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Suppression of Fine Ash Formation in Pulverized Coal Flames

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Introduction

One of the major obstacles to the economical use of coal is managing the behavior of its mineral matter. Ash size and composition are of critical importance for a variety of reasons. Fly ash size and emissivity affect radiant furnace heat transfer.[1] Heat transfer is also affected by the tendency of ash to adhere to heat transfer surfaces,[2] and the properties of these deposits.[3] Removal of ash from flue gas by electrostatic precipitators is influenced by both particle size and particle resistivity.[4] The efficiency of fabric filter-based cleaning devices is also influenced by ash size.[5] Both types of devices have reduced collection efficiencies for smaller-sized particles, which corresponds to the size most efficiently retained in the alveolar region of the human lung.[6] This special concern for finer sized particles has led to PM10 regulations in the last several years (PM10: particles of diameter less than 10 μm).

Laboratory work and studies of full-scale coal-fired boilers have identified two general mechanisms for ash production. The vast majority of the ash is formed from mineral matter that coalesces as the char burns, yielding particles that are normally larger than 0.5 μm. Flagen and Friedlander[7] proposed a simple model for this residual ash, called the breakup model. In this model, each particle is assumed to yield its mineral matter as a certain specified number of ash particles (usually in the range of 1-5). This latter value is termed the "breakup number." In this way, a known pulverized coal size distribution can be transformed into a projected ash size distribution. The presumed mechanism is that each char particle fragments during combustion, carrying mineral matter with it. The major assumptions used in the model include: (1) all coal particles contain the same percentage of mineral matter, independently of size, (2) all coal particles break into exactly the same number of char particles during combustion, (3) each char particle contains the same amount of mineral matter as the other char particles, and (4) no further fragmentation occurs, which means that each offspring char particle yields its mineral matter as a single ash particle. The breakup number has been identified in recent work as being influenced by the breakup of the char during burnout, from shedding at the burning char surface,[8] and from the fragmentation of discrete included and excluded minerals.[9,10] Recent experimental work[11] and elegant site percolation modeling[12] indicate that char macroporosity is the single most important factor governing char breakup and residual ash size. Despite the severity of the assumptions, the basic breakup model has proven to be a useful engineering and interpretative tool.[13]

The second major mechanism is the generation of a submicron aerosol through a vaporization/condensation mechanism. When the ash size distribution is plotted in terms of number density, the submicron mode generally peaks at about 0.1 μm.[4] When plotted in terms of mass, this mode is sometimes distinct from the residual ash mode,[13] and sometimes merged into it.[14] During diffusion-limited char combustion, the interior of the particle becomes hot and fuel-rich. The non-volatile oxides (e.g., Al_2O_3, SiO_2, MgO, CaO, Fe_2O_3) can be reduced to more volatile suboxides and elements, and partially vaporized.[15-17] These reoxidize while passing through the boundary layer surrounding the char particle, thus becoming so highly supersaturated that rapid homogeneous nucleation occurs. This high nuclei concentration in the boundary layer promotes more extensive coagulation than would occur if the nuclei were uniformly distributed across the flow field.[18] The vaporization can be accelerated by the overshoot of the char temperature beyond the local gas temperature.[19]

Although these particles represent a relatively small fraction of the mass, they can present a large fraction of the surface area. Thus, they are a preferred site for the condensation of the more volatile oxides later in the furnace. This leads to a layering effect in which the refractory oxides are concentrated at the particle core and the more volatile oxides reside at the surface.[20] This also explains the enrichment of the aerosol by volatile oxides that has been noted in samples from practical furnaces.[21] These volatile metal oxides include the majority of the toxic metal contaminants, e.g., mercury, arsenic, selenium and nickel. Risk assessment studies suggest that toxic metal emissions represent a significant portion of the health risk associated with combustion systems.[22]

Previous work has shown that pulverized bituminous coals that were treated by coal cleaning (via froth flotation) or aerodynamic sizing exhibited altered aerosol emission characteristics. Specifically, the emissions of aerosol for the cleaned and sized coals increased by as much as one order of magnitude. At least three mechanisms have been proposed to account for this behavior.

Objectives

The goals of the present program are to:

1. Perform measurements on carefully characterized coals to identify the means by which the coal treatment increases aerosol yields.
2. Investigate means by which coal cleaning can be done in a way that will not increase aerosol yields.
3. Identify whether this mechanism can be used to reduce aerosol yields from systems burning straight coal.

Current Activities

The current experimental series focuses on the use of artificial char to study sodium vaporization and aerosol formation associated with dispersed sodium and mineral inclusions. Artificial char has the advantage over natural coal in that the composition can be precisely controlled, such that the influence of specific mineral composition and content can be investigated.

Artificial char was manufactured using the sucrose pyrolysis technique.[23] The base composition was formed by adding 0.5 grams of sodium oxalate ($Na_2C_2O_4$) to a 50 gram sucrose /50 gram carbon black solution in distilled water. Sodium oxalate was chosen as a sodium source because of its solubility in sucrose solution, and low decomposition temperature (250-270C). Sized pyrite, bentonite and calcite were added in selected quantities to produce a matrix of chars. One batch of 75 grams sucrose / 25 grams carbon / 0.5 grams sodium oxalate was also prepared, to evaluate the effect of porosity on aerosol formation. The chars produced are shown in table 1.

	Dry Mass in Grams Prior to Pyrolysis (Form of Component)					
Char Batch	Sucrose (in solution)	Carbon Black (40-60 nm)	Sodium Oxalate (in solution)	Pyrite (9-10 μm)	Bentonite (0.9 -1 μm)	Calcite (15-17μm)
A	50	50	0.5			
B	75	25	0.5			
C	50	50	0.5	0.925		
D	50	50	0.5	1.850		
E	50	50	0.5	2.775		
F	50	50	0.5	3.700		
G	50	50	0.5		1.25	
H	50	50	0.5		2.50	
I	50	50	0.5		3.75	
J	50	50	0.5		5.00	
K	50	50	0.5			0.25
L	50	50	0.5			0.50
M	50	50	0.5			0.75
N	50	50	0.5			1.00

Table 1. Char composition matrix

The solution was devolatilized at 600C in a nitrogen environment. A ball mill was used to pulverize the resulting char into particles on the order of 40 um.

The chars were combusted in the down-fired furnace described in previous progress reports. Excess oxygen was set at 7.0% by volume, with the main burner operating at 66,000 BTU/hr. Residence time was about 1.4 seconds. The average temperature measured down the center of the furnace was 1100 C, as sensed by a type K thermocouple, with no radiation correction.

A portion of the residual ash was collected in an Andersen cascade impactor, as described in previous progress reports. The mass of particles in a given aerodynamic size range was recorded, and is presented below. All data is normalized to the total mass collected on the impactor stages. Mass collected in the preseperator is not included.

The pyrite series is shown in figure 1. Mass was concentrated in the larger diameters for the pyrite series, as compared to the sodium only tests. The mass fraction collected on the backup filter (particles with aerodynamic diameters less than 0.4 microns) was significantly reduced, in general, as initial pyrite concentration was increased. It is yet to be determined if this can be attributed, in part, to aerosol suppression, or solely to large iron compound particles in the higher size ranges.

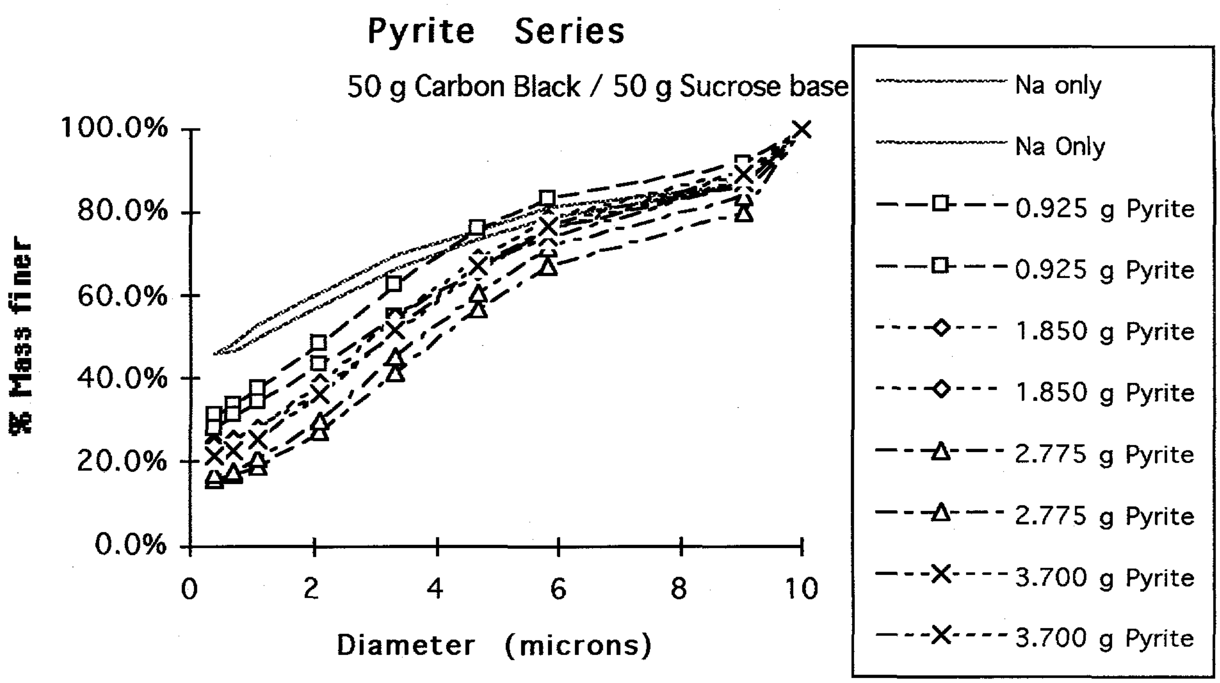

Figure 1

The bentonite series results are shown in figure 2. Note again that the mass distribution favors the larger diameter particles as mineral matter is increased.

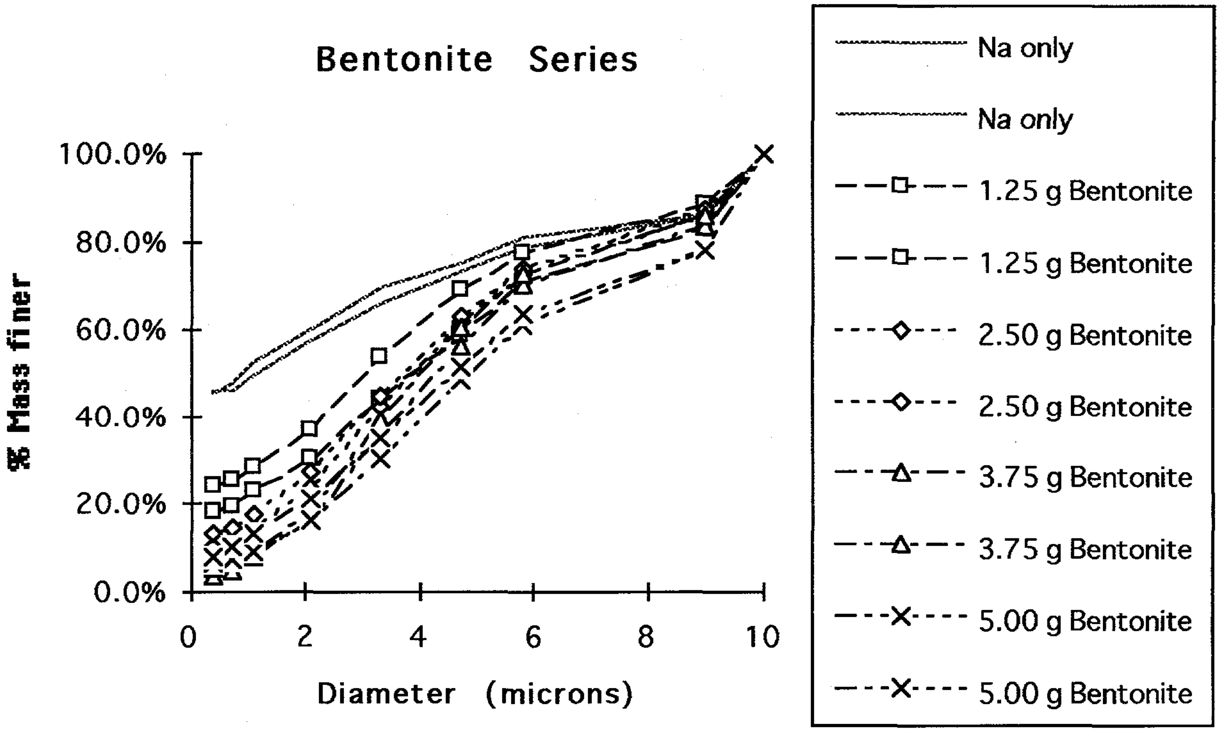

Figure 2

The Calcite series is shown in figure 3. Post-combustion size distributions for Calcite doped char was similar to the undoped char. The significance of the distribution is under investigation.

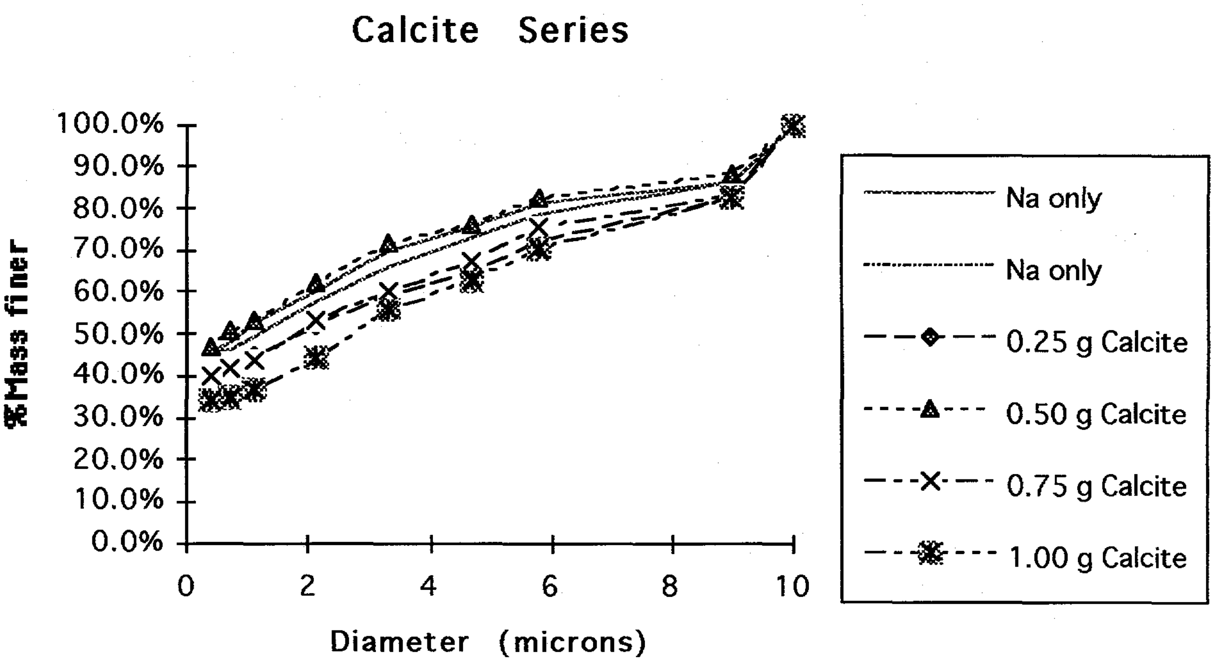

Figure 3

The effect of porosity, studied by comparison of Char A and Char B post combustion ash, was inconclusive. Run to run variation was significant, and further testing will be required in order to clarify its influence.

Future Work

Further analysis of the combusted char data will be the focus of the next contract period. Model development has been suspended until after the current test series has been concluded.

References

1. Gupta, R. J. Radiative Transfer Due to Fly Ash in Coal Fired Furnaces, Ph.D. Dissertation 1983, University of Newcastle.
2. Walsh, P. M., Sayre, A. N., Loehden, D. O., Monroe, L. S., Beér, J. M., and Sarofim, A. F. Prog. Energy Combust. Sci. 1990, 16, 327.
3. Field, M. A., Gill, D. W., Morgan, B. B., and Hawksley, P. G. W. Combustion of Pulverized Coal. 1967, The British Coal Utilization Research Assoc.
4. McCain, J. D., Gooch J. P., and Smith, W. B. Journal of the Air Pollution Control Association 1975, 25, 117.
5. Friedlander, S. K. Smoke, Dust and Haze 1977, Wiley.
6. Morrow, P. E. Amer. Ind. Hyg. Assoc. J. 1964, 25, 213.
7. Flagen, R. C., and Friedlander, S. K. Recent Developments in Aerosol Science. (D. T. Shaw, Ed.) 1978, Wiley, Chapter 2.
8. Helble, J. J., and Sarofim, A. F. Combust. Flame 1989, 76, 183.
9. Baxter, L. L. Prog. Energy Combust. Sci. 1990, 16, 261.
10. Srinivasachar, S., Helble, J. J., and Boni, A. A. Prog. Energy Combust. Sci. 1990, 16, 281.
11 Helble, J. J., and Sarofim, A. F. Combust. Flame 1989, 76, 183.
12. Kang, S., Helble J. J., Sarofim A. F., and Beér, J. M. Twenty-Second Symposium (International) on Combustion 1988, The Combustion Institute, p. 231.
13. Flagen, R. C. Seventeenth Symposium (International) on Combustion 1979, The Combustion Institute, p. 97.
14. Linak, W. P., and Peterson, T. W. Aerosol Sci. Technol. 1984, 3, 77.
15. Neville, M., Quann, R. J., Haynes, B. S., and Sarofim, A. F. Eighteenth Symposium (International) on Combustion 1981, The Combustion Institute, p. 1267.
16. Senior, C. L., and Flagen, R. C. Aerosol. Sci. Technol. 1982, 1, 371.
17. Quann, R. J., and Sarofim, A. F. Nineteenth Symposium (International) on Combustion 1982, The Combustion Institute, p. 1429.
18. Damle, A. S., Ensor, D. S., and Ranade, M. B. Aerosol Sci. Technol. 1982, 1, 119.
19. Quann, R., Neville, J. M., and Sarofim A. F. Combust. Sci. Technol. 1990, 74, 245.
20. Gladney, E. S., Small, J. A., Gordon, G. E., and Zoller, W. H. Atmos. Environ. 1976, 10, 1071.
21. Linak, W. P., and Peterson, T. W. Twenty-First Symposium (International) on Combustion 1986, The Combustion Institute, p. 399.
22. Smith, A. H., and Goeden, H. M. Combust. Sci. Technol. 1990, 74, 51.
23. Helble, J. J., Ph.D. Dissertation, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA (1987).