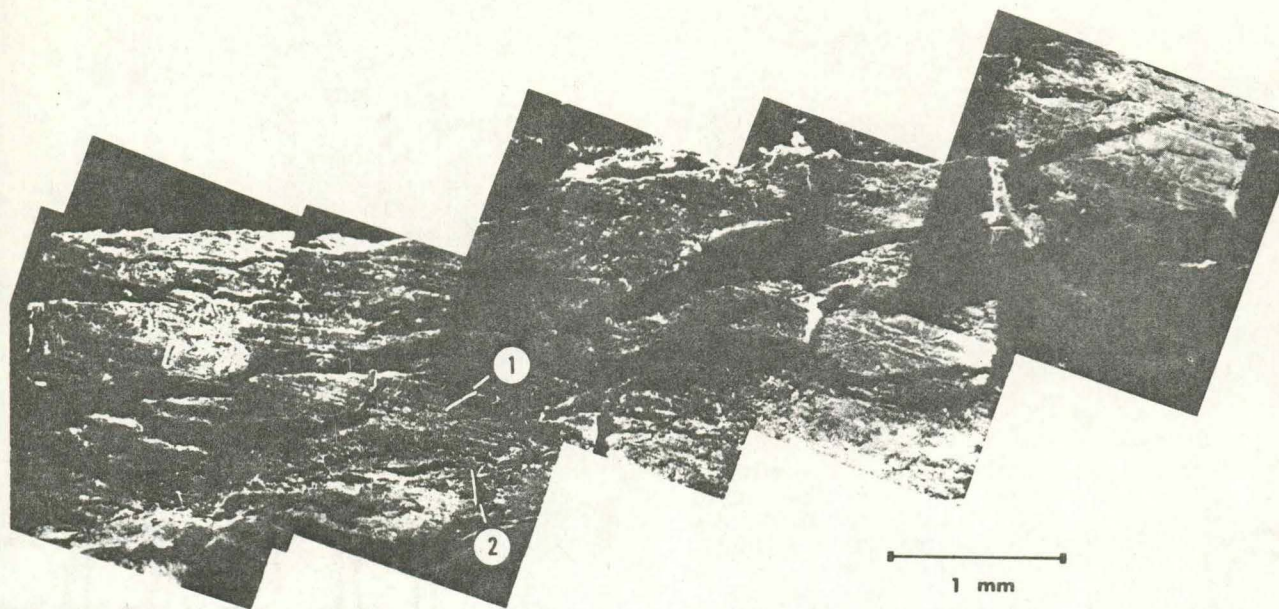


Figure 5. Star mine coal sample comminuted with anhydrous liquid ammonia. Scanning electron microscope image (25kV). Region 1 is seen at higher magnification in Fig. 6. Region 2 is shown at higher magnifications in Figs. 1c and 1d. The coal fragments in association with constituent macerals and pyrite deposits. Separation can occur on a very fine scale, down to the cellular level.



Figure 6. Fracture pattern through a deposit of pyrite crystallites in chemically comminuted coal of region 1 in Figure 5. Pyrite crystals are indicated by the arrow.

In Table 2, two items are of primary interest: 1) the size (particle diameter) below which 50% of the pyrite is present in the seam, and 2) the amount of pyrite present that could pass through a 200 mesh sieve. From these data, it is not surprising that the Star mine coal would be difficult to clean with so much pyrite

being present in a very small size range. The amount of pyrite present of a size of 76 micrometers or less in diameter is of direct practical interest. Most utilities in the U.S. crush coal to <200 mesh just prior to combustion. Thus, the significance of this information relates to the potential for additional sulfur removal at a power plant after final coal crushing. There may be a very important potential present to decrease the coal sulfur content by removal of the very fine sulfur bearing phases (predominantly pyrite) at this stage.

To show variations observed in scanning electron microscope secondary electron images, Figure 7 is included. This figure is recorded as a photographic strip and represents microstructural detail for the Mich mine (Iowa; lower seam). The strip is seen as a function of depth in the seam. This pictorial presentation is useful for showing the variation of maceral detail as well as the distribution of pyrite crystallites and framboids (and occasionally, gypsum) with depth. Pyrite framboids are easily recognized. Most of the individual crystallites seen are pyrite.

The practical implications of Figure 7 are basically two: 1) size, shape, orientation, and distribution features for macerals and coal constituents such as pyrite are very variable within a coal seam, and 2) ASTM test procedures for sulfur determinations<sup>26</sup> stipulate that the material be ground to pass a 60 mesh screen. This corresponds to particle sizes  $\leq 250$  micrometers. Taking into account the scale bar of



Figure 7, it is clear that in a particle size of 250  $\mu\text{m}$  most of the pyrite is encapsulated by relatively acid resistant organic material. Neither dilute HCl nor dilute  $\text{HNO}_3$ , the acids used as leachants in these tests, has a noticeable effect on the organic material of the coal as confirmed by scanning electron microscope observations as well as determinations by other techniques referred to in the literature.<sup>23, 36, 37</sup>

In Figure 8, the concept of encapsulation is shown on an individual micrometer size pyrite crystal basis. Notice the single pyrite crystals within individual remnant plant cells.

Methods for determination, difficulties and precautions, limitations, and uses for sulfur analyses are discussed by Fieldner and Selvig<sup>15</sup> and Rees.<sup>25</sup> The effect of time of digestion of pyrite by nitric acid has been examined by Belcher and Spooner<sup>29</sup>, and the effect of particle size (-60, -200, and -400 mesh) on pyrite removal has been compared by Kuhn, Kohlenberger, and Shimp.<sup>30</sup> Limits of repeatability for the ASTM methods are for total sulfur,  $\pm 0.10\%$ , for pyritic sulfur,  $\pm 0.05\%$ , and for sulfate sulfur,  $\pm 0.02\%$ . However, a question of accuracy exists concerning the complete removal of finely-dispersed pyrite by extraction with nitric acid. Incomplete removal would yield low pyritic sulfur values and erroneously high organic sulfur values.

From Figures 4-8 it can be seen that the pyrite is finely-dispersed for these samples. If the ASTM procedures for sulfur determination were inadequate for coals of this type because of the inability to account for all of the pyritic sulfur, it is clear that standards could vary throughout the country depending on the coal types burned. Coals of this type would have a large uncertainty associated with sulfur values when compared with coals in which the average pyrite particle size was much larger ( $\gg 250 \mu\text{m}$ ) and therefore more likely to be removed by the nitric acid.

To test for the completeness of removal of pyrite in a standard pyritic sulfur determination, the solid residue remaining after treatment with  $\text{HNO}_3$  was examined by scanning electron microscopy and energy dispersive analyses for several samples. The organic sulfur values were high (ranging from 3 to 5%) and correspond to the sulfur remaining in the solid residue. Energy dispersive X-ray analyses were performed on each sample. Pyrite was found in each residue sample showing incomplete dissolution of the pyrite by the  $\text{HNO}_3$  treatment for the ASTM standard determination of pyritic sulfur. Thus the organic sulfur values were high and uncertain. Figure 9 shows a scanning electron micrograph of a region in which the analysis was performed on one of the samples. It is clear that the pyritic framboids were incompletely dissolved in the  $\text{HNO}_3$ .

## Future Work

Several research areas are suggested for further study:

1. Pyrite: distribution, occurrence, nucleation, growth, nature and origin of morphology; but most important, how to get it out of the coal either prior to or during combustion
2. Development of a more complete and comprehensive "petrographic" classification scheme (correlation of microstructural features with properties: combustion, electron spin resonance, and so on) by SEM, scanning transmission electron microscopy, and energy dispersive X-ray microanalyses.
3. Microstructural control of chemical comminution as related to *in situ* mining applications
4. Microstructural control as related to chemical comminution and beneficiation to upgrade various types of coal; evaluate maceral breakup and separation capabilities; develop economical processes to break up coal to approximately a micrometer average size to facilitate pyrite removal
5. The "organic" sulfur problem: pulverize specimens to less than 37  $\mu\text{m}$  (less than 400 mesh)
6. Develop treatment schemes for the crystallite pyrite refuse either during pyrite removal or subsequent to pyrite separation.

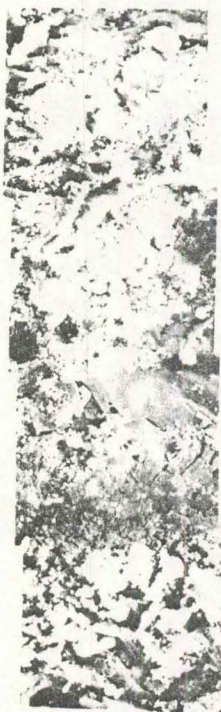


Figure 7. The ASTM tests for sulfur require that coal pass a 60 mesh sieve ( $\leq 250 \mu\text{m}$ ). As can be seen in these photos, pyrite is distributed on a finer scale, and thus in many cases, might not leach out. This contributes to an erroneous organic sulfur determination resulting in very large uncertainties. At 18 mm below the top of the lower coal seam, pyrite concentrations of framboids and single crystals are seen. Scale bar is 40  $\mu\text{m}$ . The photograph is oriented as the coal seam would be viewed in cross section at this location. (Mich mine)



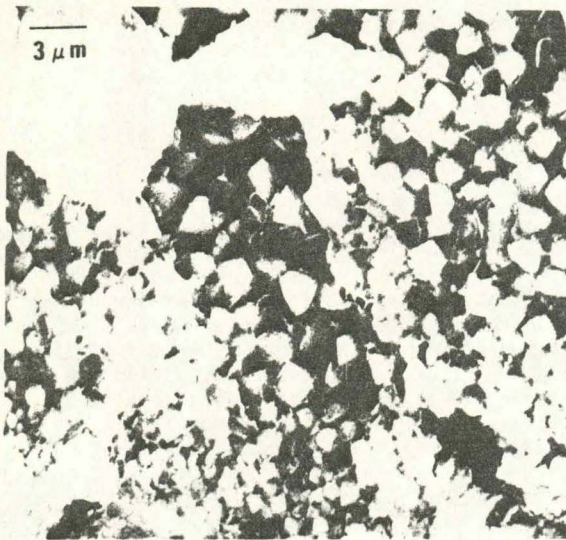


Figure 8. Fresh fracture surface showing pyrite crystals within cellular network. Notice, for example, in the lower central region of the photograph that the individual pyrite crystals were encapsulated by cell walls as indicated by fractured cell walls around crystals and by crystals visible below cell wall coverings. (Mich mine)

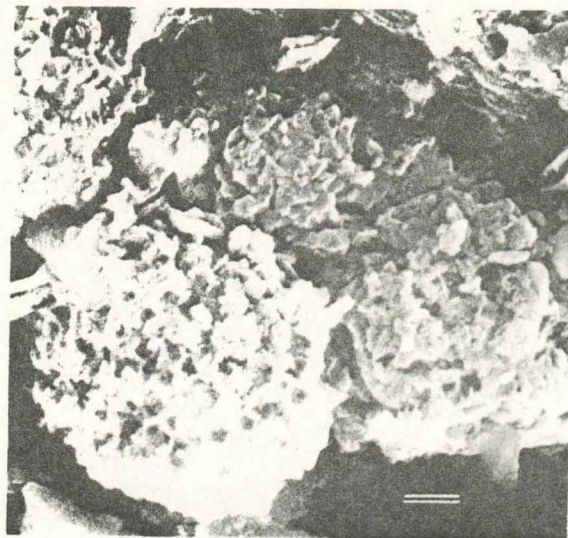


Figure 9. Scanning electron micrograph of residue from a sample which had been leached with  $\text{HNO}_3$  (ASTM method). The  $.15 \mu\text{m}$  diameter spherical form in the lower left portion of the micrograph is an incompletely leached pyritic framboid. Features of this type show that significant uncertainties are associated with organic sulfur values. Scale bar is  $3 \mu\text{m}$ .

#### Summary

Several practical implications of the research findings can be summarized as:

1. useful insight has been gained in understanding the difficulty of sulfur removal using conventional techniques
2. Microstructural-chemical information suggests an important basis of coal cleaning variations to be expected from mine to mine.
3. Large uncertainties are to be expected for standard sulfur chemical determinations (much of the pyrite may never get into solution and this can contribute to large inaccuracy in total sulfur, pyritic sulfur and organic sulfur values)
4. Coal is generally crushed to <200 mesh at most utilities, but is then burned directly without attempts to clean it at this stage. For this size (<76 micrometer diameter particles), due to the presence of large amounts of pyrite at this stage, innovative cleaning techniques may offer an important potential to upgrade the coal through additional sulfur removal.

#### Acknowledgment

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#### DISCUSSION WITH REVIEWERS

**Reviewers I and II:** Can you comment on the feasibility of determining complete pyrite size distributions within representative coal volumes (which would include the framboids as well), and do you think a determination of such distributions for various coal deposits might be useful?

**Author:** Results of pyrite type and size distributions are shown in Figures A and B. Details of the proportionation of pyrite for these two mines (Lovilia and Star) for various size ranges are shown in Figure A. From these figures, the percentage of pyrite (less than a particular size of pyrite) present can be obtained. Also in this figure (d) for example, for the Star mine, the single crystal form of pyrite predominates below 1  $\mu\text{m}$  particle diameters; framboids are an important form of pyrite over a size range of a few micrometers to 30  $\mu\text{m}$  diameter, and slightly more than 50% of the pyrite present of a diameter of 5 to 10  $\mu\text{m}$  is of the framboidal form. This complements the information presented in Tables 1 and 2. The proportion of pyrite in various size ranges offers an insight into difficulties in



pyrite removal by conventional techniques as well as considerations for establishing the degree of confidence in precision and accuracy of sulfur determinations in coal by conventional chemical analytical techniques.

This, coupled with how the various forms are distributed with depth in a particular mine (refer Figure B), provides an interesting basis for some general comments. Most of the sulfur seems to be accounted for by the various forms of pyrite. For the Lovilia mine (shaft mine; top of coal seam is approximately 260 feet below the surface), the pyrite is highly concentrated at the top of the seam and this rapidly tapers off with depth in a seam (the bottom 50% exhibits almost no pyrite). In strong contrast, the Star mine (strip mine with coal approximately 42 feet below the surface) pyrite is more widely distributed. A significant fraction of the pyrite is present as colloidal crystals and framboids (generally <40 micrometers in diameter). Distribution information for the three forms of pyrite (single crystals, framboids, and other larger, massive forms) and the total of all pyrite forms is shown as a function of depth in the Lovilia mine (Figures a-d) and in the Star mine (Figures e-h). This represents the first complete energy dispersive X-ray analyses on a micrometer size scale for continuous seam series of face-channel coal specimens. These results indicate a clear difference in the way the three forms are distributed.

Reviewers II and III: How were the figures in Tables 1 and 2 obtained? Were individual grains in each micrograph counted?

Author: Considerable characterization work has been performed on these samples (several reports and papers are available from the author). Phase identification was established by X-ray diffraction (broad survey; useful for identifying major phases down to a few % detection level), by optical microscopy (e.g., birefringence; reflectance), by energy dispersive (ED) X-ray analysis (e.g., Fe in FeS<sub>2</sub> compared with Zn in ZnS<sub>2</sub>) and by electron microprobe wavelength dispersive (WD) X-ray analysis (especially the distribution of C, Ca, S and Fe to distinguish between calcite and pyrite infillings within the C-cell walls, or massive vitrinite). For the ED and the WD analyses, a thin carbon coating is recommended. This prevents some of the difficulties in discriminating Au from S in ED analysis, for example, and still permits an evaluation of the primary carbon distribution by WD analysis.

In the specific samples discussed, the major phases present in the coal are pyrite (FeS<sub>2</sub>, cubic) and calcite (CaCO<sub>3</sub>, trigonal) with minor amounts of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O, monoclinic), quartz (SiO<sub>2</sub>) and marcasite (FeS<sub>2</sub>, orthorhombic), and trace amounts of sphalerite (ZnS, cubic) and galena (PbS<sub>2</sub>, cubic). The reflectivity of pyrite is well documented, and can be used as a standard for reflectivity measurements on other minerals. Using an optical microscope, polished surfaces of pyrite and marcasite are examined in polarized light (pyrite appears to be isotropic or weakly birefringent). The other minerals have charac-

teristic responses which will not be detailed as we are primarily concerned with pyrite. Sulfides such as pyrrhotite (Fe<sub>7</sub>S<sub>8</sub>-FeS, monoclinic (pseudo-hexagonal), occurring mainly in basic igneous rocks) or troilite (FeS, found in meteorites) are not found in these materials as related to the pressure-temperature conditions required for their occurrence, for example.

In the SEM analyses both the particular crystal form and the ED X-ray information quickly narrow the possibilities for crystal identification on fracture surfaces. Fe alone is a good indicator of the pyrite, and Fe and S are monitored along with Zn and Pb for the trace sulfides occasionally found. Since cell fillings are generally calcite or pyrite, ED analyses for Ca, Fe and S are of value (especially on fairly smooth surfaces where the crystal shapes are not obvious).

From a particular channel sample, complete polished specimens were prepared for optical microscopy to note all pyrite 50 μm or greater in diameter along a single line from top to bottom of a seam. The detailed occurrence and distribution of maceral types were also recorded. To check the representativeness, three line measurements were made across each block (D. Biggs). WD analysis and SEM were used to study certain polished samples especially in cases to establish the presence and distribution of pyrite crystals which were found to fill cell features.

From the same channel sample, a complete set of fresh fracture specimens was prepared from material in close proximity to the surfaces which were polished for optical microscope analysis. Thus, SEM analyses were performed along a continuous line from top to bottom of a seam on fracture surfaces. In this way complete data for each form of pyrite (crystal, framboid, recrystallized mass) were recorded on a micrometer scale basis to provide very detailed volume fraction data for each form and for the total amount of pyrite in the coal. This was recorded with depth and numerous complementary ED analyses. The data were then grouped to provide the distribution information of Tables 1 and 2 and Figures A and B. Also this permitted the evaluation of the fractional contribution of each form to the total pyrite present. This technique is very time consuming; however, it is necessary to be able to see the trends with depth as well as the significant presence of very fine pyrite (single crystals and framboids). This approach is slower than point count analyses or automated analyses techniques, but offers a superior reliable approach to give insight into phase type and distribution. This is particularly important in studying such a complex material.

Reviewer I: In your concluding section entitled Future Work, you indicate that getting the sulfur out of the coal is most important. What additional SEM analysis and characterization do you see as contributing directly to the sulfur removal problem in addition to those features already illustrated and discussed in the results presented?



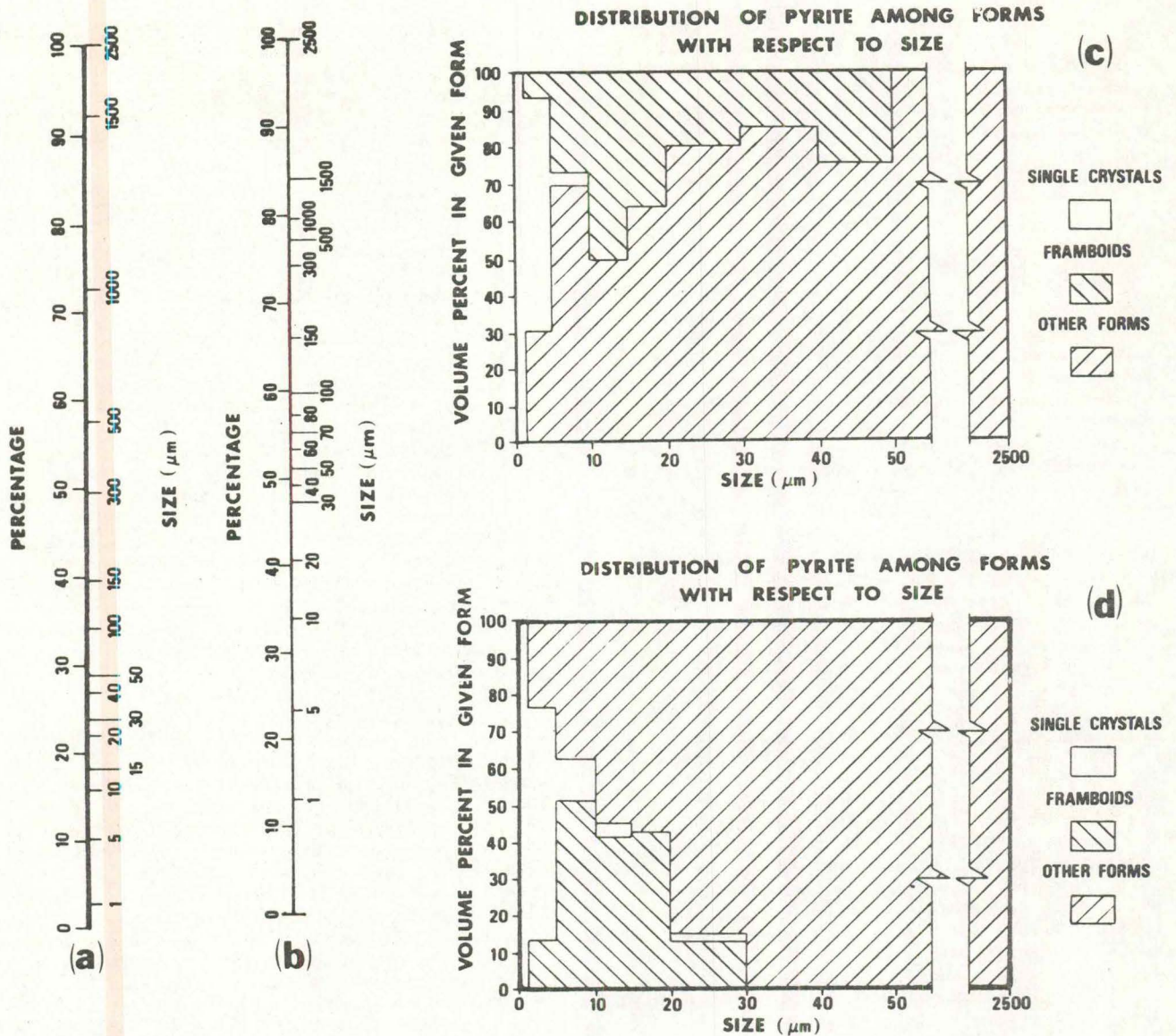


Figure A. Distribution of pyrite in the Lovilia and in the Star mines.  
 (a) Proportionation of pyrite for the various size ranges observed for the Lovilia mine (percentage of pyrite less than a particular size). For example, 30% of the pyrite is less than 76 μm in diameter (i.e., 200 mesh).  
 (b) Proportionation of pyrite for the various size ranges observed for the Star mine (percentage of pyrite less than a particular size). For example, 57% of the pyrite is less than 76 μm in diameter (i.e., 200 mesh).  
 (c) Distribution of pyrite in the Lovilia shaft mine seam among three forms: single crystals, framboids, and other larger, massive forms. The distribution is shown with respect to size (in micrometer intervals) for the range of sizes observed.  
 (d) Distribution of pyrite in the Star strip mine seam among three forms: single crystals, framboids, and other larger, massive forms. The distribution is shown with respect to size (in micrometer intervals) for the range of sizes observed.



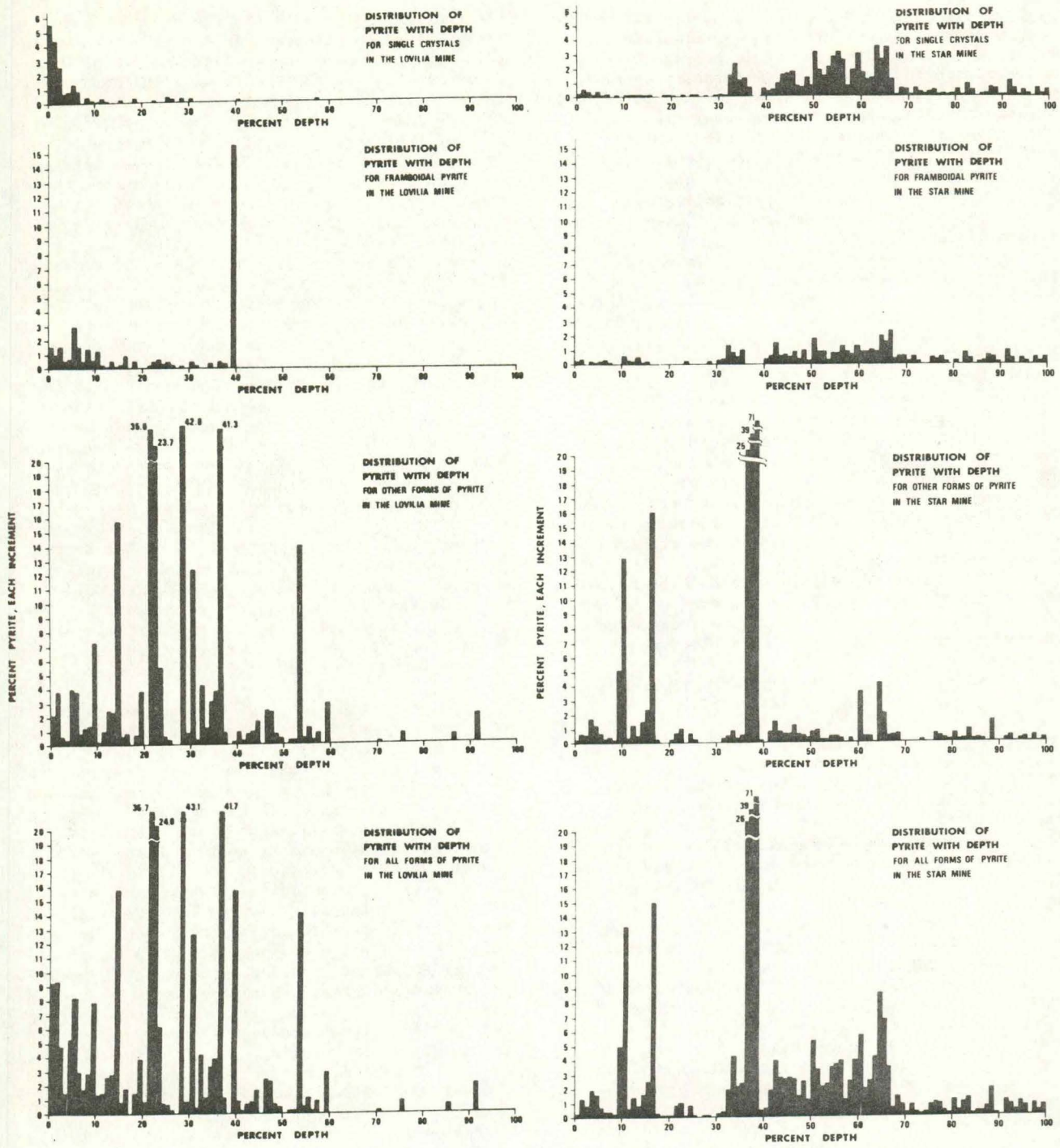


Figure B. The distribution of pyrite in the Lovilia mine (a-d) and in the Star mine (e-h) with depth in a seam. Data are shown for each mine in four ways: single crystals; framboidal formations; other larger, massive forms; and total contribution of the three forms for that mine. For example in graph b, for the 1% interval at a depth of 39 to 40% of the thickness of the seam, almost 16% of the material in this portion of the seam is framboidal pyrite. The Lovilia seam thickness is 183.0 cm, and the Star seam thickness is 105.1 cm.



Author: Extensive SEM examinations of strip and deep mined bituminous steam and metallurgical coals as well as lignites should provide a working approach to correlating important property-behavior parameters of interest in the following areas: phyteral and maceral-mineral structural characteristics; nature and distribution of pyrite; aspects of mechanical and chemical comminution (break-up), beneficiation, and conversion and associated desulfurization improvements; and precision and accuracy of chemical determination of sulfur.

Auger analyses will be of use in characterizing surface films (e.g., in Figure 9 the pyrite particles are partially dissolved; factors affecting dissolution may be better understood).

In work describing the chemically induced break-up of coal (chemical comminution) where almost forceless break-up may be induced, various environments such as liquid ammonia, liquid methanol, trichloroethylene, methylene chloride, etc. can be investigated in detail. The basic mechanism of chemical comminution is not fully understood. The cleavage occurs preferentially along coal-mineral interfaces, and it seems mineral matter may be separated without as small a particle size reduction as required by mechanical break-up.

Agglomeration of particulates and of relative types of particulates can be studied by SEM-ED analysis and related to solution treatments to change the surface character of pyrite, for example.

Desulfurization schemes in liquefaction of coal are under study by SEM-ED analyses.

Reviewer III: One of the most difficult problems associated with TEM and SEM work is the question of sample representation. Considering the total volume of sample you examined and the total volume of the coal seams you seek to characterize, do you feel you have seen enough under the SEM to generalize the occurrence of microcrystallites of pyrite to other coal deposits? To low sulfur deposits?

Author: A broad range of coals of various rank are being studied. Large differences in local and regional variability in coal seams exist. However, it is useful to detail microstructural features of coal to develop an understanding of the presence and distribution of pyrite in the coal. Suggestions can be offered to improve coal treatment schemes for removing sulfur and potential ash components. This paper may serve to further outline advantages now foreseen which are dependent on knowledge of coal constitution and functional behavior of separable constituents. The importance of micrometer size pyrite in certain coals is clearly established. Data of the type presented offer the potential to establish new lines of approach to solving current technical problems in the utilization of coal.

Reviewer II: How would the author propose to apply the textural data that he has collected in this study and data on the distribution of pyrite in coal to the Ilok fine grinding process in which liberation of the pyrite from the coal is a definite problem though the order of magnitude of the crystals would seem to suggest this as a real possibility. I would also be interested in hearing of any practical examples that the author might be able to think of in which fine grinding of coal or coal-related products to the level described, that is to minus two microns, has been accomplished on a large scale. There has been some work on fine grinding which indicates that a significant explosion hazard may exist in fine grinding coal and coal-related products down to such fine levels.

Author: In 1910 Rudolf Diesel developed the idea of burning finely ground coal directly in engines. The difficulty was to prepare fine enough coal. By 1940 Hans Rohrbach patented a pulverizing process to obtain 4 micrometer diameter coal for this application. In the late 1950's another modification was developed, the Rohrbach-Ilok Attrition Mill. The 4 micrometer coal is still a paper idea. Briefly, the Stephen Krajcovic-Ilok process is to break coal down to this size by fracturing and heating coal in a multichambered mill. The very general proposal is that both inorganic and organic sulfur could be removed, leaving the carbon; however, no details of the proposal have been released and no process has been demonstrated on a small-scale basis.

Commercial devices exist to pulverize coal to a micrometer diameter size (e.g., Retsch, Düsseldorf, West Germany); techniques of interest for potential large scale application in the utility industry such as pneumatic fragmentation have been demonstrated in bench scale operations and offer a possibility for practical scale-up (e.g., L. Buechler and R. Eccles, Systems Research Laboratories, Dayton, Ohio).

The work presented in this paper shows the significant potential for removing almost all of the pyrite in certain coals. Coals vary in the relative proportion of inorganic (primarily pyrite) and organic sulfur. For example, numerous analyses indicate that the general characteristics of both Iowa and Illinois<sup>28</sup> coal are that the pyritic sulfur exceeds the organic sulfur (roughly, a 3 to 2 ratio). Thus, important amounts of sulfur could potentially be removed prior to combustion (and to scrubbing of off gases when and if appropriate). Even the high sulfur coals of Iowa might then meet the State's environmental standards for currently operating utility plants. Also, the situation exists in certain coals, that not all the pyrite may appear in the chemical analyses. This would be manifested as erroneously high organic sulfur values. This would be the result of the pyrite distribution factors discussed in this paper. The pyrite larger than a micrometer in diameter would then be in a form appropriate for separation from the coal macerals.



It is important to note that not only pyrite and potential ash components might be separable, but also that maceral types might be separable as well. If the vitrinite (high BTU material) could be separated from the inertinite and exinite, the coal would be upgraded significantly.

The explosion hazard of fine particulate coal can be controlled by using appropriate gas concentrations or by subsequent agglomeration, for example.

Reviewer II: How would you propose to separate the sulfur-bearing components in coals after the fine grinding of the type you propose, and what practical means would you suggest and how could they be implemented? Have such techniques been tested in previous pilot plant or laboratory types of evaluations and what were the results of those evaluations?

Author: Potential techniques are under intensive study at this laboratory and at many other facilities. These include the use of cyclone separators, centrifuge modifications (e.g., Sharples; Zonal), precipitation-floatation, oil agglomeration and mechanical flow modifications. A primary consideration is economics. Data are needed for comparative energy consumption among processes, or for the % recovery of coal which is required for a particular level of pyrite removal, for example. The components can be separated, and current studies are providing a practical framework for potential large-scale implementation.

Reviewer I: Have you made any observations of pyrite crystals and pyrite aggregates in comminuted coal? Certainly it would be of interest, and a very simple problem using SEM to investigate the pyrite particulates in relation to coal aggregate size.

Author: Yes. This is a complex problem to establish mechanisms, and a variety of systems are being studied.

Reviewer I: In the comminuted form, some fraction of the ash in coal might also be separated along with the sulfur. If SEM studies of comminuted coal have been performed, there might be some observations of ash or other noncombustible inclusions. Have you made any observations of such inclusions and their size distributions?

Author: This work is far from being complete. Such studies will require the contributions of many investigators. My work has concentrated on pyrite. Potential ash components such as clays will vary with the coal being studied, and introduce another level of complexity to SEM-ED analyses.

Reviewer III: In Figures 5 and 6, you show a pyrite vein and indicate that the crack has formed in association with the pyrite treatment. How can one be certain this crack was subsequent to the formation of the pyrite? It seems to me that the micrograph strongly suggests the opposite and that the pyrite may have possibly been deposited along the walls of the crack after it opened.

Author: The original surface was studied in detail prior to treatment by using an optical microscope, and the matching untreated surface was also viewed by SEM for a variety of magnifications. The natural boundaries, especially where inorganic phases occur, tend to separate usually without significant dissolution of the coal matrix or the inorganic phases (observed on a micrometer scale for liquid ammonia, for example). The size distribution of the fragments is influenced by bedding features, the comminuting solution, and the exposure time.



Additional discussion of "Applications of Scanning...." by J. W. Neasham continued from p. 108.

Reviewers IV and V: Will the vacuum in the specimen chamber and the potential heating effect of the electron beam tend to damage the oil shale kerogen, resulting in erroneous morphological characteristics, and could the contorted kerogen in Figure 20 be the result of such damage? Was the cold stage of value in observing kerogen?

Author: Examination of kerogen for extended periods of time under the electron beam has never detected morphological changes which might result from heating. The rate of kerogen thermal decomposition at temperatures below approximately 600°F is very low, and localized sample surface heating effects from the electron beam (raster pattern) are thought to be far below this temperature level.

We have not used a cold sample stage to examine kerogen on the SEM.

Reviewer IV: Were Figures 13 and 14 obtained with an SEM voltage of 10 kev?

Author: The particular photomicrographs illustrated in Figures 13 and 14 were obtained with an SEM beam voltage of 25 kev. Our SEM work with uncoated rock samples, however, has shown that photomicrographs of comparable quality to those in this report can be obtained with a 10 kev beam voltage.

Reviewer V: Do you have any procedure that you can recommend for examining oriented thin sections or chips in the SEM/ED; particularly those containing elongated grains and oriented micropores?

Author: We can maintain a particular sample orientation in the sample chamber by scratching a reference mark on the rock sample or thin section surface and continually monitoring this reference point at lower magnifications.