

Development of Computer-Controlled Scanning Electron Microscopy (CCSEM) Techniques for Determining Mineral-Maceral Association

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I. INTRODUCTION

The solutions to several important problems in coal science depend critically on being able to determine mineral-maceral association. Perhaps the most obvious of these is physical coal cleaning. Liberated or nearly liberated mineral matter will normally be most easily removed in advanced physical cleaning processes, such as froth or microbubble flotation or oil agglomeration. Although the oxidation state of the coal and mineral particle surfaces also plays an important role,⁽¹⁾ it is generally felt that liberation is the primary factor in determining coal cleanability by physical methods.

A second topic that is receiving increasing attention is the effect of mineral-maceral association on ash slagging and fouling behavior during coal combustion.⁽²⁾ Slagging behavior is usually more severe under reducing combustion conditions than under oxidizing conditions. This is primarily because ferrous iron derived from pyrite reacts more readily with clay minerals and quartz to form molten slag than does ferric iron.⁽³⁾ Thus, quantitative determinations of the amounts and types of mineral matter and carbonaceous material associated together in coal particles may be useful in predicting slagging distributions on a particle by particle basis.

Recently, Straszheim, Markuszewski and coworkers⁽⁴⁾ have succeeded in making the first quantitative measurements of the association of mineral matter with the organic coal matrix using CCSEM. By mounting the crushed coal in carnauba wax, which has an average atomic number that is somewhat lower than coal, they were able to clearly distinguish between the mounting medium and the coal in the backscatter electron imaging (BEI) mode. A CCSEM automatic image analysis (AIA) procedure was used to determine the amounts of different minerals and the amount of organic matter ("coal") associated with each particle on a particle by particle basis. This allowed them to determine the amounts of each major mineral (pyrite, kaolinite, illite, etc.) associated with various amounts of coal (0 - 20%, 20 - 40%, etc.).

In the current research, we have investigated mineral-maceral (the term "maceral" is used here in the generic sense) association using a somewhat different approach. Specifically, we are attempting to combine the use of a digital imaging technique called "microimaging"^(5,6) with ternary and quaternary representations^(7,8) of particle chemistry determined from energy dispersive x-ray (EDX) spectra obtained using a light element detector. The results indicate that this approach is rather promising.

II. EXPERIMENTAL PROCEDURE

Ternary diagram representation of CCSEM EDX data has proven to be very useful in allowing graphic interpretation of trends that develop in particle chemistry as a result of various types of processing or reaction. Previously, we have used this method for investigating reactions that occur between different minerals during coal combustion^(7,8) and carbonization⁽⁹⁾. Briefly,

three elements are selected and one or more thresholds are set as a basis for admitting a given particle into the data set. For example, in the current investigation, mineral-maceral association is of primary interest, so we have examined C - S - Fe diagrams, which are representative of pyrite - coal maceral association. The approximate chemical compositions of the particles are calculated from the raw EDX spectra using the background-subtracted peak areas. Several variations on this basic presentation proved to be very useful. For example, the sum of two or more elements can be used as a vertex and the diagram C - (Fe + S) - (Al + Si) is effectively a coal - pyrite - clay/quartz diagram. Additionally, the number or percentage of particles in a given compositional increment can be displayed in a four dimensional graph, which provides a much more vivid representation of the particle-by-particle compositional trends. Such frequency-composition dependence may also be presented in binary form across any linear strip of the ternary diagram. Finally, particle size histograms for any user-selected composition range are readily generated in a cursor-window mode.

The coals investigated in this study were Illinois #6 samples obtained from the Argonne Premium Coal Sample Bank (APCSB)⁽¹⁰⁾ and from the University of Kentucky Center for Applied Energy Research (CAER).⁽¹¹⁾ The APCSB coal was hand ground to 100% -200 mesh (<75 microns) before investigation; a simple laboratory cleaning process was used for this sample, which consisted of floating the coal in carbon tetrachloride and centrifuging. The CAER sample was micronized to <10 - 20 microns and cleaned using a column flotation process discussed in detail elsewhere.⁽¹²⁾

One method of sample preparation used was essentially identical to that developed by Straszheim et al.,⁽⁴⁾ that is, the coal powder was mixed with molten carnauba wax, pressed into a pellet in a hydrostatic press, and polished using petrographic methods with diamond paste (< 1 micron) finish. The second method consisted of dispersing the particles directly onto a beryllium (Be) substrate.

The basic CCSEM analysis is conducted in the usual manner,^(13,14) by moving the electron beam over the sample in discrete increments, measuring the backscattering electron intensity (BEI) at each stopping point, and collecting an energy dispersive x-ray spectrum (EDX). In the current work, the discrimination level discerning particles from background was set low enough to allow coal maceral material to be detected, as opposed to the usual CCSEM mode for coal^(13,14), in which only minerals are detected. The EDX spectra were then collected over a period of 15 seconds while the electron beam was rastered over the whole coal particle. Since a light element detector was used, the resulting EDX spectra were characteristic of whole coal particles, including both mineral and maceral material. An additional novel feature of the current work was the simultaneous acquisition and storage on disks of digital images of all particles, a procedure called microimaging,^(5,6) which will be addressed in a future paper.

III. RESULTS AND DISCUSSION

The principal results are best summarized by perspective plotted phase diagrams in which number percentage is shown as a fourth, vertical dimension. The C-S-Fe diagrams in figures 1 and 2 illustrate the degree of liberation of pyrite in the -200 mesh Illinois No. 6 coal and the extent of its removal in a simple laboratory cleaning operation, centrifugation in carbon tetrachloride. These diagrams have been drawn using a rather low threshold value of C + S + Fe > 15%; therefore most of the coal particles examined are represented in the diagrams. It is seen by comparison of Figures 1 and 2 that the two sample preparation methods gave results that are qualitatively similar. Presumably, the samples prepared by dispersal of the coal particles onto beryllium give EDX spectra that are more characteristic of the coal particle surfaces than the polished carnauba wax samples, since the electron beam penetrates only a few

microns into the coal and the particles in the polished specimens are cross-sectioned, on average. This suggests that the distribution of pyrite on the surfaces of the crushed coal particles is not markedly different from its bulk distribution for this particular coal.

It is evident that most particles containing < 30 - 40% C on the basis of the EDX spectra have been removed in the cleaning operation. It must be noted, however, that the compositions shown in these diagrams have not been corrected for preferential absorption of the low energy carbon X-rays (277 eV) relative to the absorption of the higher energy sulfur (2308 eV) and iron (6404 eV) X-rays, which occurs primarily in the thin window of the light element detector. Such corrections are important if we wish to use such diagrams as quantitative composition guides. For example, the particles having compositions along the C-S border represent coal particles that contain primarily organic sulfur. With appropriate calibration of the relative strengths of the C and S X-rays, such data could be used to make direct measurement of the organic sulfur content on a particle by particle basis.

An alternative way of presenting the data is shown in Figures 3 to 5. Here, the corners of the diagram are C, (Fe + S), and (Al + Si), and the threshold is taken as 80%. As seen from the number of particles plotted, this encompasses nearly the whole data set. With this representation, the vertices for these diagrams are effectively coal (that is, mineral free coal particles), pyrite, and clay plus quartz (Figures 3 - 5). This representation has the advantage of illustrating the efficiency of a given cleaning process for removing all of the major minerals in coal, not just pyrite. It is seen from the perspective plotted ternary diagrams (Figures 3 - 5) that the two methods of sample preparation give results that are significantly different for the clay/quartz abundance in the as-crushed coal. Presumably, this indicates that this coal fractures most easily along clay-coal interfaces. This would cause the sample prepared by dispersion of the coal particles onto beryllium to exhibit a higher percentage of clay/quartz rich particles than the polished carnauba wax-mounted specimen, since the EDX spectra are derived primarily from the top 1 - 2 microns of the coal. The results for the cleaned coals are again qualitatively similar for the two sample preparations, with most of both the pyrite and clay/quartz having been removed.

A sample of Illinois No. 6 coal was also examined before and after a column froth flotation cleaning process described in more detail elsewhere.⁽¹²⁾ Only the sample preparation method of dispersing coal particles onto a beryllium disk was used for these samples. Results for the feed coal, which is micronized to < 10 to 20 microns, are shown in the top half of Figure 11. It is seen that these coal particles exhibit a heavy preponderance of clay minerals, again indicating a tendency of the coal to fracture at coal-clay interfaces. In the column flotation process, both the ash and pyritic sulfur are dramatically reduced, as shown by the perspective ternary diagram in the bottom half of Figure 5.

Such CCSEM diagrams could be very useful in predicting cleaning behavior of individual mineral species. One can easily envision cases where it is easier to remove pyrite than clays and quartz and vice-versa. Certain types of cleaning operations could then substantially change the slagging and fouling behavior of a coal.

IV. SUMMARY AND CONCLUSIONS

In this research, the feasibility of determining mineral-maceral ("maceral" is used in the generic sense) association using four-dimensional ternary composition - number percentage diagrams generated from CCSEM data has been investigated. The results indicate that this approach is promising. The degree of liberation of pyrite and its removal during physical cleaning is perhaps most clearly illustrated by perspective plotted C - S - Fe diagrams with number percentage shown as a fourth vertical ordinate (Figures 1 and 2). Alternatively, a C -

(Fe + S) - (Al + Si) ternary diagram is effectively a coal - pyrite - clay/quartz ternary. Four dimensional frequency of occurrence - coal - pyrite - clay/quartz diagrams (Figures 3 - 5) illustrate the degree of liberation and removal during cleaning of most of the principal minerals in coal. They also indicate a marked tendency of Illinois #6 coal to fracture at coal - clay interfaces.

Future papers will discuss other aspects of this work, including particle size distributions, direct measurement of organic sulfur content and variation, and analysis of stored digital particle images.

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REFERENCES

1. Attia, Y.A.; Elzaky, M.; and Ismail, M.; Processing and Utilization of High-Sulfur Coals III, Eds., R. Markuszewski and T.D. Wheelock, 1990, Elsevier, 187 - 196.
2. Helble, J.J.; Srinivasachar, S.; and Boni, A.A.; Idealized Combustion Determination of Ash Particle Formation and Surface Stickiness; Task 8 - Model Development and Integration, Phase I Final Report, U.S. DOE Contract No. DE-AC22-86PC90751, March, 1990, pp.8-1 to 8-195.
3. Huffman, G. P.; Huggins, F. E.; and Dunmyer, G. R.; Fuel, 60 585-597 (1981).
4. Straszheim, W.E.; and Markuzewski, R.; Energy & Fuels 1990, 4, 748-754.
5. Schwoeble, A. J.; Dalley, A. M.; Henderson, B. C.; and Casuccio, G. S.; Journal of Metals, August 1988, pp. 11-14.
6. Casuccio, G. S.; Schwoeble, A. J.; Henderson, B. C.; Lee, R. J.; Hopke, P. K.; Sverdrup, G. M. "The Use of CCSEM and MicroImaging to Study Source/Receptor Relationships." Receptor Models in Air Resources Management, Air Pollution Control Association, Pittsburgh, PA, 1989.
7. Huffman, G.P.; Huggins, F.E.; Shah, N.; and Shah, A.; Prog. in Energy & Combustion Sci., 1990, 16(4), 243-252.
8. Shah, N.; Huffman, G.P.; Huggins, F.E.; Shah, A.; Mershon, W.J.; and Casuccio, G. "Graphical Representation of CCSEM Data for Coal Minerals and Ash Particles." To be published in ACS Div. of Fuel Chem. Preprints, Atlanta Meeting, April, 1991.
9. Huffman, G. P.; Huggins, F. E.; Shoenberger, R. A.; Walker, J. S.; Gregor, R. B. and Lytle, F. W.; Fuel 65, 621-632 (1986).
10. Vorres, K.S. Users Handbook for the Argonne Premium Coal Sample Program, Oct. 1, 1989.
11. Samples provided by B.K. Parekh of the University of Kentucky Center for Applied Energy Research.
12. Parekh, B.K.; Groppo, J.G.; Stotts, W.F.; and Bland, A.E.; Column Floatation 88, Chapt. 24, 227-233.
13. Huggins, F. E.; Kosmack, D. A.; Huffman, G. P.; and Lee, R. J.; Scanning Electron Microscopy/1980/I, 531-540, SEM Inc., AMF O'Hare, Chicago, IL 60666, USA.
14. Huggins, F. E.; Huffman, G. P.; and R. J. Lee, ACS Symposium Series No. 205, pp. 239-258, Coal and Coal Products: Analytical Characterization Techniques, Ed., E. L. Fuller, Jr., American Chemical Society, 1982.

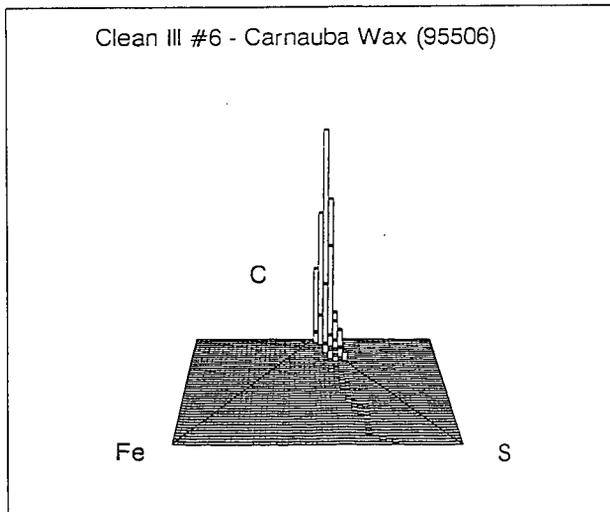
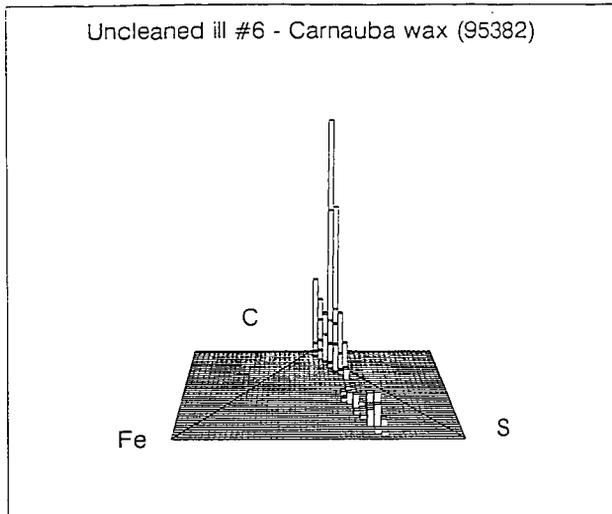


Figure 1. CCSEM number percentage (vertical ordinate) versus composition in a ternary C-Fe-S diagram for raw (top) and cleaned (bottom) Illinois #6 coal mounted in carnauba wax.

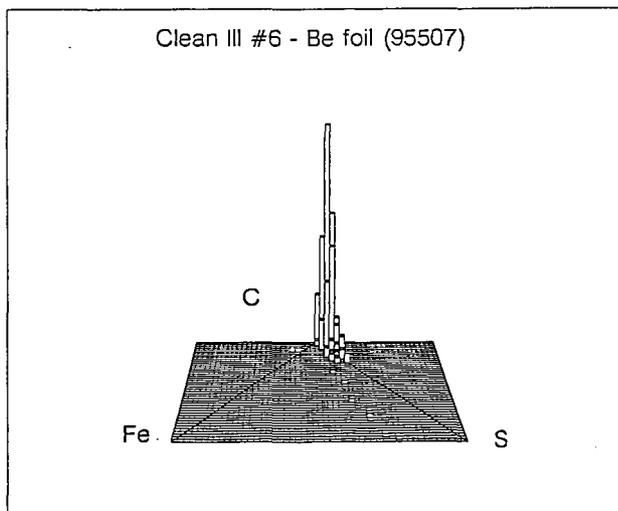
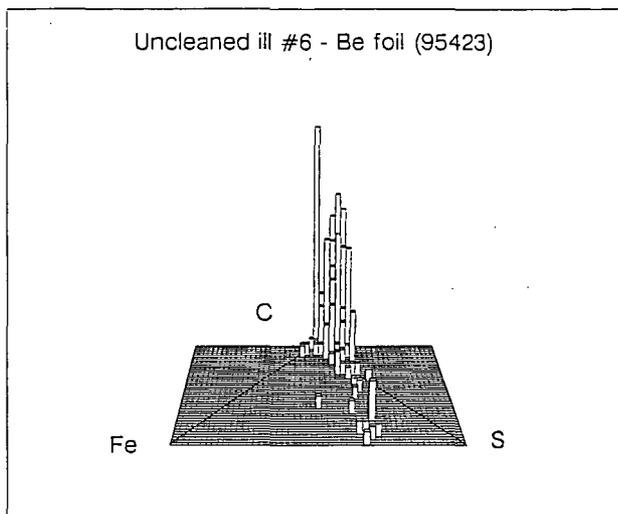


Figure 2. CCSEM number percentage - composition data for raw and cleaned Illinois #6 coal dispersed on beryllium.

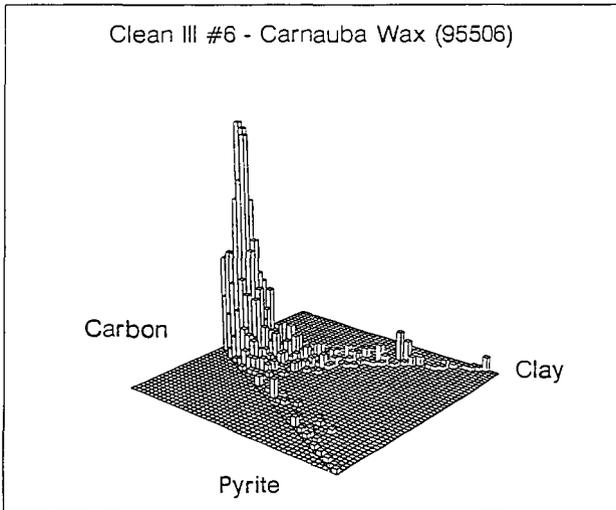
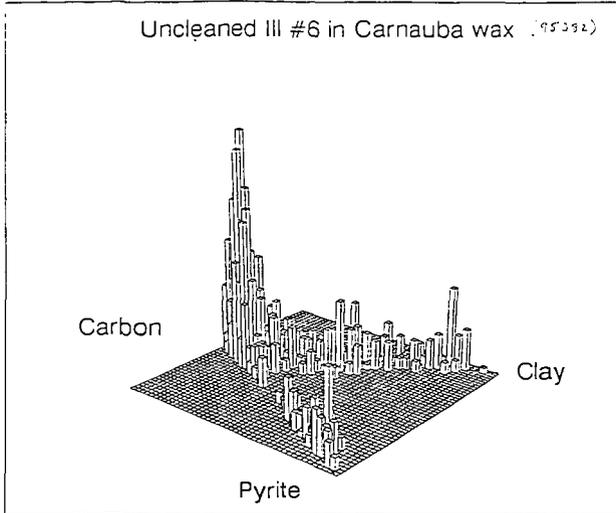


Figure 3. CCSEM number percentage vs. composition in a coal (C) - pyrite (Fe + S) - clay/quartz (Al + Si) diagram for raw (top) and cleaned (bottom) Illinois #6 coal mounted in carnauba wax.

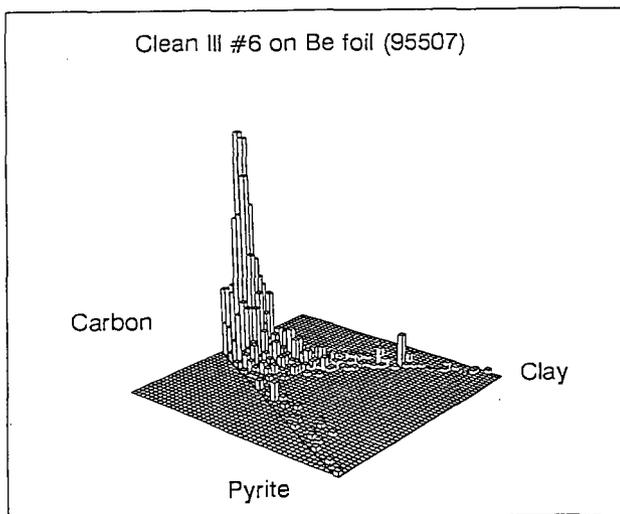
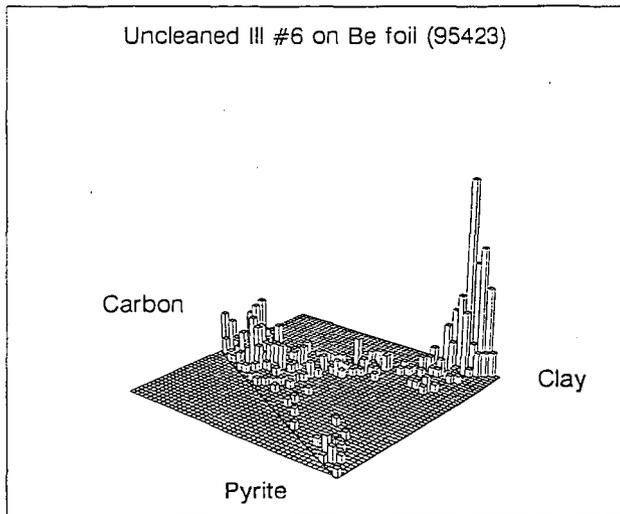


Figure 4. CCSEM number percentage vs. "composition" in a coal-pyrite-quartz/clay diagram for raw (top) and cleaned (bottom) Illinois #6 dispersed on beryllium.

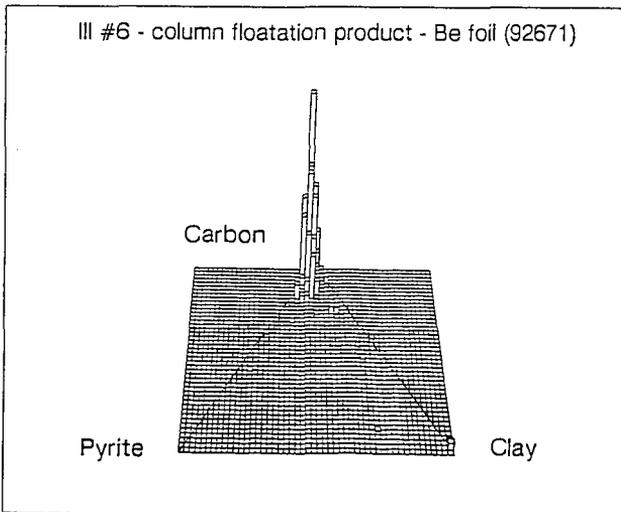
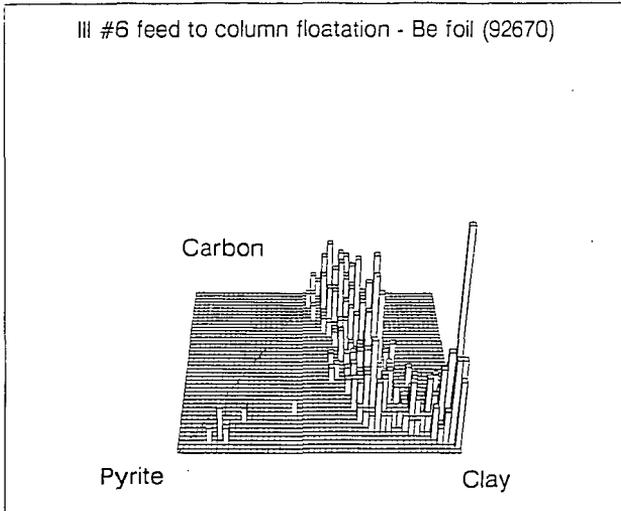


Figure 5. CCSEM number percentage vs. coal-pyrite-clay/quartz composition for Illinois #6 coal before and after column floatation cleaning.