Title
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CHARACTERISTICS OF FLY ASH FROM LABORATORY COMBUSTION OF PULVERIZED COAL

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September 1981

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ABSTRACT

Submicron particles generated from pulverized coal combustion show an enrichment of certain trace elements that may be a health hazard when ingested into the lung. Sieved pulverized coal was entrained in an air/methane/oxygen mixture and burned in an enclosed bunsen type burner fitted with a chimney. Cold secondary air was injected at the chimney exit. The fly ash samples were separated into two size categories (diameter < 2.5μ and 2.5μ < diameter < 15μ) and analyzed by x-ray fluorescence. Results show enrichment of several volatile elements in the small size fraction compared to the large size fraction. There is also indication of depletion of some refractory elements. The results support suggestions of several earlier observations which were made on full scale modern boilers.
INTRODUCTION

Pulverized coal combustion produces fly ash particles that comprise a wide range of size and toxic trace element distributions. The smaller fly ash particles have a significant enrichment of volatile trace elements. A commonly used model for the formation and distribution of elements in fly ash particles is the vaporization condensation model. Trace elements are volatilized in the hot combustion zone and, depending on the cooling rate, condense to form small particles or coalesce to form large particles. The larger surface to volume ratio of smaller particles leads to an enrichment of volatile trace elements upon condensation. Pollution control devices presently being used or being considered all have high overall mass collection efficiencies which, however, decrease considerably for the smaller particles. The smaller particles also have much longer atmospheric residence times than do the larger particles. This longer residence time coupled with volatile (usually toxic) enrichment and the ease of ingestion into the lungs may make the small particulate output from utility boilers more important than their weight fraction would indicate (1, 2, 3, 4).

This paper is a continuation and extension of an investigation into the effects of combustion and heat transfer parameters on the formation of submicron particulates and their chemistry (5). Combustion and heat transfer parameters have been varied, particulate samples have been collected and the concentrations of 29 elements have been determined.
APPARATUS AND PROCEDURE

A small amount of Pittsburgh seam pulverized coal, whose properties are given in Table 1, was entrained in an air/methane/oxygen mixture and burned in an enclosed bunsen type burner fitted with a chimney. This arrangement was able to simulate the temperature-time history of a pulverized coal burner. The coal, which was already pulverized when received, was sieved through a 200 mesh screen to remove the larger particles. Particulate sampling was done with a Lawrence Berkeley Laboratory automated dichotomous air sampler which divides the particulates into two size ranges, those with stokes diameters in the range between 2.5 and 15 μm and those with stokes diameters less than 2.5 μm. The samples were collected on one micron pore size Teflon filters, obtained from GHIA Corp., Pleasanton, CA, 32 mm in diameter and mounted in 5 cm square frames. The mass collected was determined by electron beam attenuation (Beta gage) and the elemental composition by x-ray fluorescence.

A schematic diagram of the burner is shown in Fig. 1. Pulverized coal is entrained in a small amount of air in a hopper by using a jet of air to sweep coal particles from the surface of a fluidized bed. The coal hopper is placed on a balance to continuously monitor the weight. The coal mixes with methane, oxygen, and additional air in a 10 mm diameter tube. A ceramic flameholder is inserted coaxially into the end of this tube and stabilizes the flame at the entrance to the chimney. The chimney controls the rate at which the mixture cools; the residence time is sufficient for the coal particles to burn out in the first 1/4 to 1/3 of the chimney length. Two chimney configurations were used; an uninsulated ceramic tube 44 mm in diameter and 355 mm long, and a similar tube provided
with a layer of insulation to reduce the heat loss and thereby operate at higher temperatures. At the downstream end of each chimney, secondary air is injected to rapidly cool the combustion products in a short 75 mm length section (see Fig. 1). The initial cooling rate of the insulated chimney is less than that of the uninsulated chimney, but upon quenching the cooling rate becomes greater for the insulated chimney. The chimney without insulation will be referred to as the low exit temperature chimney while the chimney with insulation will be referred to as the high exit temperature chimney. The sampling tube is placed 200 mm downstream of the quenching tube exit.

Complete details of the Lawrence Berkeley Laboratory automated dichotomous sampler are given in Reference 6. Particle size selection is achieved with a virtual impactor that uses the principle of inertial separation (see Fig. 2). After separation the sampling material is collected on Teflon filters. Analysis of the filters is done with an automated Beta gage(7) and x-ray fluorescence system(8) developed at Lawrence Berkeley Laboratory for analyzing such filters.

The combustion and heat transfer conditions are controlled by varying both the methane/oxygen/air mixture and the chimney condition. A total flow rate of 30 l/min of secondary air is injected at the chimney exit. Approximately 0.2 seconds are required for the products to travel to the location of secondary air injection.

The temperature as a function of the distance from the flame holder is shown in Fig. 3. The initial cooling of the combustion gases is due to convection to the chimney wall. The curves all follow the expected exponential decrease in the temperature with increasing distance from the
flame holder. Average cooling rates of 3000 to 5000°K/sec are obtained for the high exit temperature chimney and 5000 to 8000°K/sec for the low exit temperature chimney. The higher rate corresponds to the run with the 2500°K peak temperature and the lower rate to the run with the 2000°K peak temperature. The mixing of injected quenching air with the hot products takes place in a short 80 mm section of the chimney and occurs in less than 0.04 sec. There is further mixing and cooling downstream of the chimney with the ambient air (see Fig. 1). Table 2 lists the flowrates, peak temperatures, equivalence ratios and the fraction of oxygen in the oxidizer. The equivalence ratio listed is based on two liters of oxygen per gram of coal, plus two liters of oxygen per liter of methane for stoichiometric conditions.

The sampling procedure involves collecting a sample of fly ash over a period of 2 minutes. This sampling time gave, under all operating conditions, an adequate amount of sampling material for both x-ray analysis and Beta gage mass determination. Approximately 1 gram of coal was combusted in this sampling time. The dichotomous sampler regulates itself to sample at a constant flow rate of 30 l/min, so that the same volume was sampled every run.
RESULTS AND DISCUSSION

The normalized percentages of 14 elements in the small size fraction for various runs are listed in Table 3. The elemental concentration on a given filter is first normalized to the silicon concentration on that filter, then the percent in the small size fraction is calculated for each run. The percent in the small size fraction is defined as the ratio $(100)\cdot\left(\frac{s}{s+L}\right)$ where $s$ is the normalized elemental concentration on the small size fraction filter for a given run, and $L$ is similar except for the large size fraction filter. The normalization is made to account for any sample material that may be lost from the filter between the time the sample is taken until the time it is analyzed. The usefulness of the normalization to silicon is based on the assumption that the concentration of silicon in the fly ash is independent of particle size. It was found, however, that the concentration of silicon in the small size fraction did change slightly with the peak temperature, but there was no noticeable change with the chimney exit temperature. The slight change in silicon concentration with the peak temperature does not alter the conclusions made on the relative comparison of the elements concentration in the small size fraction. The normalization was found to reduce the scatter of the elemental concentration data. The scatter for the $2000^\circ$K peak temperature case was consistently larger than that for the $2250^\circ$K and $2500^\circ$K peak temperatures.

In Fig. 4 the percent of total sample weight in the small size fraction is shown as a function of the peak temperature. From the linear least squares fit shown in Fig. 4 it is seen that the weight percentage in the small size fraction increases with increasing peak temperature.
No correlation was found between the percentage of the total sample weight in the small size fraction and the chimney exit temperature.

In Fig. 5 a comparison is made between the volatile element arsenic and the refractory element aluminum. Both elements are first normalized to silicon and then plotted as a function of chimney exit temperature. The line through the small size fraction arsenic data is a least squares fit line. The concentration of arsenic in the small size particles appears to be a function of chimney exit temperature, while the concentration of aluminum does not. The peak temperatures that correspond to the chimney exit temperatures shown in Fig. 5 are listed in Table 3.

Figure 6 is plotted to again compare the behavior of arsenic and aluminum. The percent of aluminum and arsenic in the small size fraction is shown as a function of peak temperature. This figure clearly shows the enrichment of arsenic (~90%) and the depletion of aluminum in the small size fraction (~30%). The small increase in aluminum concentration in the small size fraction with increasing peak temperature is not large enough (compared to uncertainties) to be significant.

Elements showing significant enrichment in the small size fraction besides arsenic are: iron, zinc, potassium and chromium. Other elements having significant enrichment in the small size, but a large degree of scatter at low peak temperatures, are: rubidium, vanadium, nickel, selenium, and sulfur. Calcium and titanium appear to be enriched in the small sizes but not to as great an extent. The results are inconclusive for antimony and manganese. As noted previously, aluminum was depleted in the small size fraction. Similar enrichments of arsenic, rubidium, vanadium, zinc, and nickel were found in samples from utility boilers by
Agreement was also found for the depletion of aluminum and the slight increase in titanium and iron concentrations in small particles. The enrichment of iron in the small particles increased with increasing peak temperature; this was not found in the utility boiler tests because of their constant operating conditions.

The results of this experiment appear to be in agreement with a vaporization-condensation model for the chemistry of small fly ash particles. According to the model some of the volatile elements in the coal are vaporized in the high temperature region of the flame. Changes in the chemical state or a decrease in temperature cause the vapor to become saturated and condensation may occur. From this model one would anticipate that the concentration of elements in a particle of a given size would depend on both the peak combustion temperature and the temperature at which quenching occurs (chimney exit temperature). The peak temperature dictates which elements are volatilized. It can be concluded from the elemental concentrations in the two size categories that arsenic, chromium, vanadium, nickel, zinc, selenium, tin, potassium, sulfur and rubidium volatilize to a significant extent in the combustion process. General agreement with Smith is found except in the case of iron. We found iron to be slightly enriched in the small size fraction, whereas Smith found iron to behave like aluminum and subsequently show a depletion in small size particles. The vaporization-condensation model leads one to predict a higher concentration of volatiles in smaller particles as the chimney exit temperature (or temperature at quenching) is increased; this is seen to be the case for arsenic (Fig. 5) and other volatiles (Table 3). The reason for this, using the vaporization-condensation model,
is that as the temperature at quenching is increased a larger percentage of the volatiles will be in the vapor state and upon rapid quenching they will form small particles by homogeneous nucleation.

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REFERENCES


TABLE 1
PITTSBURG SEAM COAL PROPERTIES

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Table 2. Experimental Conditions: Fuel and Oxidizer Flow Rates

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<th>Methane Concentration %</th>
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<th>Flow Rates l/min</th>
<th>Coal Flow Rate g/min</th>
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*Equivalence Ratio = \( \frac{O_2}{\text{Stoic.}} \)

\( \frac{O_2}{\text{Fuel}} \frac{\text{Supplied}}{\text{Fuel}} \)
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Table 3. Normalized Percent of Each Element in Small Size Fraction
Figure 1 Experimental Apparatus
Fig. 2  Schematic of the automated dichotomous air sampler.
Fig. 3 Chimney Temperature Profiles
Fig. 4 Sample Weight in Small Size Fraction
Fig. 5 Comparison of Arsenic and Aluminum (△ Low Exit Temperature Chimney, Small Size Fraction; ○ High Exit Temperature Chimney, Small Size Fraction; □ Low Exit Temperature Chimney, Large Size Fraction; ■ High Exit Temperature Chimney, Large Size Fraction)
Fig. 6 Comparison of Aluminum and Arsenic (▲, △ Low Exit Temperature Chimney; ●, ○ High Exit Temperature Chimney)
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