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CHARACTERISTICS OF FLY ASH FROM LABORATORY COMBUSTION OF PULVERIZED COAL

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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 exptected 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 $(100)\cdot(\frac{s}{s+L})$ 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 usefullness 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 noticable 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°K peak temperature case was consistently larger than that for the 2250°K and 2500°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

others[4,9,10]. 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[2,3]. 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, iton, potassium, sulfur and rubidium volatilize to a significant extent in the combustion process. General agreement with Smith[9] 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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TABLE 1

PITTSBURG SEAM COAL PROPERTIES

Proximate Analysis	moisture	1.6%
	volatile matter	35.8%
	fixed carbon	57.2%
	ash	5.4%
Ultimate Analysis	H	5.3%
	C	78.6%
	N	1.6%
	O	8.1%
	S	1.0%
	ash	5.4%

Estimated Size Distribution	Sieve Size		
	On	Thru	% Weight
	80	--	0.0
	170	80	5.0
	200	170	7.1
	325	200	31.5
	--	325	56.4

Table 2. Experimental Conditions: Fuel and Oxidizer Flow Rates

Methane Concentration %	Excess Oxygen ℓ/min	Flow Rates ℓ/min			Coal Flow Rate g/min	Equivalence Ratio*	$\frac{O_2}{O_2 + N_2}$	Peak Temp. °K
		Methane	Oxygen	Air				
8	1.5	2.4	1.9	25.7	0.5	0.79	0.26	2000
10	1.5	3.0	3.6	23.4	0.5	0.82	0.32	2250
12	1.5	3.6	5.3	21.2	0.5	0.85	0.37	2500

$$\text{*Equivalence Ratio} = \frac{\frac{O_2}{\text{Fuel}}\ \text{Stoic.}}{\frac{O_2}{\text{Fuel}}\ \text{Supplied}}$$

PEAK TEMP °K	2000	2250	2500	2000	2250	2500
EXIT TEMP °K	1000	1100	1200	1400	1600	1700
Aluminum	55 56 56 58 56 55	49 51 48 48	32 32 31 29	59 58 57 57 57 56 54 54	47 47 45 47	51 42 36 40
Antimony	64 88 0	52	47 99 99 47	79 0 98 78 99 99	61 29 99 99	99 99 66
Arsenic	77 84 70 84 84 67	92 98 92 93	91 96 93 90	98 98 95 95 96 94 95	98 97 97 96	94 99 92 93
Calcium	56 57 50 60 58 65	68 66 65 65	60 62 62 60	61 65 59 61 56 65 61	65 64 62 63	62 65 60 63
Chromium	50 81 67 76 74 88	84 83 76 70	68 63 87 76	71 77 72 70 73 73 72	87 87 86 85	73 91 82 81
Iron	57 39 57 60 59 61	70 70 70 69	69 70 71 70	59 59 58 57 59 60 60	69 68 70 71	57 71 69 72
Manganese	47 41 70 91 72 67	81 70 79 57	50 48 50 56	89 55 44 70 78 72 76	40 49 73 76	48 51 58 55
Nickel	68 78 59 69 64 86	83 86 79 84	71 79 72 77	74 79 78 70 69 73 65	77 83 77 87	70 81 72 78
Rubidium	64 58 61 56 58 73	74 75 68 75	81 81 83 81	63 67 60 57 60 0 71	80 78 83 77	66 81 76 83
Selenium	99 99 80 99 80 90 99	95 96 94 89	85 87 93 84	91 91 99 88 87 77 90	84 88 93 99	75 77 88 99
Sulfur	65 69 62 55 59 58	85 88 79 80	78 80 78 78	77 82 74 76 76 77 80	91 91 91 93	71 91 90 90
Titanium	54 58 53 67 56 58 62	69 68 65 65	65 63 64 63	60 62 62 58 58 62 57	66 64 61 65	59 67 60 63
Vanadium	54 53 71 85 79 61	80 80 79 72	65 78 75 70	74 88 74 81 78 63 75	80 83 81 82	78 76 70 89
Zinc	76 81 78 85 78 99	90 92 90 87	90 81 83 80	82 84 88 89 85 71 85	81 87 86 93	70 82 91 92

Table 3. Normalized Percent of Each Element in Small Size Fraction

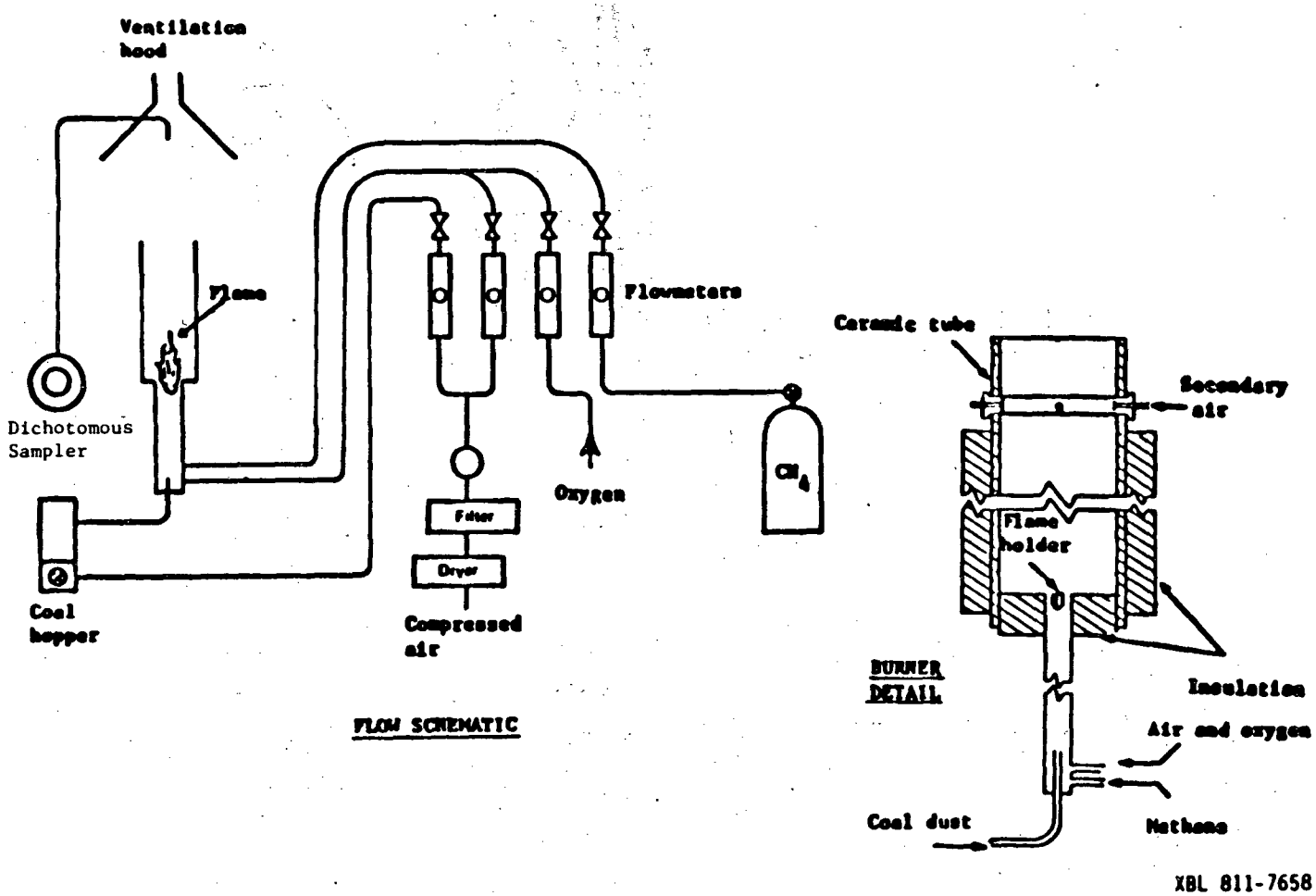

Figure 1 Experimental Apparatus

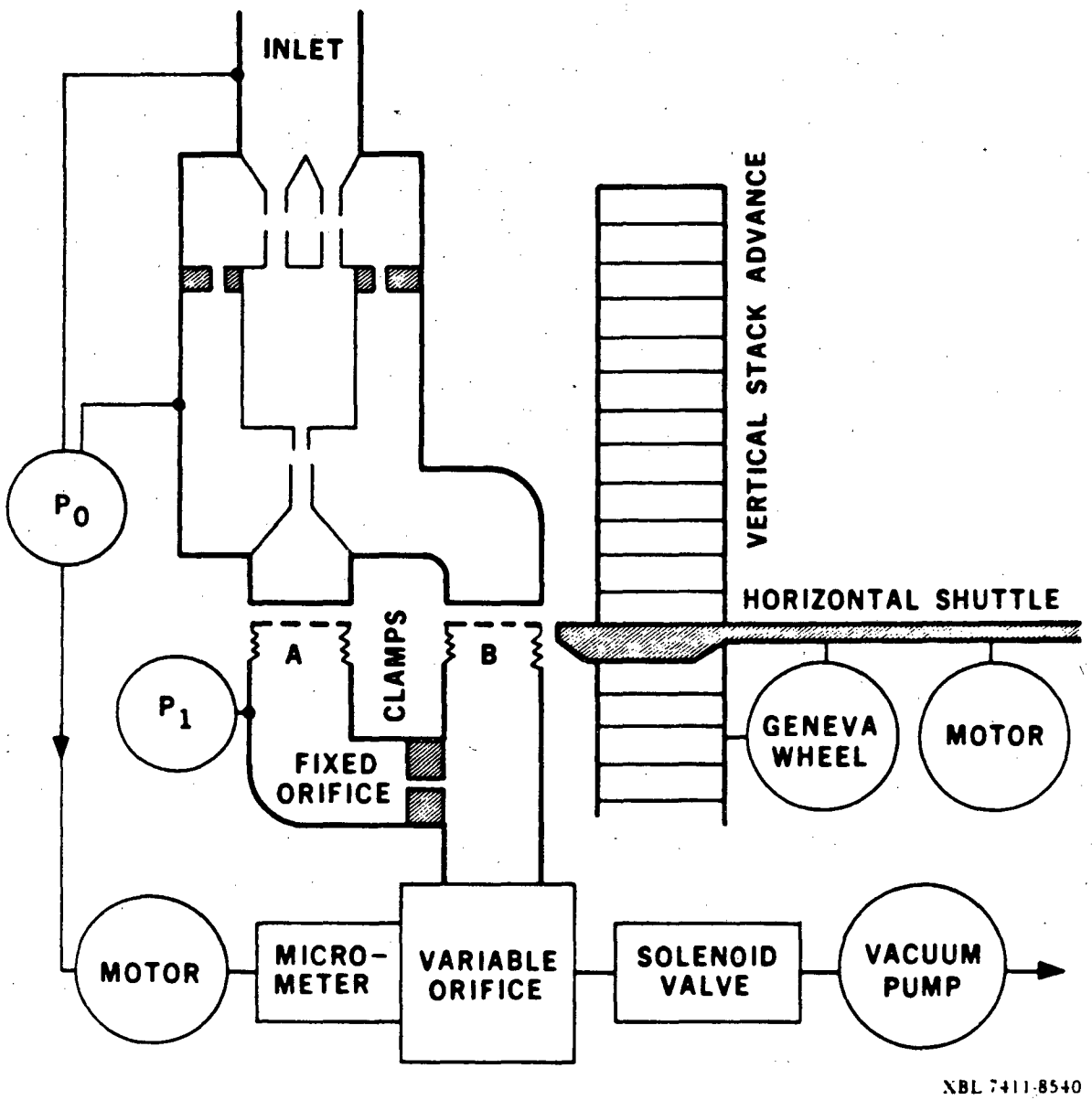

Fig. 2 Schematic of the automated dichotomous air sampler.

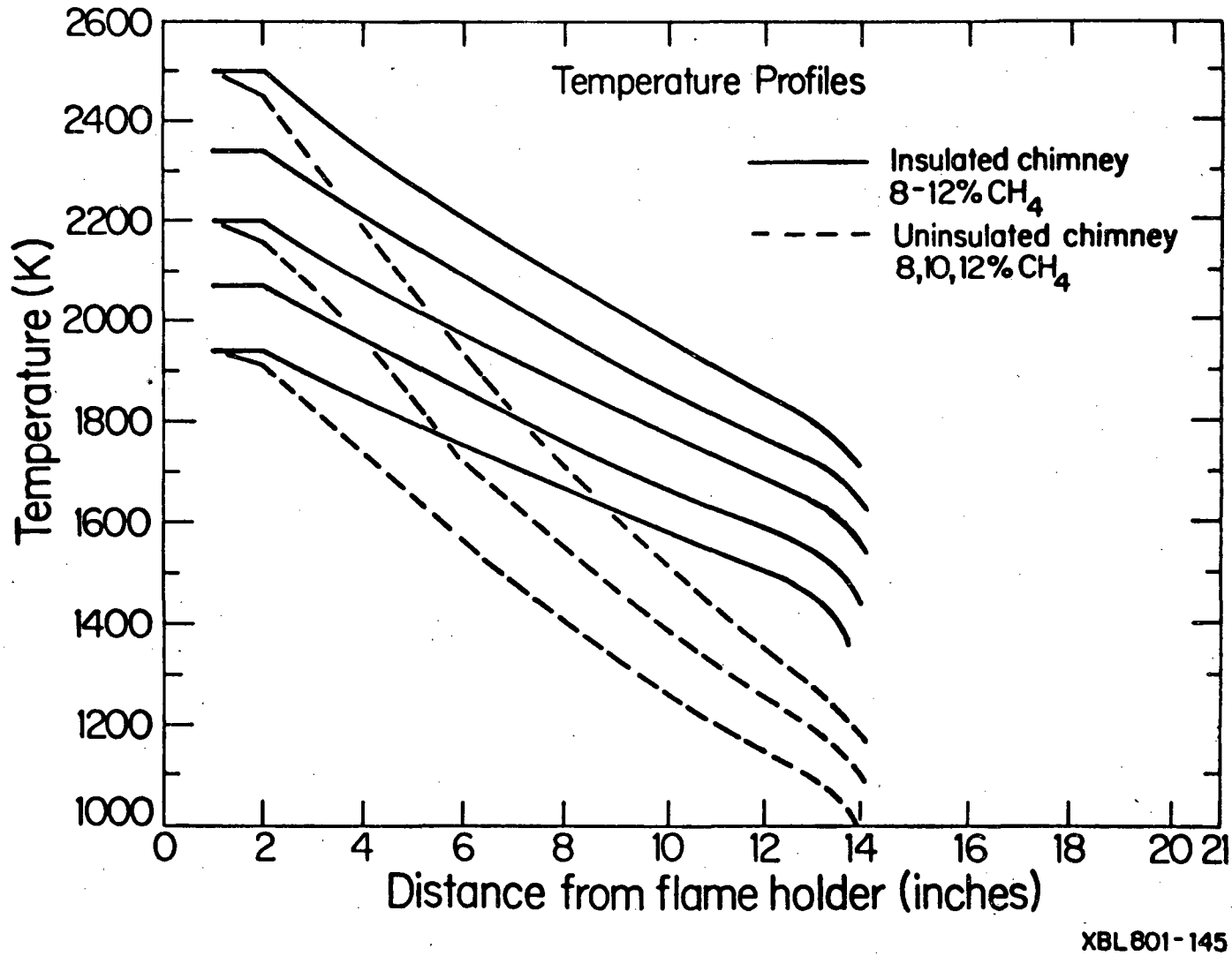

Fig. 3 Chimney Temperature Profiles

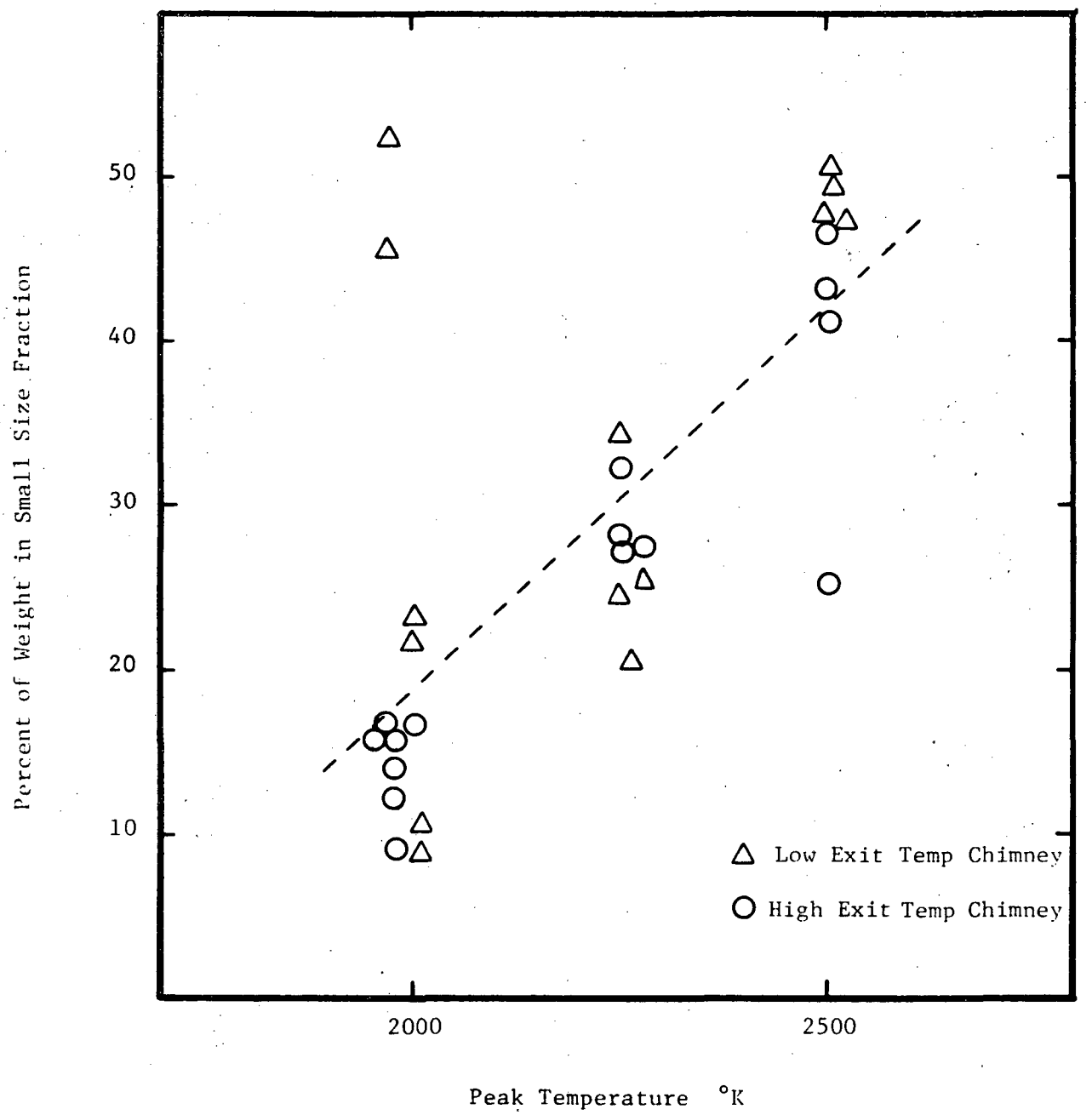

Fig. 4 Sample Weight in Small Size Fraction

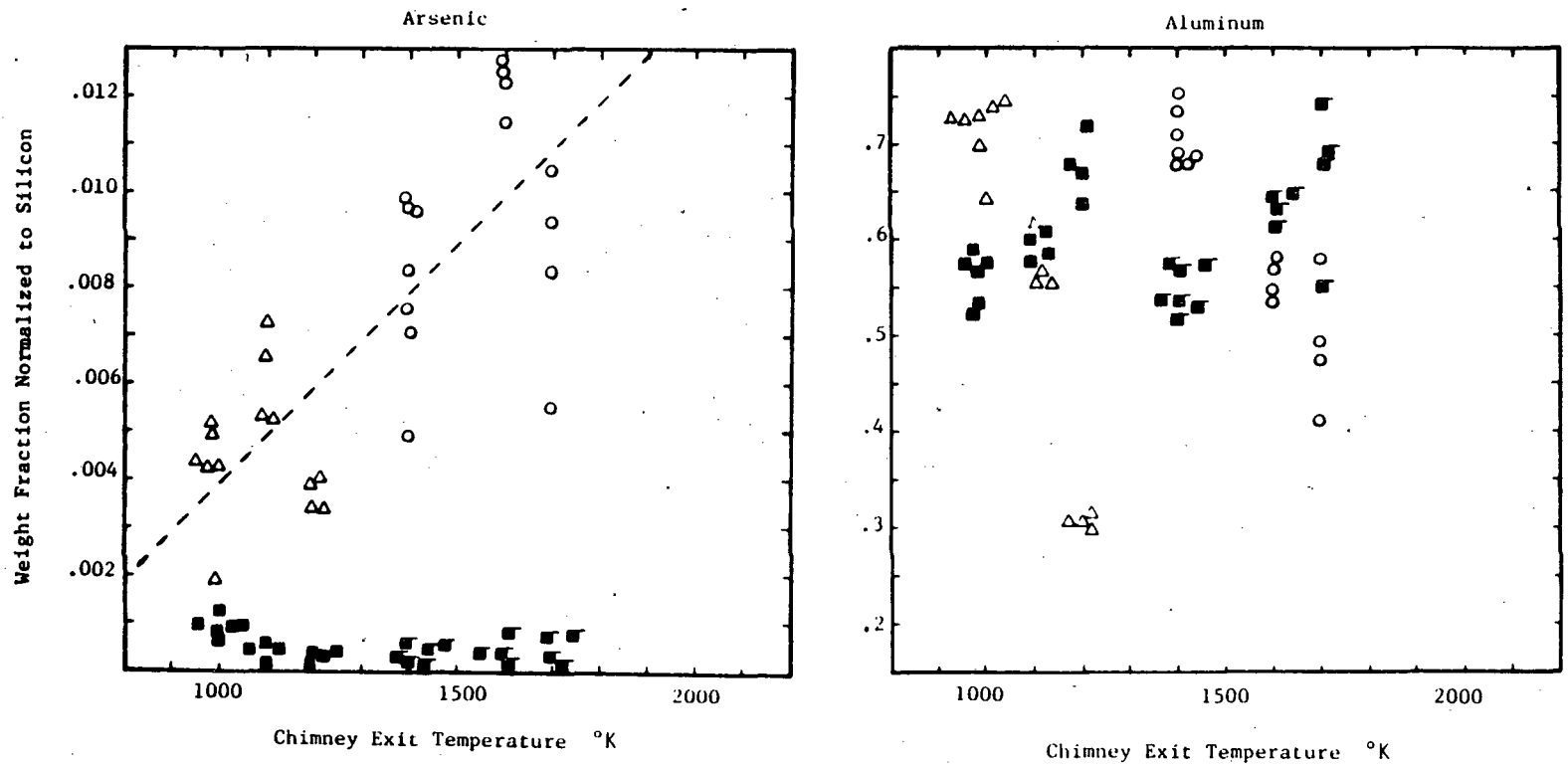

Fig. 5 Comparison of Arsenic and Aluminum (△ Low Exit Temperature Chimney, Small Size Fraction; ○ High Exit Temperature Chimney, Small Size Fraction; ■ Low Exit Temperature Chimney, Large Size Fraction; ■ High Exit Temperature Chimney, Large Size Fraction)

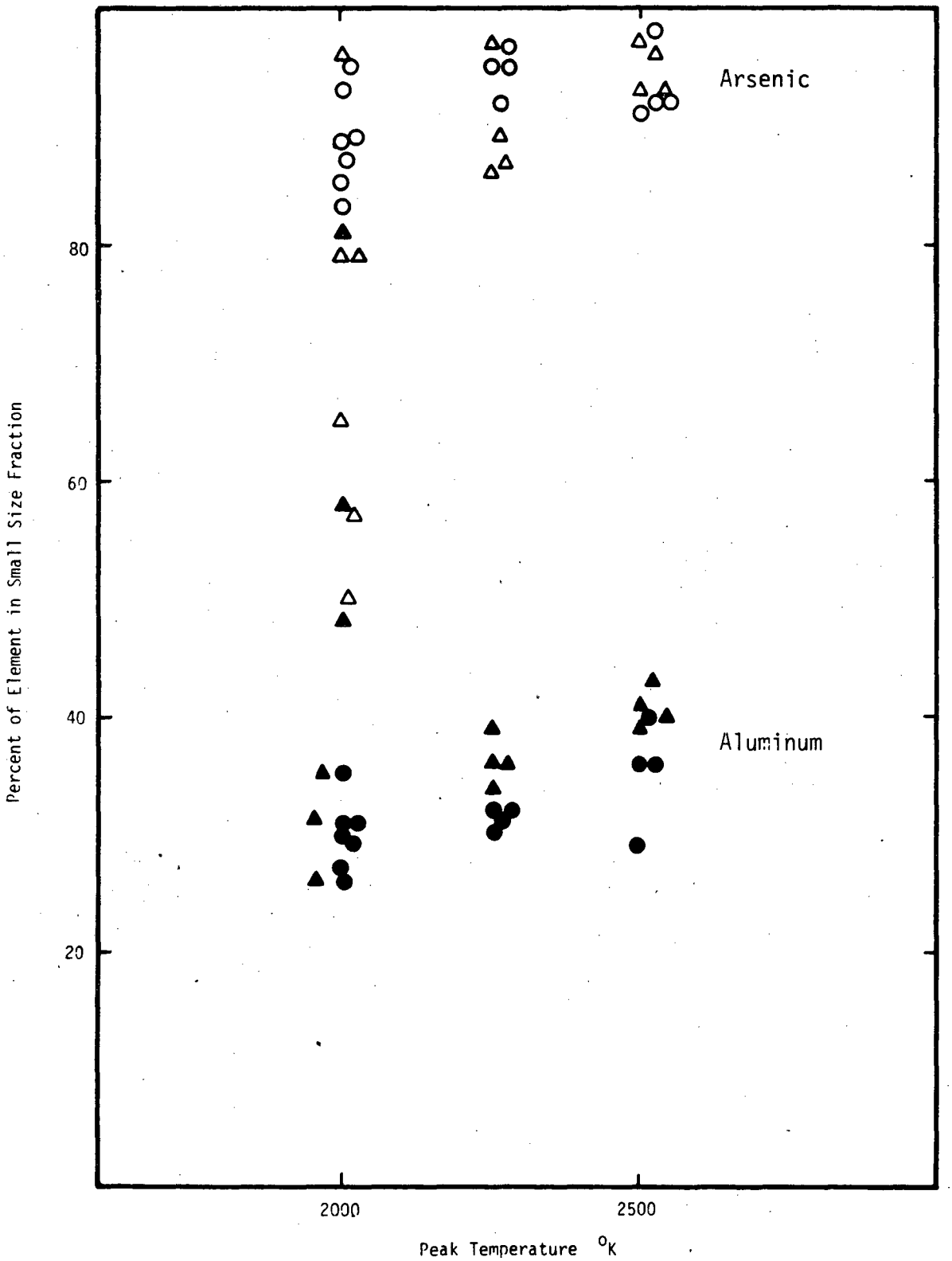

Fig. 6 Comparison of Aluminum and Arsenic (▲ , △ Low Exit Temperature Chimney; , ○ High Exit Temperature Chimney)

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