

AUTOMATED IMAGE ANALYSIS OF THE ASSOCIATION OF ASH-FORMING  
MINERAL MATTER WITH COAL PARTICLES

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ABSTRACT

Scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS) and automated image analysis (AIA) techniques were used for the characterization of the association of ash-forming mineral particles with coal particles. Mineral matter can be found as grains free from the coal matrix or embedded within particles of coal in various proportions and in a range of compositions of the mineral phases. Such mixtures will influence the chemistry of the ash particles generated from the coal, so that the behavior of the ash can be quite different from the behavior predicted by the bulk ash chemistry. SEM-based AIA conducted for several thousand composite coal and mineral particles provides data which can be used to predict the range of ash particles that will be produced from a coal. Results of analyses are reported for a number of bituminous coals.

INTRODUCTION

Over the years, changing practices in coal combustion have led to a need for more detailed characterization of the ash-forming mineral matter in coal. Traditional characterization methods have been performed on bulk samples of ash derived from burning off the coal at relatively large particle sizes (1). That ash is compacted during fusibility tests, so that there is considerable opportunity for interaction of the ash particles and so the ash may be expected to behave in accordance with its average chemistry. Such a test is suited to the ash environment in a stoker-fired boiler where the ash particles do have extensive contact with other ash particles. However, in many modern pulverized coal boilers, ash particles are more likely to result from single particles of coal and remain relatively unaffected by other ash particles. Thus, ash behavior might be expected to be more dependent on the mineral/ash chemistry of individual particles rather than on the bulk ash chemistry. This hypothesis appears to be born out by operating experience where coals of similar bulk ash chemistry can lead to significantly different ash behaviors (2).

Scanning electron microscopy (SEM) along with energy-dispersive x-ray spectroscopy (EDS) offer many insights into coal and mineral particles which should be helpful in predicting ash behavior. These techniques are able to characterize samples for size and elemental composition on a scale appropriate for determining particle ash chemistry. In conjunction with automated image analysis (AIA) techniques, the above analyses can be automated to provide statistical significance in the results.

For the past few years, methodologies have been developed and applied at the Ames Laboratory and elsewhere for the characterization of mineral grains in coal (3,4,5). In much of that work, attention was focused on the fundamentals of measuring particle size and determining a mineral particle's identity from its x-ray spectrum. Less work has been directed toward determining the association of the minerals grains with the coal. Moza et al. (3) reported rather interesting efforts to measure the average elemental content of composite coal and mineral particles. However, there were certain limitations to their approach and the work was not followed up. At the Ames Laboratory, we have continued to develop AIA methodology for the determination of the association of

mineral grains with coal. Work has focused on determining the weight fraction of the mineral and coal phases within the particles. The results have been used primarily in the field of coal preparation to predict the partitioning of phases during physical cleaning (6). However, the data on particle mineral content could just as well be presented in a manner suitable for predicting the nature of the resulting ash particles based on information about their mineral precursors.

#### METHODOLOGY

Coal samples were prepared for analysis by embedding approximately 2 g of coal in 10 g of carnauba wax according to procedures described elsewhere (7). Samples were embedded at the particle size of interest (i.e., approximately 80% passing 200 mesh for pulverized coal). The ground coal was mixed with molten carnauba wax and the mixture was poured into a cylindrical mold where it was allowed to cool and harden under pressure. The cylindrical pellet was cut vertically along its axis to expose a section through the coal and mineral particles. The exposed section was polished using standard petrographic procedures and then coated with 150 Å of carbon to provide electrical conductivity during SEM examination.

Samples were characterized with an image analysis system consisting of a JEOL JSM-840A electron microscope, a KEVEX model DELTA V energy-dispersive x-ray analyzer, and a LeMont Scientific model DB-10 automated image analyzer. Samples were imaged using the backscattered electron (BSE) signal at magnifications of 100, 200, and 500 times, and with a resolution of 512 pixels (i.e., sampling points) across the field of view. The multiple magnifications were used to provide sufficient resolution across the range of particle sizes present in the sample. Coal and mineral particles were identified, based on the brightness of their BSE signal, and were then characterized for particle area, diameter, perimeter, and other basic parameters. The electron beam was then returned to the center of each mineral particle and the x-ray analyzer was used to collect an x-ray spectrum (2 to 4 seconds acquisition time). The integrated intensities were determined for 20 common mineral-forming elements ranging from oxygen to zinc, and those intensities were compared with up to 20 sets of mineral definitions based on the relative abundance of the elements to identify the mineral phase (4,5). Minerals were identified as the first phase with elemental definitions matching the measured intensities.

The size and elemental data for each coal and mineral phase were recorded on magnetic disk for later data reduction. Significantly, the LeMont Scientific image analysis software recorded the data for associated coal and mineral particles together in such a manner that it was possible to determine the association of particles. For a composite assemblage, the measured areas of each of the phases present were used in conjunction with tables of densities of the phases to calculate the weight fraction of each phase within the particle.

The above measurements were made for thousands of composite coal-mineral particles in order to achieve a measure of statistical reliability. It then remained to tabulate the particle data in a format that was of technological interest.

For this paper, 200-mesh samples of Upper Freeport and Pittsburgh No. 8 coals were used to illustrate the capabilities of the AIA measurements. The general characteristics of these coals are summarized in Table 1. Both coals are bituminous coals with about 15% mineral matter. The amount of pyritic sulfur varied and thus the pyrite fraction of the mineral matter was considerably different between the two coals.

Table 1. General characteristics of the Upper Freeport and Pittsburgh No. 8 coals (results are on a dry basis unless otherwise noted).

	Upper Freeport	Pittsburgh No. 8
Moisture <sup>a</sup>	1.74	3.50
Total S	2.36	4.27
Pyritic S	1.98	3.15
Sulfate S	0.02	0.12
Organic S	0.36	1.00
Ash	12.4	11.4
Mineral Matter <sup>b</sup>	14.9	14.4

<sup>a</sup> As-received basis

<sup>b</sup> From modified Parr formula  $MM=1.13(Ash)+0.47(Pyr.S)$  (ref. 8, in which MM = mineral matter)

#### RESULTS AND DISCUSSION

Typical measurements available using the current technology are shown in Table 2 for some selected coal-mineral particles. The identity of each phase is given along with its area, average diameter, and significant x-ray signals. These results were used to calculate the abundance of phases within the particle as shown in Table 3. The total area of each phase was multiplied by that phase's density to estimate its weight contribution. These tables illustrate that a wide range of particles are encountered in coal, including nearly pure coal particles with very small, isolated mineral particles, coal particles with a large amount of a single mineral phase, and coal particles with a mixture of two and more minerals in a wide range of relative abundances.

The particles can be classified in any number of ways depending on the characteristics of interest. Currently, particles are tabulated according to the weight fraction of the combined minerals within them. This results in distributions as shown in Table 4 and in Figures 1 and 2. Such distributions indicate significant differences between these coals regarding the closeness of association of the mineral phases with coal. Minerals are more closely associated with the coal matrix in the Pittsburgh sample than they are in the Upper Freeport sample. Also, relatively more of the mineral matter in the Pittsburgh coal is pyrite which is somewhat more closely associated with the coal than it is in the Upper Freeport coal. Relatively more of the mineral matter in the Pittsburgh sample consists of quartz, clays, and other silicates.

These formats were developed with utility for density-based coal cleaning in mind. The particle density can readily be calculated, given the mineral composition of each particle. Predictions can then be made about the amount of sample and which phases and particles are likely to report to the clean coal stream.

However, weight fractions calculated from AIA results could also be used to calculate the overall elemental composition for the particles. Such compositions could then be used in conjunction with ash modeling efforts to predict ash particle characteristics.

For the prediction of ash characteristics, the particles may be treated in two ways. One model of ash formation assumes that each mineral grain will

Table 2. Typical SEM-AIA measurements for selected particles of Upper Freeport coal.

Phase	Area ( $\mu\text{m}^2$ )	Avg. Diam. ( $\mu\text{m}$ )	X-ray elemental intensities (as % of all x-rays)
Coal	561	26.7	none
Coal	1650	45.8	none
Pyrite	89	10.6	S=81, Fe=19
Coal	11	3.8	none
Quartz	30	6.2	O=4, Si=93, K=3
Illite	36	10.5	O=4, Al=33, Si=49, K=14
Coal	17	4.7	none
Coal	362	22	none
Misc.	10	3.7	O=5, Al=95
Quartz	62	8.9	O=3, Si=97
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Total	2267	53.7	
Coal	1320	41.0	none
Kaolinite	20	5.1	O=7, Al=43, Si=50
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Total	1340	41.3	
Coal	181	15.2	none
Iron Sulfate	157	14.2	O=9, Al=7, S=68, Fe=16
Quartz	24	5.6	O=5, Si=95
Coal	347	21.0	none
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Total	709	30.0	
Coal	59	8.7	none
Coal	81	10.2	none
Iron Sulfate	821	32.3	O=12, S=62, Fe=26
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Total	961	35.0	

Table 3. Abundance of coal and mineral phases for the particles shown above in Table 2 (as weight % of particle).

	Identified Phase and its Density ( $\text{g/cm}^3$ )						
	Coal 1.30	Pyrite 5.00	Fe Sulfate 3.00	Quartz 2.65	Kaolinite 2.65	Illite 2.75	Other 2.50
Particle 1	100.0	---	---	---	---	---	---
Particle 2	78.9	13.2	---	7.2	---	2.9	0.7
Particle 3	97.0	---	---	---	3.0	---	---
Particle 4	56.0	---	38.6	5.4	---	---	---
Particle 5	6.9	---	93.1	---	---	---	---

Table 4. Association of coal and ash-forming minerals in Upper Freeport coal as a function of particle mineral content.

Category	Mineral content %						Sum
	0	1-20	21-40	41-60	61-80	81-100	
Coal	55.05	22.42	5.42	2.53	1.37	0.33	87.10
Mineral Matter <sup>a</sup>	0.00	1.87	2.23	2.38	3.09	3.33	12.90
Total	55.05	24.29	7.64	4.91	4.46	3.66	100.00
<sup>a</sup> Where "Mineral Matter" includes:							
Pyrite	0.00	0.32	0.66	0.87	0.91	1.96	4.73
Fe sulfate	0.00	0.04	0.06	0.06	0.04	0.15	0.35
Kaolinite	0.00	0.30	0.28	0.38	0.18	0.11	1.24
Illite	0.00	0.25	0.28	0.40	0.44	0.16	1.53
Quartz	0.00	0.20	0.30	0.13	0.68	0.46	1.77
Silicates	0.00	0.52	0.47	0.46	0.67	0.39	2.51
Other	0.00	0.25	0.17	0.07	0.18	0.10	0.76

produce one mineral particle, while another model assumes that all of the mineral grains in a single coal particle coalesce to form a single ash particle. For either model, AIA results could be used to predict the overall composition and mass/size distributions of the ash particles. The appropriate phase diagrams could then be used to help predict the character of the ash particles. For example, some particles may contain clay particles along with pyrite. The iron could serve as a flux and lead to a low melting point (i.e., sticky) ash particle, whereas clay particles associated with quartz or with no other minerals could lead to more refractory ash particles.

Or again, predictions could be made using both scenarios. First, each mineral particle could be assumed to follow a known transformation during combustion, apart from the influence or contribution of other mineral grains in the same composite. For example, quartz by itself would be relatively unaltered during combustion, while pyrite would lose its sulfur and form a particle of iron oxide,  $Fe_2O_3$ . Secondly, for each composite particle, the mineral grains could be assumed to interact. The iron from pyrite might be expected to serve as a flux for clay particles and lead to a low melting point mixture when both are present in the same composite.

However, we are not currently involved in developing models of mineral transformations during combustion. Instead, we are involved in developing the unique capabilities of SEM-based AIA to provide the necessary data for those who are interested in modeling mineral transformations to ash. We leave it to other researchers to determine the relative importance of the various modes of production of ash particles, whether they are produced one per mineral grain, are produced one per composite particle, or are produced as a result of ash particles agglomerating during combustion. We do seek to provide reliable data as input for those models.

#### CONCLUSIONS

AIA is able to provide detailed characterization of ash-forming mineral particles which can be used as input to models of ash formation and behavior. Significant differences have been observed in the distribution of mineral particles in different coals in the areas of mineral abundance, mineral size distributions, and the extent of association of mineral particles with coal.

Since such differences exist, it is not surprising that coals behave in markedly different ways even though they have the same nominal ash chemistry.

Further development of AIA applications for the prediction of ash behavior is necessary. Particularly, more work needs to be done on preparing the results into formats that are directly applicable to ash modeling efforts. Perhaps elements of the ash models can be incorporated into the AIA programs to directly provide the desired results. Much work also needs to be done to validate results and predictions based on AIA results. There is nearly always concern over how well two-dimensional AIA measurements can represent three-dimensional reality. And the accuracy of the ash models themselves will need to be determined. Nevertheless, the combination of detailed AIA characterization and ash modeling should provide a much improved indicator of ash behavior than older methods of ash characterization which are less than appropriate in view of current combustion technology.

#### ACKNOWLEDGEMENT

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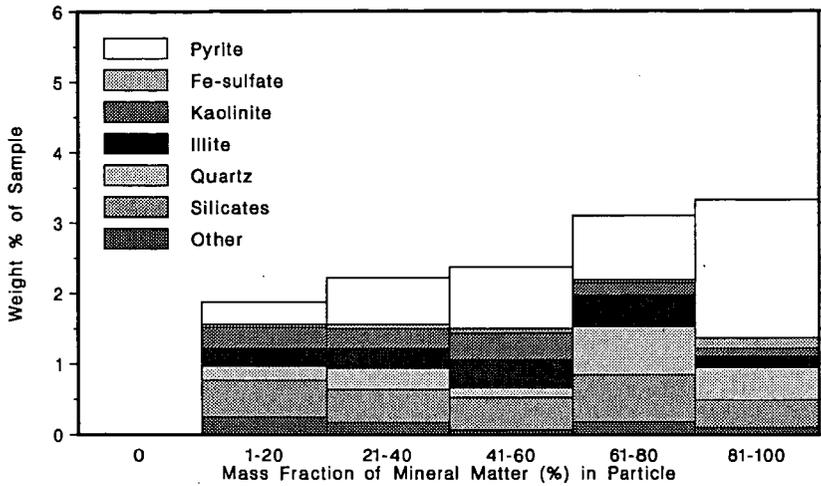


Figure 1. Distribution of ash-forming minerals in Upper Freeport coal as a function of particle mineral content.

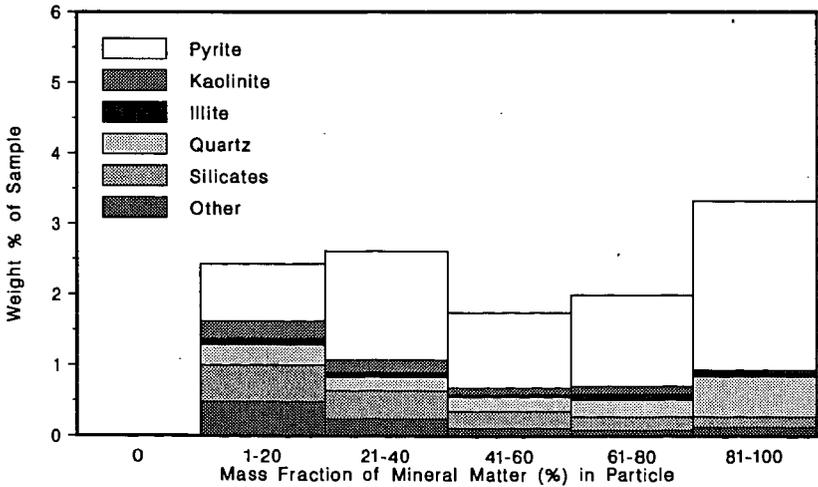


Figure 2. Distribution of ash-forming minerals in Pittsburgh No. 8 coal as a function of particle mineral content.