MINERAL TRANSFORMATIONS IN SELECTED COALS - SIZE AND COMPOSITION OF THE ASH

J.J. Helble, S. Srinivasachar, C.B. Katz, and A.A. Boni
PSI Technology Company
Research Park P.O. Box 3100
Andover MA 01810

ABSTRACT

The transformation of minerals during pulverized coal combustion has been examined by burning utility sized coals (70% < 200 mesh) in a laboratory-scale combustor. Experiments were conducted with several coals possessing different mineralogies, with particular attention paid to Kentucky #11 bituminous. Size and composition of the initial minerals and the resulting ash were measured by a variety of techniques, including computer controlled SEM, low temperature ashing, deposition on a cascade impactor, and optical (Malvern) particle size analysis. Results for the Kentucky #11 coal suggest a large degree of coalescence is occurring between illite, kaolinite, and quartz minerals, with occasional iron incorporation into the resulting glass. Partitioning of the acid-leachable potassium was found to split between incorporation into the glass and vaporization. For other coals, such as Beulah lignite, mineral fragmentation was inferred from the data, presumably due to large quantities of large (>40 microns) pyrite present.

BACKGROUND

Deposition of ash on heat transfer surfaces is the most costly problem associated with the combustion of pulverized coal. Although much research is currently focused toward obtaining a better understanding of the factors giving rise to deposition, current industry practice is to address the problem in an empirical manner which often proves unsatisfactory and inaccurate (1). In determining deposition indices, ash is treated as a homogeneous medium, possessing uniform properties. This neglects the fact that combustion generated ash is actually comprised of individual particles, of a wide variety of sizes and compositions. By treating the ash as disparate particles rather than as a homogeneous medium, it is possible that better deposition indices could be developed.

There are several components which must be addressed in determining the deposition behavior of an ash particle, and by extension, of a particular coal. Size, chemical composition and adhesive properties of the surface layers (i.e. stickiness) are all important considerations. The stickiness of ash particles has been addressed elsewhere (2,3); preliminary results of an experimental study of the factors giving rise to the observed size and composition distributions of ash are discussed herein. Several recent laboratory studies have utilized the size of the ash particles to infer the importance of various phenomena such as fragmentation, fines carry-over, and coalescence (4-9). Utilization of size information coupled with mineral and

ash compositional information for a particular coal to provide an overall picture of the important processes, is the focus of this study. Several U.S. coals and one Australian coal are being examined, with the results from one particular coal - Kentucky #11 bituminous - highlighted.

EXPERIMENTAL APPROACH

Combustion experiments were conducted in a laboratory scale drop-tube combustor which incorporates a gas-fired swirl-stabilized section on the front end to increase residence time and simulate particle concentrations present in an actual combustor. Details of this system are provided elsewhere (2). Ash particles were sampled isokinetically, quenched, and collected with a variety of techniques depending upon the desired information. Size distributions were obtained both by deposition on a Pollution Control Systems Mark III cascade impactor, and by filtration and subsequent sizing with a Malvern Instruments particle sizer. Chemical composition of coal minerals and individual ash particles was determined by computer controlled scanning electron microscopy (CCSEM) at the University of Kentucky.

RESULTS AND DISCUSSION

By comparing the initial distribution of minerals present in a pulverized coal with the final distribution of ash particles, it is possible to infer the major mechanisms of mineral transformation occurring. Kentucky #11 was chosen for this study, as it has finely disseminated minerals compared to other bituminous coals, with a relatively low degree of extraneous or excluded mineral matter. As it contains fairly large amounts of illite and kaolinite, it presents an ideal opportunity for examining the transformations undergone by clay minerals in the presence of carbon. The mineralogy of this coal is summarized in Table I.

TABLE I
Kentucky #11 Mineralogy and Ash Composition

Fuel Analysis*		Ash Analysis	
Fixed Carbon	41.9	SiO_2	45.8
Volatile	33.8	Al_2O_3	19.0
Ash	20.3	Fe_2O_3	20.4
Moisture	4.0	CaO	4.4
		MgO	0.9
Mineral Analysis		K_2O	2.5
		Na_2O	0.3
Quartz	19	SO_3	5.2
Kaolinite	8		
Illite	16		
Mix. Silicates	23		
Pyrite	24		

* for as-received coal

Mineral size distributions for this coal were obtained by two techniques: CCSEM analysis of the minerals in the utility grind coal, as well as Malvern analysis of a small sample of the low temperature ash. Results from these two measurements are compared in Fig. 1 with an ash particle size distribution, obtained upon combustion of the coal in 7% oxygen at 1500 K gas temperature. As the curves in the figure indicate, the mineral distributions agreed at small diameters, but varied somewhat at the larger mineral sizes. While the CCSEM indicates 80% by volume of the mineral matter to be < 13 microns in diameter, the low temperature ash measurement indicates that 80% of the mineral matter is less than 30 microns in size. As the two techniques measure size on a different basis (the CCSEM measures a cross-section and infers diameter, while the Malvern is a volume-based technique), this level of agreement is encouraging. Preliminary results with coals having a high percentage of extraneous mineral matter (Kentucky #9 bituminous and San Miguel Texas lignite) yields better agreement across the entire distribution.

Examination of the ash size distribution, measured by a combination of cascade impaction and Malvern techniques and also plotted in Fig. 1, reveals that upon combustion, a large degree of coalescence is taking place. This is evidenced by the uniform shift to larger particle diameters for the entire distribution. Although both char and mineral fragmentation may be occurring, the effects are lost when the utility grind coal is burned and the overall distribution examined. For this coal under these combustion conditions, mineral agglomeration and coalescence dominate.

Examination of the chemical composition of individual ash particles collected under these conditions also suggests that coalescence is the primary mechanism governing ash evolution. Figure 2 presents composition data for all ash particles containing potassium + silicon + aluminum in greater than 80% levels, excluding oxygen. Composition ranges for typical illite and kaolinite particles are also presented. Pure quartz can be assumed to occur at 100% Si on the diagram. Several conclusions can be drawn from this compositional information. First, it is evident that neither pure quartz, illite, nor kaolinite dominate the final ash. The resulting final ash composition is clearly a mixture of these three minerals. The compositions suggest that quartz is incorporated into both clay minerals, though the mixed silicates present in the initial coal are likely contributing as well. Analysis of the data on a particle by particle basis is currently under way to help resolve the effect of the mixed silicates. It is also interesting to note from the Figure that potassium levels do occasionally increase above the baseline present in the initial illite, but it is not a dramatic increase. This observation, coupled with fume measurements reported elsewhere (2), indicates that acid-leachable potassium present in the raw coal can vaporize in addition to being incorporated into the glassy ash particles.

The fate of the pyrite present in the coal can also be deduced from examination of the final ash composition. Mossbauer analyses of ash collected from combustion at two different oxygen levels are presented in Table II. It is evident that only a small portion of the iron is incorporated into a glassy phase under both oxygen levels. As anticipated, the level of iron present as hematite increases as the oxygen level is raised, due to an increase in the kinetically limited magnetite oxidation rate (10).

Table II
Kentucky #11 Mossbauer Results

Conditions	Magnetite	Hematite	Glass
5% O_2, 1500 K	70	21	9
21% O_2, 1500 K	57	33	10

Different behavior was noted in experiments conducted with a North Dakota Beulah lignite coal under this program. This coal was selected both for the large amount of large (>40 micron) pyrite minerals present, and the large amount of acid-leachable calcium. As the size distribution results presented in Fig. 3 indicate, combustion at both 7% and 21% oxygen levels yielded ash particles with distributions shifted toward smaller sizes relative to the initial minerals. What this suggests is that pure minerals may be fragmenting and influencing the distribution. It is anticipated that pyrite is the major species contributing to this observed behavior, as pyrite fragmentation has been noted in the literature under several conditions (11). Further experimentation with both the Beulah lignite and synthetic chars containing only pyrite is under way to test this hypothesis.

SUMMARY

Laboratory combustion experiments conducted with Kentucky #11 bituminous coal at low oxygen levels (7% oxygen in the bulk gas) demonstrate that agglomeration and coalescence of the included minerals is the dominant transformation mechanism occurring. Results suggest a large degree of coalescence is occurring between illite, kaolinite, and quartz minerals, with occasional iron incorporation into the resulting glass. Lack of iron incorporation was demonstrated by Mossbauer measurements, where approximately 10% of the iron was present as a glass under both oxygen levels studied. Acid-leachable potassium occasionally added to the glassy ash, as evidenced by relatively high potassium concentrations in some particles, though vaporization of the acid-leachable potassium was found to occur as well. For the second coal discussed in the study - Beulah lignite - mineral fragmentation was suggested by comparison of the ash distributions with initial mineral distributions measured by CCSEM. This presumably is due to large quantities of large (greater than 40 micron) pyrite present.

ACKNOWLEDGMENTS

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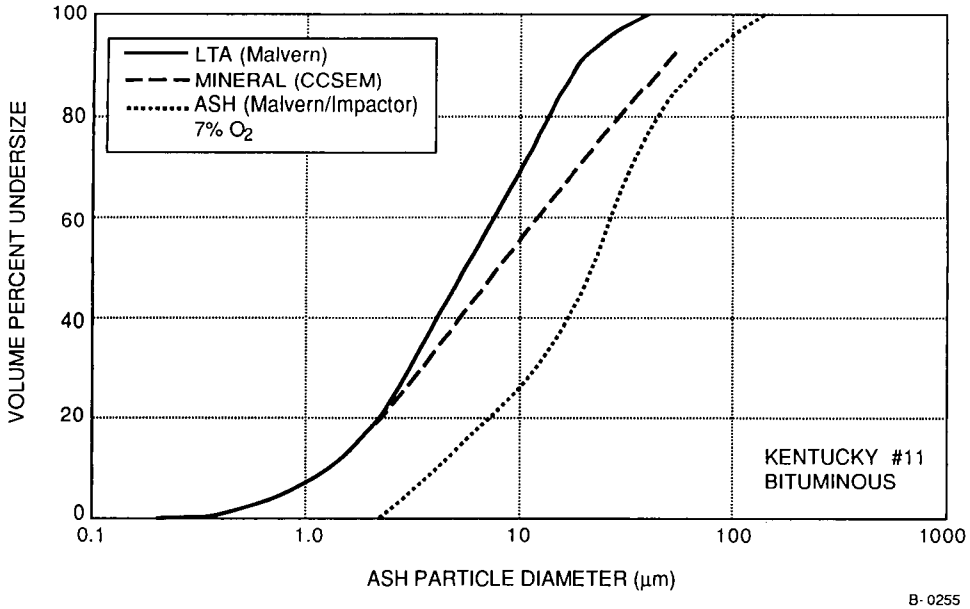


Figure 1: Mineral and Ash Particle Size Distributions - Kentucky #11

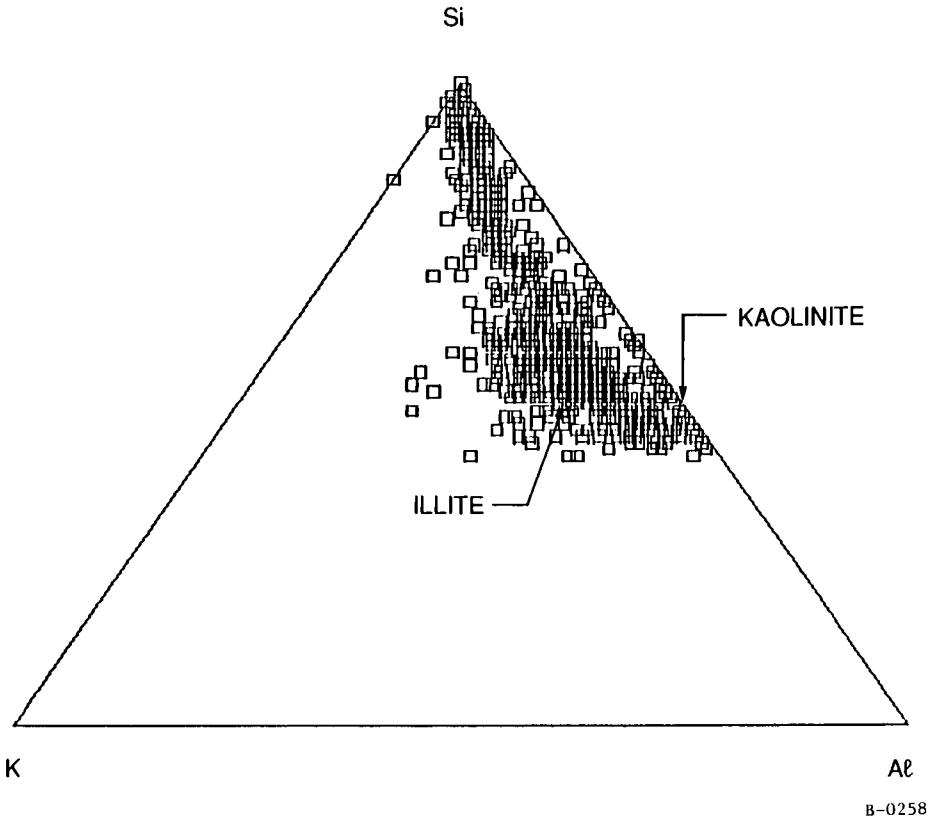
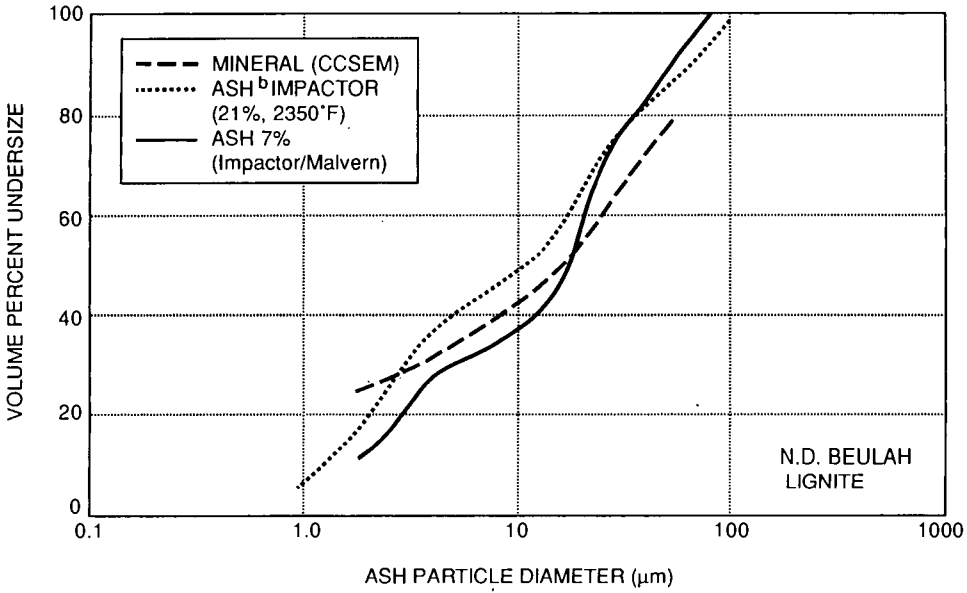


Figure 2: Individual Particle Composition, K+Al+Si>80%, Kentucky #11



[b] NORMALIZED TO 0% VAPORIZATION

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Figure 3: Mineral and Ash Particle Size Distributions - Beulah