

THE BEHAVIOR OF CLAY MINERALS UNDER COMBUSTION CONDITIONS

J.J. Helble, S. Srinivasachar, and A.A. Boni
PSI Technology Company
20 New England Business Center
Andover MA 01810

Keywords: Coal Combustion, Ash, Deposition

ABSTRACT

The mineral matter in pulverized coal contains a significant amount of clays such as kaolinite, illite, montmorillonite, and other aluminosilicates. During combustion, these minerals often melt and coalesce to form larger ash particles which, if their composition and viscosity are in the appropriate range, may stick to wall surfaces upon impact, leading to deposition. To assess the importance of these transformations in determining ash particle stickiness, combustion and deposit initiation experiments were conducted with montmorillonite, two forms of kaolinite, and several U.S. coals. For the montmorillonite, which contained calcium, magnesium, and iron as modifier ions, vitrification was evident upon exposure to 1500°C oxidizing atmospheres. For the kaolinites - essentially pure aluminosilicates - however, little morphological change was noted. As a result of the difference in modifier ions concentrations, the montmorillonite produced lower viscosity "stickier" particles more prone to adhere to tube surfaces. A comparison of these results with those obtained in a pulverized coal combustion study displayed similar trends. During combustion, if coalescence between clay minerals and dispersed modifier ions such as calcium occurred, the resulting ash particles readily adhered to high temperature tube surfaces. In the absence of modifier species coalescence, reduced values of ash stickiness were observed.

BACKGROUND

To properly select coals for a particular boiler, a reliable prediction of the extent of deposition is clearly desirable. Historically, many empirical indices have been employed for this purpose, but these are only reliable for a limited range of fuels under certain well-defined conditions (1,2). Much of the uncertainty associated with these indices stems from their use of *bulk* ash chemistry to describe processes which are initiated by *individual* ash particles. Fundamental laboratory studies have presented convincing evidence for the need to identify individual ash particle properties and determine how these are derived from the parent coal's mineralogy in addressing deposit initiation and growth (3,4). Although much can be learned from studies conducted with pulverized coals, the importance of individual mineral and ash species may be lost in such a complex system. For this reason, studies with individual minerals have been conducted to isolate their transformations in a combustion environment, and to determine whether the resulting ash particles may contribute to inertial deposition. In previous efforts, the role of pyrite and illite have been explored (5,6) and compared to results obtained with synthetic glass particles where viscosity was identified as a key parameter in

deposit initiation. Here we extend our study to two commonly encountered clays - kaolinite and montmorillonite - and explore their role in deposit initiation.

EXPERIMENTAL APPROACH

Equipment

All experiments were conducted in an externally heated laminar flow drop tube furnace, described in detail elsewhere (5). In brief, particles were injected at the top of the reactor into premixed, preheated gases containing 0 - 3 percent O₂ in N₂. Temperatures in the reaction zone were held constant during an individual experiment in the range 1000 to 1500°C. At the exit of the reactor, particles were either (a) sampled isokinetically via a water-cooled nitrogen-quenched collection probe and deposited in a filter for subsequent analysis, or (b) inertially impacted on a deposit collection probe. In the deposit collection probe, particles accelerated through a ceramic converging section to impact uncooled 1.25-3.2 mm diameter mullite tubes oriented perpendicular to the flow. Particles which were sufficiently deformable - "sticky" - adhered to the substrate. Morphological examination of the particles was subsequently conducted by scanning electron microscopy (SEM) on an Amray Model 1820 SEM. Chemical analysis of individual particle and deposit samples was by energy-dispersive x-ray analysis (EDAX).

Sample Selection

Kaolinite and montmorillonite clay samples were obtained from the Source Clays Depository at the University of Missouri - Columbia. Samples were mined from several well-characterized locations, steam dried, pulverized in a hammer mill, remixed, and then riffled prior to shipping. No additives were used in the preparation of these clays. The well-crystallized kaolinite was taken from Washington County Georgia; the poorly crystallized kaolinite from Warren County, Georgia; and the montmorillonite, from Apache County, Arizona. Detailed analyses of these samples have been collected and published in reference (7); chemical composition analysis of each sample taken from (7) is presented in Table I (weight loss on heating is the additional term which will sum the compositions to 100%).

The San Miguel lignite presented for comparison has been discussed in detail elsewhere (3). High clay contents in the parent coal made it an ideal choice for comparison with the clays of this study. Mineralogy of the high-ash San Miguel (51% ash on a dry basis), obtained by computer-controlled SEM at the University of Kentucky, was dominated by zeolite silicates (64 weight percent of the minerals), with significant quantities of montmorillonite (16%) and quartz (12%) also present. Kaolinite levels were only 2% in this lignite, which is lower than the 6-20% levels often encountered in U.S. coals. Note that the coal sample was utilized in an as-received form, with 70% < 75 μm in size. Clay samples were dry-sieved to 38/53 μm prior to testing.

RESULTS AND DISCUSSION

Experiments were first conducted with the well-crystallized kaolinite (K-WC) to determine whether melting or vitrification occurred during combustion processing.

In Figure 1, an SEM micrograph shows typical large kaolinite crystals surrounded by a fairly high concentration of submicron-sized fine particulate. The chemical composition of the larger particles was typically 42-44% Al_2O_3 , with the balance silica. Little was noted in the way of modifier ions in the untreated K-WC particles examined. Poorly crystallized kaolinite samples (K-PC) also contained a large number of fine particles in the feed material. Silica-to-alumina ratios for the individual K-PC particles examined were comparable to those observed for the K-WC sample. In contrast to the well-crystallized sample, however, low levels of titania (1-2%) were frequently observed. Silica-rich particles containing nominal 5% potassium (as oxide) were also observed as impurities in the K-PC sample.

Subsequent to reaction in 3% oxygen at 1500°C for 2.9 seconds, little change was noted in either the K-WC or the K-PC samples as shown in Figure 2. In the well-crystallized sample, titania levels of 1-2% were occasionally noted, with no apparent change in the silica-to-alumina ratio observed. For the K-PC sample, some coalescence of the submicron fines is evident upon close examination of the micrograph (Fig. 2b). The chemical composition of these particles, as determined by SEM-EDAX, was comparable to that of the parent K-PC particles. Titania was again consistently observed as an impurity at the 2-6 percent level (oxide, by weight). Iron oxide levels of ≤ 2 weight percent were noted in several particles.

Examination of the third clay in this study - montmorillonite - yielded strikingly different results. Initially the particles were similar to the raw kaolinite in that they were of angular shape as seen in Figure 3. Silica-to-alumina ratios in these particles were approximately 3.5/1, with 10% of the particle composed of the modifier ions magnesium, calcium, and iron; most particles sampled were similar in composition to the bulk composition reported in Table I. Subsequent to processing at 1500°C for one second, however, vitrification is apparent in several of the particles seen in Figure 4a. After complete processing at 1500°C for 2.9 seconds (similar to what minerals might encounter in a boiler environment), nearly complete melting was apparent (Fig. 4b).

Because of the high modifier ion content of the montmorillonite, it was expected to produce sticky ash particles prone to deposit over a fairly wide range of conditions. In contrast to this, little deposition was expected from either the K-PC or the K-WC samples. To test this, deposition experiments were conducted with all three samples at deposit impaction surface temperatures of 1275 to 1675 K. Under all conditions examined to-date, little or no deposition was noted with either kaolinite sample as shown in Figure 5. For the montmorillonite, however, capture efficiencies comparable to those of the San Miguel lignite ash previously examined were obtained. Detailed examination of the San Miguel lignite ash had indicated that calcium plus magnesium plus potassium levels of most particles were greater than 10% as oxides, by weight, yielding viscosities below the 10^8 poise believed necessary for adhesion (3). This produced particles with viscosities low enough to permit the particle to remain on the impaction surface subsequent to contact -i.e., viscosities were low enough to absorb the energy of collision. For the calcium

montmorillonite ash particles examined herein, the sum of the modifier ions calcium plus magnesium plus iron was in the range 6-12% for the individual particles studied. Note that this range is comparable to the San Miguel ash particles so similar viscosities are expected. Exact computation requires analysis for the final form of iron (ferrous v. ferric) and is currently underway.

A marked difference in deposit morphology was also noted between the kaolinite and montmorillonite samples, as expected. As Figure 6a shows, only a few glassy particles were retained on the tube surface for the K-WC sample. EDAX analysis of these particles showed them to be illitic in nature and therefore expected to adhere under the conditions of this study (cf. Figure 5). In Figure 6b, the molten adhesive nature of the montmorillonite particles at 1425°C deposition conditions is clearly evident. For this deposit, chemical composition was comparable to that noted both for the raw sample and for individual transformed particles: 20 wt% silica, 67% alumina, 5% each of magnesia and calcia, and 2.4% iron (ferric) oxide.

These results suggest that any mineral interactions which produce aluminosilicate ash particles with approximately 10% modifier ion concentration will give rise to extremely sticky ash particles, prone to deposit upon inertial impaction with wall surfaces. Kaolinite alone is of little concern because of a relative absence of modifier ions, but interactions with dispersed species such as calcium and magnesium could produce ash particles prone to adhere to tube surfaces. Ash particles derived from minerals such as illite and montmorillonite which are rich in modifier ions can deposit without the need for interaction with other species.

ACKNOWLEDGEMENTS

The authors wish to thank Mr. Jeffrey Moore of PSIT for performing many of the experiments described herein. Financial support of the US DOE Pittsburgh Energy Technology Center, grant DE-AC22-86PC90751, is also gratefully acknowledged.

REFERENCES

1. Bryers, R.C., *Proc. EPRI Conf. on the Effects of Coal Quality in Power Plants*, October (1987).
2. Winegartner, E.C., *ASME Research Committee Report on Corrosion and Deposits from Combustion Gases* (1974).
3. Srinivasachar, S., Helble, J.J., and Boni, A.A., *Proc. 23rd Symposium (Int'l) on Combustion*, The Combustion Institute (in press) (1990).
4. Baxter, L.L., Hencken, K.R., and Harding, N.S., *Proc. 23rd Symposium (Int'l) on Combustion*, The Combustion Institute (in press) (1990).
5. Srinivasachar, S., Helble, J.J., and Boni, A.A., *Progr. Energy and Combust. Sci.* **16**, 281 (1990).
6. Srinivasachar, S., Helble, J.J., Boni, A.A., Shah, N., Huffman, G.P., and Huggins, F.E., *Progr. Energy and Combust. Sci.* **16**, 293 (1990).
7. Van Olphen and Fripiat, eds., *Data Handbook for Clay Materials and Other Non-Metallic Minerals*, Pergamon Press, New York (1979).

Table 1. Clay Chemical Composition

	Weight Percent								
	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O
Kaolin-well crystallized	44.2	39.7	1.39	0.13	0.08	0.03	-	0.013	0.05
Kaolin-poorly crystallized	43.9	38.5	2.08	0.98	0.15	0.03	-	-	0.065
Ca-montmorillonite	60.4	17.6	0.24	1.42	0.08	6.46	2.82	0.063	0.19

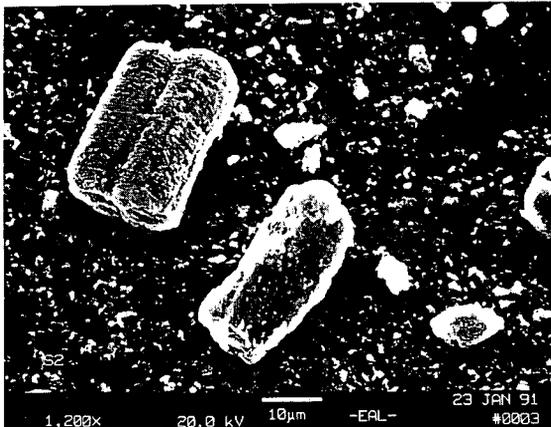
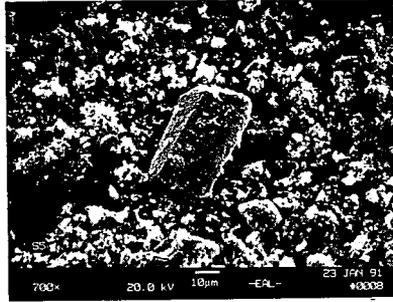
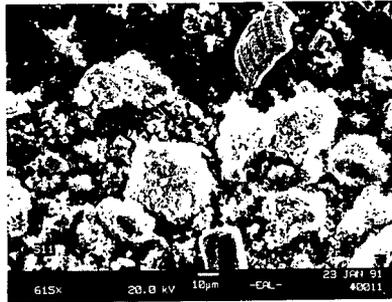


Figure 1. Raw Sample of Well-Crystallized Kaolinite



(a) Well Crystallized Kaolinite



(b) Poorly Crystallized Kaolinite

Figure 2. Kaolinite Samples After Processing at 1500°C in 3 Percent O₂ for 2.9s

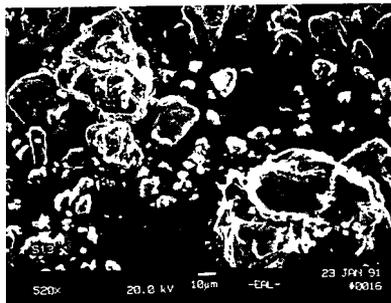
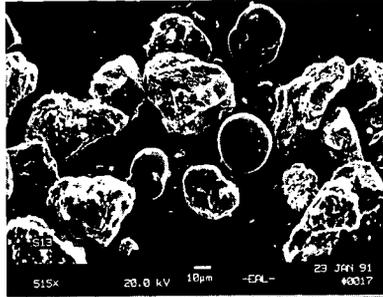
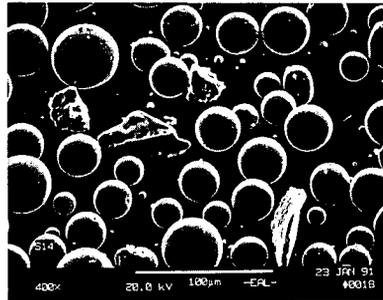


Figure 3. Raw Sample of Calcium-Montmorillonite



(a) 1s



(b) 2.9s

Figure 4. Montmorillonite Samples After Processing at 1500°C in 3 Percent O₂

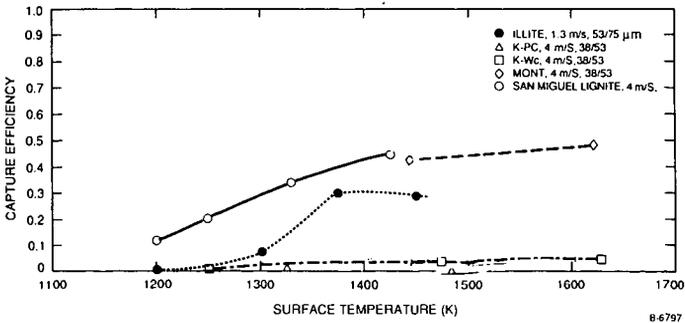
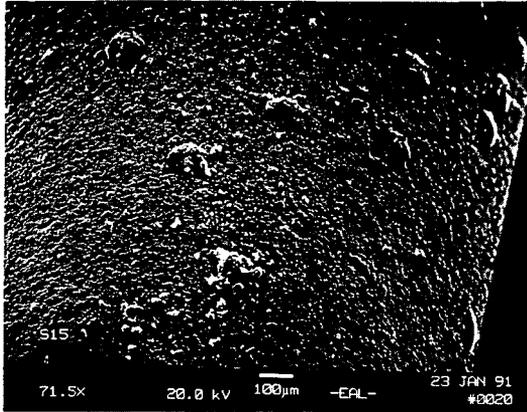
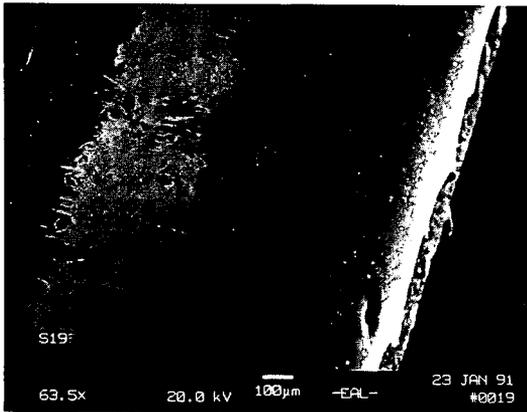


Figure 5. Comparison of Clay Sample Collection Efficiencies with Coal Ash Collection Efficiencies. Combustion conditions as noted



(a) Well Crystallized Kaolinite



(b) Ca-Montmorillonite

Figure 6. Morphology of Initial Deposits Collected at 1425°C After Processing at 1500°C, 3 Percent O₂