FLY ASH DEVELOPMENT FROM SODIUM, SULFUR AND SILICA DURING COAL COMBUSTION

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Introduction

The formation of ash during the combustion of coal is a very complex environmentally dependent reaction. Significant parameters include the combustion conditions and association and relative sizes of the inorganic constituents present. During pulverized coal combustion the inorganic constituents undergo chemical and physical transformations in the flame and during gas cooling to form inorganic vapors, liquids, and solids. These chemical and physical transformations dictate the size and composition distribution of the final ash product. Previous studies of the final ash product (fly ash) indicate that the size distribution is usually bimodal (Sarofim, 1977; Flagan and Friedlander, 1978; and Damle, 1982). The submicron size particles have an average diameter of about 0.1 microns. These small particles form as a result of the homogeneous condensation of flame volatilized species. These flame volatilized species may also condense heterogeneously on the surfaces of larger particles. The larger size fraction of the particles, referred to as the residual ash, are largely a result of the minerals present in the coal. The size and composition distributions of the larger particles are a result of the transformations and interactions of the minerals and other inorganic components in the coal. Physical processes such as coalescence, fragmentation of minerals and char, and shedding of inorganic components occur which effect the properties of the ash.

A furfuryl alcohol polymer containing Na, S, and SiO_2 was used to study the effect of combustion temperature on the formation of fly ash particles. Of specific interest to low-rank coal combustion systems is the interaction between sodium, sulfur and silica to form low melting point phases that can cause deposition problems (Jones, 1987). In order to identify key processes associated with the formation of ash in combustion systems carefully controlled combustion experiments using a laminar flow furnace system were performed. A precisely formulated synthetic coal/mineral mixture was produced, combusted in a laminar flow furnace, and the composition and size of the ash was examined. The synthetic coal was formulated to include only a specific composition of inorganic species in a specific form and size to facilitate the examination of the effects of combustion conditions on the final ash particles formed.

Experimental Approach

A furfuryl alcohol polymer was catalyzed with p-toluenesulfonic acid as outlined by Senior (1984) and modified by Erickson (1990). The coal was synthesized to include 10% by weight SiO_2 in the crystalline form of quartz. Computer Controlled Scanning Electron Microscopy (CCSEM) (Steadman et.al., 1990) and Inductively Coupled Plasma (ICP) analysis determined the synthetic coal to contain 9.3 and 11.3 % by weight quartz, respectively. CCSEM analysis determined the quartz to range in diameter from 1 to 10 microns with the average size, based on a volume percent basis, to be 5.06 microns. Sodium (5% by weight) was added to the coal in the form of sodium benzoate in an alcohol solution. The solution was then allowed to evaporate off with the sodium remaining attached to the coal. This method gives a form of sodium which is easily volatilized (Mills, 1989) similar to the ease of the volatilization of sodium in low rank coals. Sublimed sulfur was added extraneously to comprise 1% by weight. The final coal was ground in a ball mill and sized to 46-106 microns with a sonic sieve.

The synthetic coal was combusted in a laminar flow furnace at 900, 1100, 1300, and 1500°C. The residence time of the coal was approximately 1.4 seconds with slight variations dependent upon temperature. After exiting the furnace the fly ash was cooled instantly with a quench probe and collected on a bulk filter.

After combustion the samples were mounted on a carbon plug with double stick tape, carbon coated and studied with the use of a JEOL Scanning Electron Microscope/Microprobe (SEM/EMPA). The SEM/EMPA is equipped with an ultra-thin window energy dispersive detector with a Tracor Northern 5600 processing system. The system also has the abilities of a Tracor Northern 8500 image analysis system. These three tools together create a flexible mechanism for determining the composition, size, and various characteristics of fly ash samples.

Results

Figures 1-4 show the fly ash formed at 900, 1100, 1300, and 1500°C, respectively (all four figures are at the same magnification). The particle size decreases with increasing combustion temperature. Virtually all of the particles are spherical in nature and were assumed to be for all subsequent calculations. Table 1 gives the average particle size of each of the samples. The particles were sized manually by randomly measuring 125 particles with the aid of the image analysis system. Figure 5 gives a graphical representation of the same data with the addition of: 1) the theoretical diameter of a fly ash particle assuming 100% coalescence of inorganics, and 2) the diameter of the original quartz prior to combustion. It should be noted that some of the particles at 900 and 1100°C show some evidence of either cenosphere formation or unburned carbon in the center. The combustion of the synthetic coal appears to be dominated by coalescence, i.e. formation of one fly ash particle per coal particle, at lower temperatures as shown in Figure 6, and by fragmentation followed by coalescence at higher temperatures, shown in Figure 7.

Figure 8 is a high magnification photo of the fly ash combusted at 900°C. On the surface of the larger grey particles are very small white moieties. The same phenomenon appears in all four samples but is most abundant and largest in size at the lower temperatures. Due to the small size of the moieties it is impossible to get an accurate chemical analysis of them with the SEM/EMPA (the excitation volume of the electron beam is 8 microns in diameter as compared to the submicron size of the moieties). Table 2 compares the grey area composition, moiety composition, and bulk area composition. It is important to note that SEM/EMPA analysis of the moieties includes analysis of a substantial amount of the fly ash behind and surrounding it. These analyses are averages of 3 to 5 samplings of each of the described areas. From these analyses it appears that the moieties are sodium sulfates which homogeneously condensed and impacted onto the Na-rich silicate particles.

SOLGASMIX (Erikkson and Rosen, 1973), a theoretical program based on minimization of Gibbs free energy, predicts that the abundance of sodium sulfates will decrease with increasing temperature. This corresponds to the observed results, with fewer and smaller sodium sulfate particles found at higher temperatures.

Conclusions

The formation of fly ash in the coal studied was dominated by coalescence at low temperatures (900 and 1100°C) and by fragmentation followed by coalescence at higher temperatures (1300 and 1500°C). The fragmentation during combustion may be caused by: 1) thermal breakup of the particle, 2) rapid combustion (explosion), 3) break up of pore structure, or 4) a number of other phenomena. There was increased formation of submicron sodium sulfates at lower temperatures while higher temperatures appeared to decrease both the size and abundance of the submicron sodium sulfate particles. At the higher temperatures, the sodium appears to interact with the silica to form sodium silicates.

References

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Table 1

Average Particle Size of Fly Ash Formed From Synthetic Coal

Temperature(°C)	Diameter (microns)
900	27.0
1100	27.7
1300	17.6
1500	8.5

Table 2

Particle Surface Composition, Elemental %'s

Temperature	Bulk Composition			Grey Area Composition			White Moiety Composition		
(°C)	Na	S	Si	Na	S	Si	Na	S	Si
900	24	5	61	19	1	80	39	18	43
1500	80	1	19	5	0	95	6	1	93

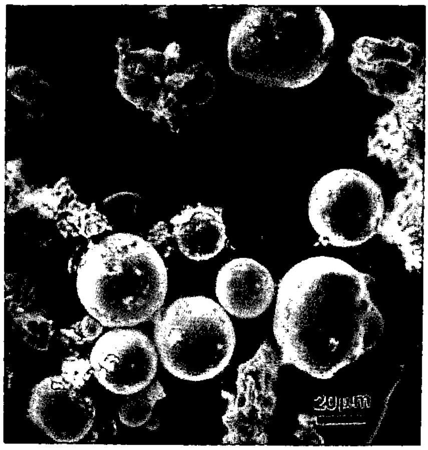

Figure 1 Fly Ash Particles Formed at 900°C, 500x.

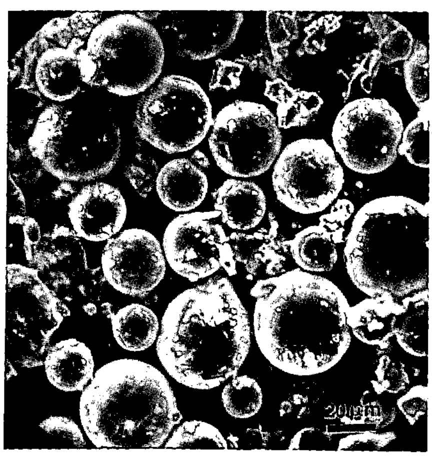

Figure 2 Fly Ash Particles Formed at 1100°C, 500x.

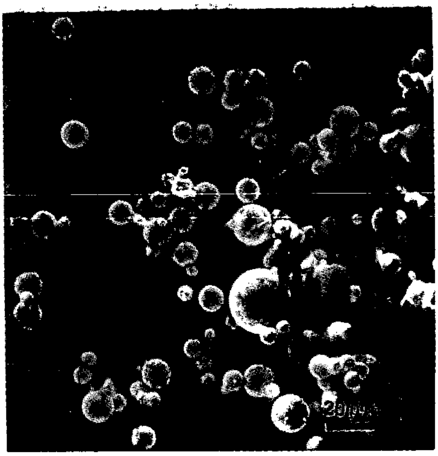

Figure 3 Fly Ash Particles Formed at 1300°C, 500x.

Figure 4 Fly Ash Particles Formed at 1500°C, 500x.

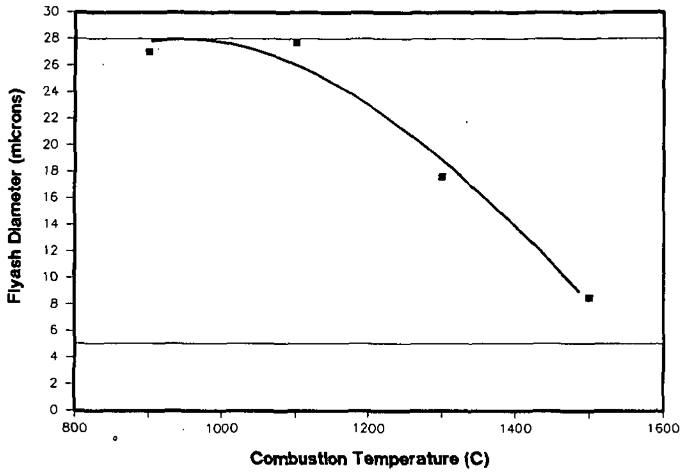

Figure 5 Particle Size versus Combustion Temperature. (upper line represents 100% coalescence and lower line represents original size of mineral grains)

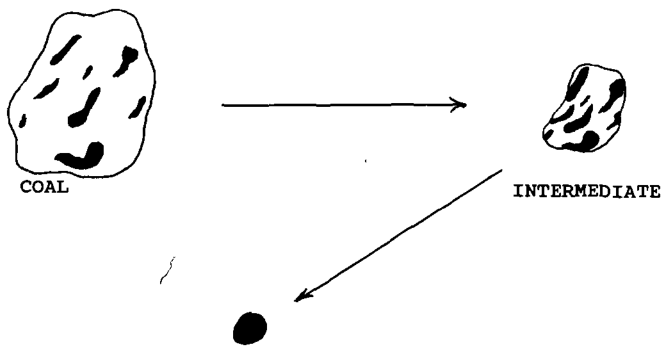

Figure 6 Diagram of the Formation of Fly Ash Particles Through Coalescence.

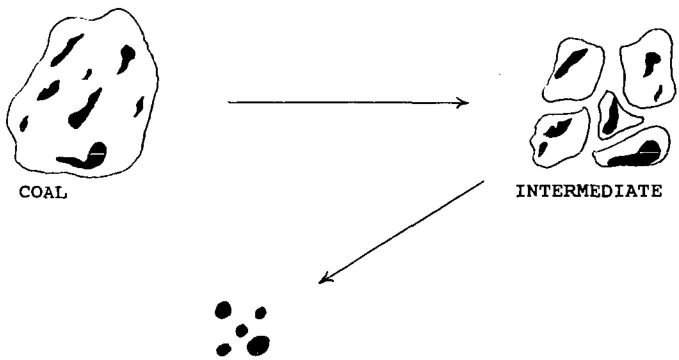

Figure 7 Diagram of the Formation of Fly Ash Particles Through Fragmentation.

Figure 8 High Magnification Photo of 900°C Fly Ash Particle Surface.