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MASTER

CHARACTERIZATION OF SUBMICRON FLY-ASH IN CYCLONE-FIRED BOILERS

MASTER

by

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ABSTRACT

CHARACTERIZATION OF SUBMICRON FLY-ASH IN CYCLONE-FIRED BOILERS

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As coal becomes increasingly important in providing the energy requirements of this country and many others, various efforts are underway to ensure that the utilization of coal will produce minimum environmental damages. Submicron fly-ash has been recognized as a potential problem in emission control, a health hazard and a major cause of boiler fouling. This study contains information concerning the submicron fraction of fly-ash produced by cyclone-fired boilers. Experimental activities involved size fractionation and chemical analyses of separated ash particles. Results have been compared with predictions developed by others in the UNH Fly-Ash Research Group.

According to this study, approximately 10 percent of the fly-ash under investigation consists of particles in the submicron range. The chemical composition of the submicron fraction is considerably different from that of the bulk. In particular, silicon and sulfur are enriched while iron and aluminum are depleted. Calcium shows slight possible enrichment trends while sodium, potassium and magnesium exhibit constant concentrations for all size ranges. Silicon enrichment is consistant with equilibrium predictions which indicate significant vaporization of this element under reducing conditions. The sulfur trends are attributed to the surface adsorption of gaseous sulfur-containing species. Enrichment of iron is also predicted whereas the opposite is found experimentally.

The morphology of submicron ash was examined extensively with the aid of the scanning electron microscope. Submicron ash can be approximately visualized as aggregates, each containing an average of 10 or so primary particles. The primary particles themselves are about 0.06 micron in diameter.

This study, intended as an aid to the theoretical development, has provided basic data on the particle size versus enrichment characteristics of fly-ash in a cyclone-fired boiler. In general, the vaporization condensation mechanism is further confirmed as a major source of submicron fly-ash. Discrepancies, particularly regarding iron enrichment, deserve further attention.

Chapter I

Introduction

The major energy source for electric power production in the U.S. has been and will probably continue to be coal. Other energy sources for electricity production include fuel oil, natural gas, hydroelectric dams, and, more recently, nuclear reactors and geothermal energy. Extensive U.S. coal reserves coupled with a lack of alternate, large, reliable or inexpensive energy sources provide assurance that coal will remain the major fuel for electric power production for the next 25 years (1). The idea of converting coal to a clean fuel by removing ash and sulfur before burning, thereby solving the problem of fly-ash formation during combustion, is attractive. However, the proposed methods for accomplishing this are only in an experimental stage at present. Thus, at least for the next 10 years, coal will be burned mainly in its natural form in conventional boilers (2).

The ash content of coal considerably greater than that of fuel oil. The potential for fly-ash emission is striking when one considers the amount of coal being burned by the utilities (over 400 million tons in 1975). Modern plants with high efficiency collectors, though capable of matching Environmental Protection Agency (EPA) standards today, must improve in cleanliness to match more stringent standards expected in the future. For particulate emission control, electrostatic precipitators have been widely used in the electric-power industry. These devices have inherent advantages in handling large volumes of flue gas with low pressure drop. Although most electrostatic precipitators have an efficiency of above 95%, they are least efficient for the collection of submicron particles. This submicron ash fraction may be as much as 10 percent of the total fly-ash, depending on the type of boiler and fuel.

Submicron fly-ash, though comprising a small fraction of total mass, causes inordinate environmental damage. These ultrafine ash particles have higher concentrations of the more volatile toxic metallic elements (3), larger specific surface area for the adsorption of gaseous toxins, and they penetrate more deeply into the respiratory system (4). Submicron particles also have an adverse effect on visibility because they are effective scatterers of light. Also the low sedimentation velocity of fine particles allows them to remain suspended in the atmosphere for long periods of time. The large number of nucleation sites thus available exerts profound effects on atmospheric condensation.

Various efforts are underway to improve the performance of particulate control devices (5,6,7). However, a complementary long range attack on this pollution problem is to develope a better understanding of ash formation and growth mechanisms and to apply this information to future boiler designs. Recently, EPA has placed tighter restrictions on fine particulate emissions. For coal-fired power generation, the emission limit of particulate matter is 0.1 lb/million Btu for the year 1975 and the limit will be reduced to 0.02 lb/million Btu in 1980 (1). To understand the significance of this, consider the Merrimack Unit 2, a cyclone-fired (CF) boiler, (Public Service Company of New Hampshire) which was employed for this study. This unit, with an electric output of 340 Mw has a typical internal ash loading of 10 to 15 percent of the total coal ash. Pervious work (8) had shown an average ash loading of 0.06 grain/cu.ft.

in the radiant section with a gas flow-rate of 3.5 million cu.ft./min at $3000^{o}R$. The total fly-ash flow rate in the furnace, therefore, is about 1800 lb/hr or 22 ton/day. To meet current EPA standards, the dust collecting equipment must clean about 1 million cu.ft./min. of hot flue gases with an efficiency of 94.2%. To meet 1980 standards, the dust collecting equipment must be 98.8% efficient. Thus, the electrostatic precipitator must remove a very high percentage of the submicron ash in order to be successful, a circumstance quite different from that existing when lower efficiencies of 95% or so were necessary. A thorough understanding of the chemical and morphological properties of submicron ash will furnish important information for the design of future boilers and dust collecting equipment.

Perceiving the need for more scientific information of fine particle formation and control, a three year project was initiated in 1976 at U.N.H. to investigate the mechanism of fly-ash formation in coal-fired utility boilers (9). The investigation has taken two directions. The first is a fundamental particle formation study using a laboratory burner. The study of the formation and growth of pure and mixed metal oxides in this burner provides basic information necessary for the modelling of real systems. Secondly, coal-fired boilers are being examined. This includes the collection and characterization of fly-ash from various boiler types. This thesis is concerned with the morphological properties and major chemical composition of submicron particles. With this information, we hope to gain insight into the origin and the mechanism of formation of these particles.

The major portion of this study was done using hopper ash collected by the electrostatic precipitator at the Merrimack Unit 2 of Public Service

Company of New Hampshire. CF boilers account for about 10 per cent of utility production and are not as widely used as pulverized-fuel (PF) boilers. However, the existing CF boilers will be in operation for many more years to come and their particulate emmission problems are not to be neglected. High operating temperatures in these boilers create both excessive nitrogen oxide emmissions (10) and a significantly larger amount of submicron ash compared with pulverized coal furnaces (11).

Hopper ash samples were fractionated by size and each size fraction was subjected to a combination of chemical analysis including atomic absorption spectroscopy (AA), energy dispersive x-ray analysis (EDAX), and inductively coupled plasma analysis (ICPA). Special attention was given to the enrichment trends of the major elements in submicron particles.

Probe samples from various locations in the operating boiler were also collected. However, because of limited sample size, detailed evaluations of these samples were not possible. Some probe samples were also extracted using membrane filters for fractionation. These were analyzed by EDAX, but results were incomplete and inconclusive.

Chapter II

Literature Survey

Work, to date, on fly-ash characterization has been concerned, primarily, with particles larger than one micron in diameter. The common approach to fly-ash characterization involves a size fractionation followed by one or more chemical analyses. Many methods and devices have been used to determine particle size distributions. These include sieving, sedimentation, centrifugal classification, cascade impaction, light scattering, diffusional sizing and microscope counting. Sedimentation was used from the 1940's to early 1960's for subsieve sizing of fly-ash, but the centrifugal classifier method now specified by ASME Power Test Code No. 28 for collector performance evaluation is widely used today. Particle size distributions from representative power plants have been obtained using sedimentation methods, the Bahco classifier (12), the cascade impactor method (13) and specialized methods such as light scattering (14).

Schulz, Engdahl and Frankenberg (15) sampled from a CF boiler. The sampling points are inlet and outlet of the electrostatic precipitator. They concluded that fifty percent of the weight of particles leaving the electrostatic precipitator was smaller than 2 microns and 15 per cent was smaller than 1 micron in diameter. Scanning electron microscopy was used for preliminary morphological studies. Additional research by scanning electron microscope and electron probe micro-analyzers to identify the composition of the sub-micron particles was suggested.

Cheng et al. (16) did qualitative studies on particles from coal-fired and oil-fired boilers with a scanning electron microscope and EDAX. They reported major morphological differences between oil-fired and coal-fired particles. Chemical compositions of ash particles were qualitative and were not reported as a function of particle size.

Linton, Loh and Natusch (17) studied the surface concentration of trace elements of fly-ash samples from two coal-fired power plants burning bituminous coals. An ion microprobe and auger microprobe were used to detect concentration changes. Arbitrary units of secondary ion intensity ratio were obtained at an estimated depth of 100 to 1300 Angstroms into the particle surface. However, only large particles (75 to 100 microns in diameter) were studied. This was done for convenience on the assumption that elemental concentration per unit surface area should be independent of particle diameter. It was shown that a number of trace elements exhibited a significant increase in concentration near particle surfaces. Matrix elements such as aluminum, iron and silicon, however, showed no signs of surface enrichment. It was suggested that the surface enrichment was due to the volatilization of certain elements in the high temperature combustion zone and then condensation onto the surfaces of entrained fly-ash particles. The possibility of surface enrichment due to surface deposition of submicron particles was ignored. Due to the lack of morphological studies in this work, the postulated vapor-condensation mechanism is inconclusive (e.g. a large population of coalescing submicron particles on the surface of the larger particles would be a good indication of enrichment due to the presence of submicron particles).

Davison, Natusch, and Wallace (18) studied the relationship between the concentration of trace elements and particle size. They studied ash from a PF boiler. Two types of ash samples were studied: hopper ash from a cyclonic precipitator and airborne ash in the immediate area of the power plant. Size fractionation of hopper ash was accomplished mechanically by sieving and also aerodynamically using a Roller particle-size analyzer (American Instrument Co.). The smallest cut-off particle diameter was 5 microns. Airborne ash samples were collected and separated by an Andersen stack sampler with the smallest size fraction of 0.65 to 1.06 microns in particle diameter. No back-up filter was attached to the Andersen impactor outlet to collect particles smaller than 0.65 microns. Certain trace elements were found to exhibit concentration increases with decreasing particle diameter. Major elements such as aluminum, iron and silicon showed limited but inconclusive dependence on particle size. Elements such as potassium and calcium showed no concentration trends at all. Size fractionations of the hopper ash samples were certainly not adequate with the smallest particle cut-off diameter at 5 microns. Airborne ash was better separated with the Andersen impactor, but the lack of an absolute back up filter ignores an important class of fly-ash particles. The concentration increase of trace elements with decreasing particle size can be explained by the increase of specific surface area or the increasing population of submicron particles in each separated fraction with decreasing particle size.

Raask and Wilkins (19) investigated the extent of silica vaporization when coal was gasified. They concluded that silica is volatilized mainly as silicon monoxide which is formed by the reduction of silica or silicate with carbon and hydrogen. They noted that direct vaporization of silica is significant at temperatures only above 2100°C.

Sarofim, Howard and Padia (20) studied the relationship between combustion conditions and ash characteristics using an electrically heated drop tube furnace. Peak furnace temperatures of $1500^{o}K$ to $2700^{o}K$ were used. Qualitative analyses of ash particles were done with a scanning electron microscope and EDAX. Particle size distributions were obtained with a Zeiss semi-automatic particle counter. There was indirect evidence of vaporization and condensation of silica. Submicron particles were not separated but found deposited on the surface of larger ash particles. The major composition of these fine particles was assumed to be vaporized and condensed silica. Mass balances showed a 4% total weight loss at $1830^{o}K$ which was attributed to the formation of submicron silica particles.

The major emphasis of previous fly-ash characterization studies has been the preferential concentration of trace elements in smaller particles. Although the health and environmental impact of submicron ash particles has been well recognized, these particles were not fractionated for separate analysis in these studies. Realizing its importance and the lack of information on submicron ash, this study was undertaken to examine it as a separate class of particles. Concentration of the matrix elements as a function of particle size was studied to compare their relative volatilities in a CF boiler environment. Previous studies have shown that given the amount of material vaporized and the growth time, particle size and morphology can be predicted (10,21).

Chapter III

Experimentation

A. Sample Collection

Fly-ash samples were collected from unit 2 of the Merrimack station, Public Service Company of New Hampshire. Unit 2 is a CF boiler with peak capacity of 340 Mw electric output. The distribution of ash produced in cyclone-fed boilers is about 15 percent fly-ash and 85 percent bottom slag. The unit consumes about 112.5 tons of coal per hour at peak load, and discharges flue gas through its own electrostatic precipitator to the stack. Coal burned at the Merrimack station during sample collection period was a medium-volatile, West Viginia, bituminous coal (Loveridge Mine, 36.9 percent volatile matter, 7 percent ash).

Two types of samples were collected: a) fly-ash retained in the electrostatic precipitator (hopper ash) and b) fly-ash from the gas stream of the operating boiler. Hopper ash was collected in bulk. Fly-ash in the gas stream was collected from boiler ports representing three locations: 1) half way up the radiant section (5th floor), 2) in front of the secondary supper heater (7th floor), 3) the reheat superheater (7th floor) (See Fig. 1). These sampling points represent ash residence times of 1.1, 1.5 and 2 seconds respectively. Samples were collected isokinetically.

B. Size Fractionation

To determine the size distribution and the dependence of chemical composition on particle size, ash samples were separated into size fractions and each of these fractions was subjected to chemical analysis. Three techniques were used to separate the hopper ash. In the first, ash samples were dispersed in a fluidized bed and then fed to an eight stage Andersen cascade impactor followed by an absolute filter.

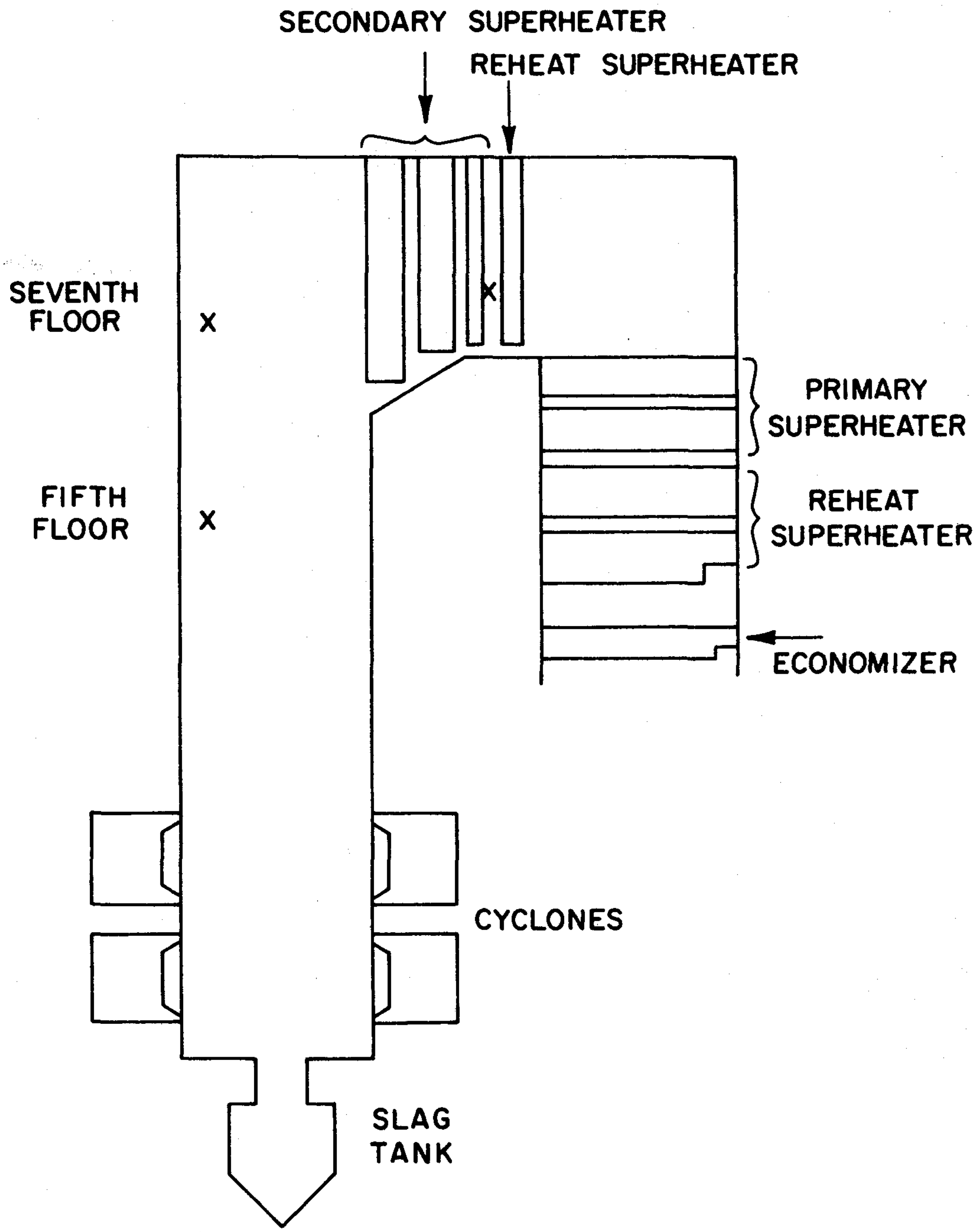

Figure 1 Approximate locations (marked X) of sampling points in the boiler.

Only samples separated by this method have size fractions large enough for chemical analysis. In the second technique, samples were dispersed ultrasonically in water and then fractionated by a serious of Nuclepore filters. A Joyce-Loebl disc centrifuge was used in the third method to differentiate particles in the submicron range. Samples collected by probe were fractionated into two size fractions by two Millipore membrane filters in series while sampling.

Figure 2 shows the flow diagram of the fluidized bed and the cascade impactor arrangement used in this study. The eight stage cascade impactor was designed to separate the particles into 8 fractions from 11 microns and above down to 0.4 micron in diameter. A backup filter gave absolute collection of the submicron particles. Particle size distribution of each impactor stage was also obtained experimentally by microscope counting using scanning electron micrographs. These results were compared with the impactor manufacturer's information on "effective cut-off diameter" for each stage. Substantial discrepancies were found for the first two stages while results for the rest of the stages showed good agreement. This is attributed to the partial size separation in the fluidized bed feeder before particles enter the impactor. Figure 3 shows the relationship between the average particle diameter and impactor stages as obtained by the impactor manufacturer's calibration and by scanning electron micrograph calibration.

Separations by Nuclepore filters and Joyce-Loebl disc centrifuge were done at Cabot Corporation, Billerica, Massachusetts. Figure 4 shows the cumulative weight percentages verse particle size of hopper ash as separated by the three methods. It must be noted that the Joyce-

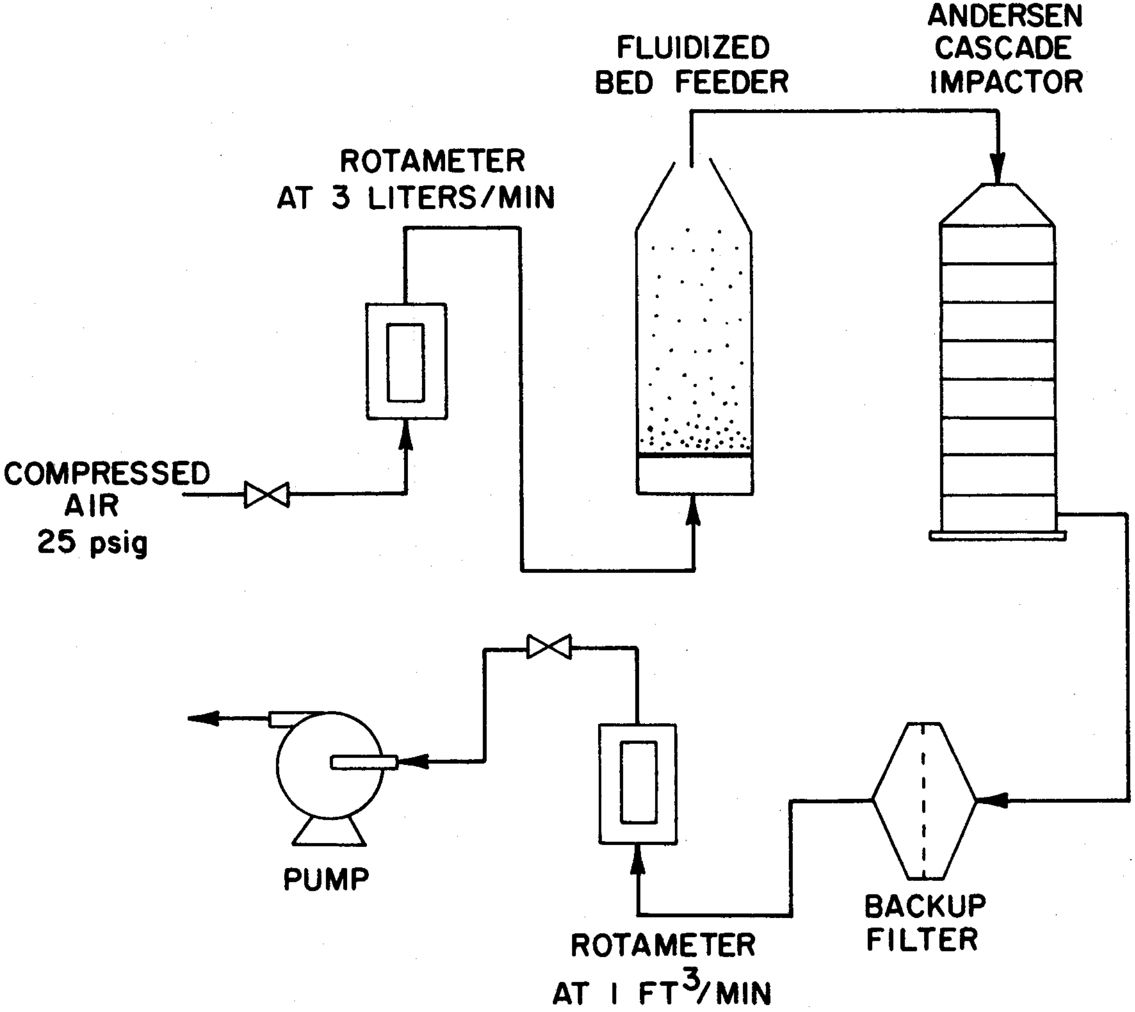

Figure 2 Flow diagram for cascade impactor separation.

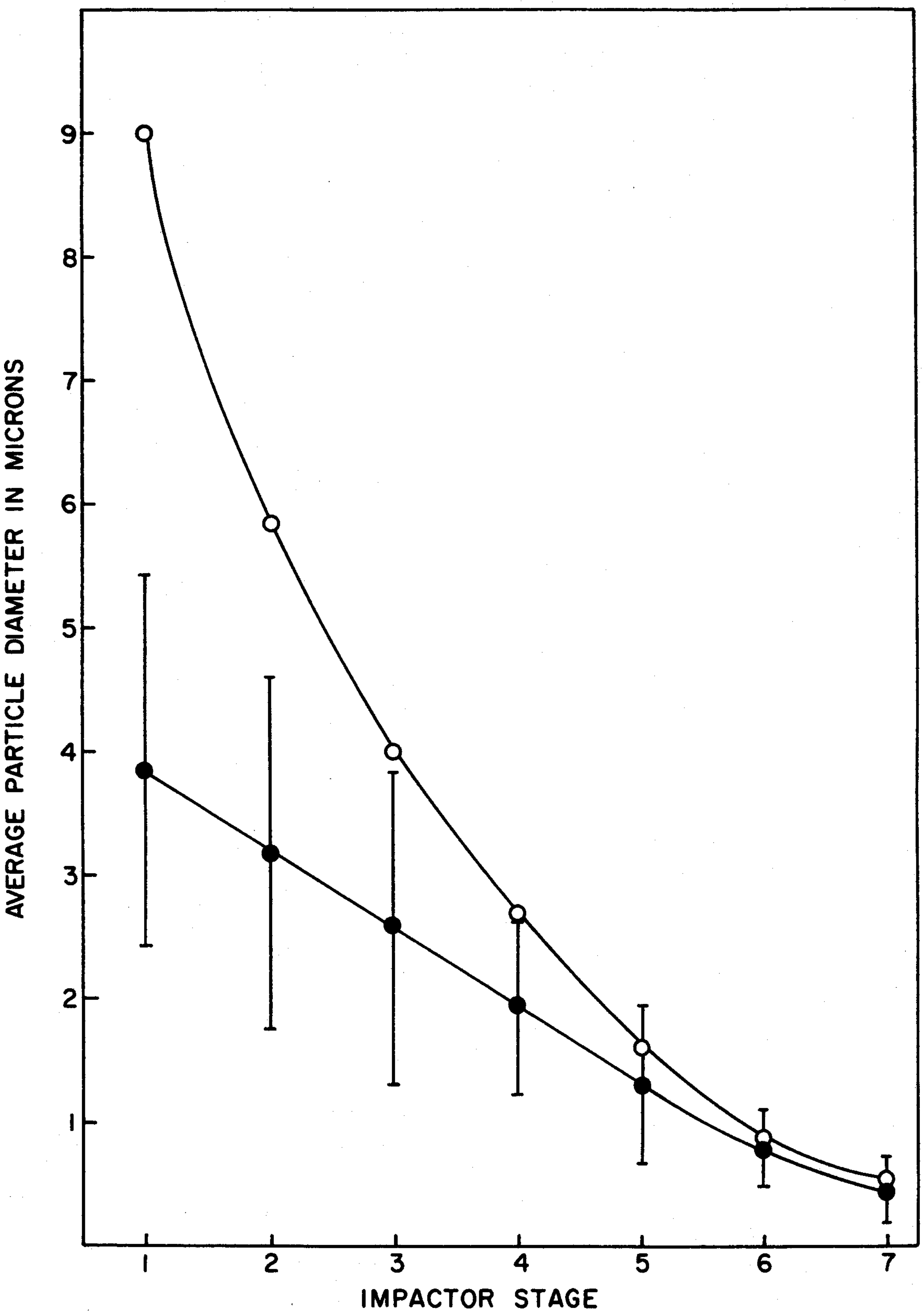

Figure 3 Average particle diameter of fly-ash separated by cascade impactions. Open symbols represent the impactor manufacturer's calibration. Filled symbols represent calibration done by microscope counting. Vertical bars indicate the maximum and mimimum particle size on corresponding impactor stages.

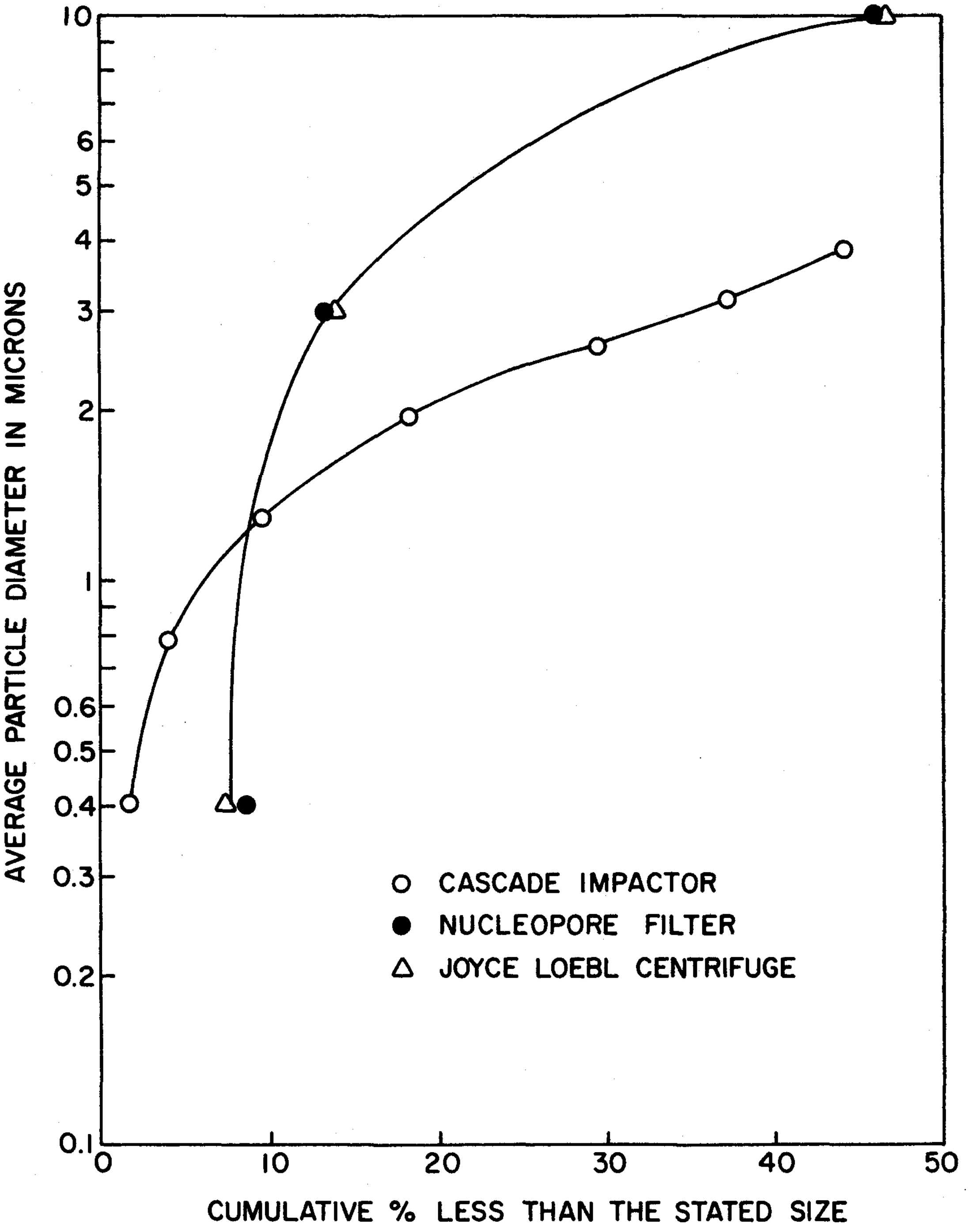

Figure 4 Cumulative weight percentages verses particles of hopper ash. Separations was done by cascade impactor, Nuclepore filters, and Joyce-Loebl disc centrifuge with normalization by Nuclepore filtration data.

Loebl result is not independent. Because of inability to detect rapid settling large particles, the result was arbitrary normalized using the Nuclepore results. The Joyce-Loebl size distribution, based on this normalized submicron fraction is, however, valid.

In a Nuclepore filter separation, the sample was first ultrasonically dispersed in water before filtering. This procedure enhances the disengagement of physically attached particles, which was verified by scanning electron micrographs (See Figure 9). Particle dispersion in a impactor separation was achieved in the fluidized bed but disengagement of the fine particles was poor. However, cascade impactor has certain advantages over the other two methods: 1) there is little carry-over of larger particles 2) results are reproducible 3) samples separated by the impactor method have fractions large enough for a variety of chemical analysis.

C. Particle Size and Morphology

Ash samples were examined by scanning electron microscopy (SEM). The mounting procedures employed are described in Appendix B.

SEM photographs of samples from selected stages of the impactor and back-up filter are shown in Figure 5. This series of pictures illustrates reasonable size separation in the impactor. Carry-over of the larger particles is not generally observed. Significant amounts of submicron particles are, however, found attached to the larger ones on early stages. Supermicron particles are usually discrete spheres. A significant number of fine particles having rather uniform primary diameters of about 0.06 micron are observed. This class of particles is thought to be condensation ash.

Figure 6 shows a high magnification micrograph of the ultra-fine particles. The dark background is carbon paint used for specimen mounting. These particles are noted to form aggregates consisting of roughly 10 to 15 primary particles. The aggregates have average lengths of about 0.3 microns. As noted, larger particles found on early stages of the impactor are heavily coated with fine particles. In some cases, the fine particles are partially fused onto the surface of the larger particles. The size of these partially fused particles is approximately the same as the size of primary particles of the aggregates (See Figure 7). In other cases, it is apparent that the fine particles are only physically attached to the larger ones (See Figure 8). Since the calculated collision frequency for the larger particles is rather low, the fact that they are heavily coated with submicron fines suggests they are artifacts. Electrostatic precipitators, like all dust collecting equipments, must promote particle collisions. This probably explains the heavy coating of physically-attached fines on the large particle shown in Figure 8. Probe samples, apparently, do not escape this dilemma. The membrane filters used in sample collections also enhance particle collisions. Particles entering the probe at first will be deposited on a relatively "clean" filter while particles entering later will have increasingly high probabilities of colliding with particles already on the filter. Thermal deposition in the probe will also promote collisions. The fact that submicron particles are frequently fused to the surfaces of larger particles suggests that quenching temperatures in the sampling probe were not low enough to prevent fusion of the smaller particles.

Figure 9 illustrates samples separated by Nuclepore filters. The backgrounds in these micrographs are the filters used for separation. The

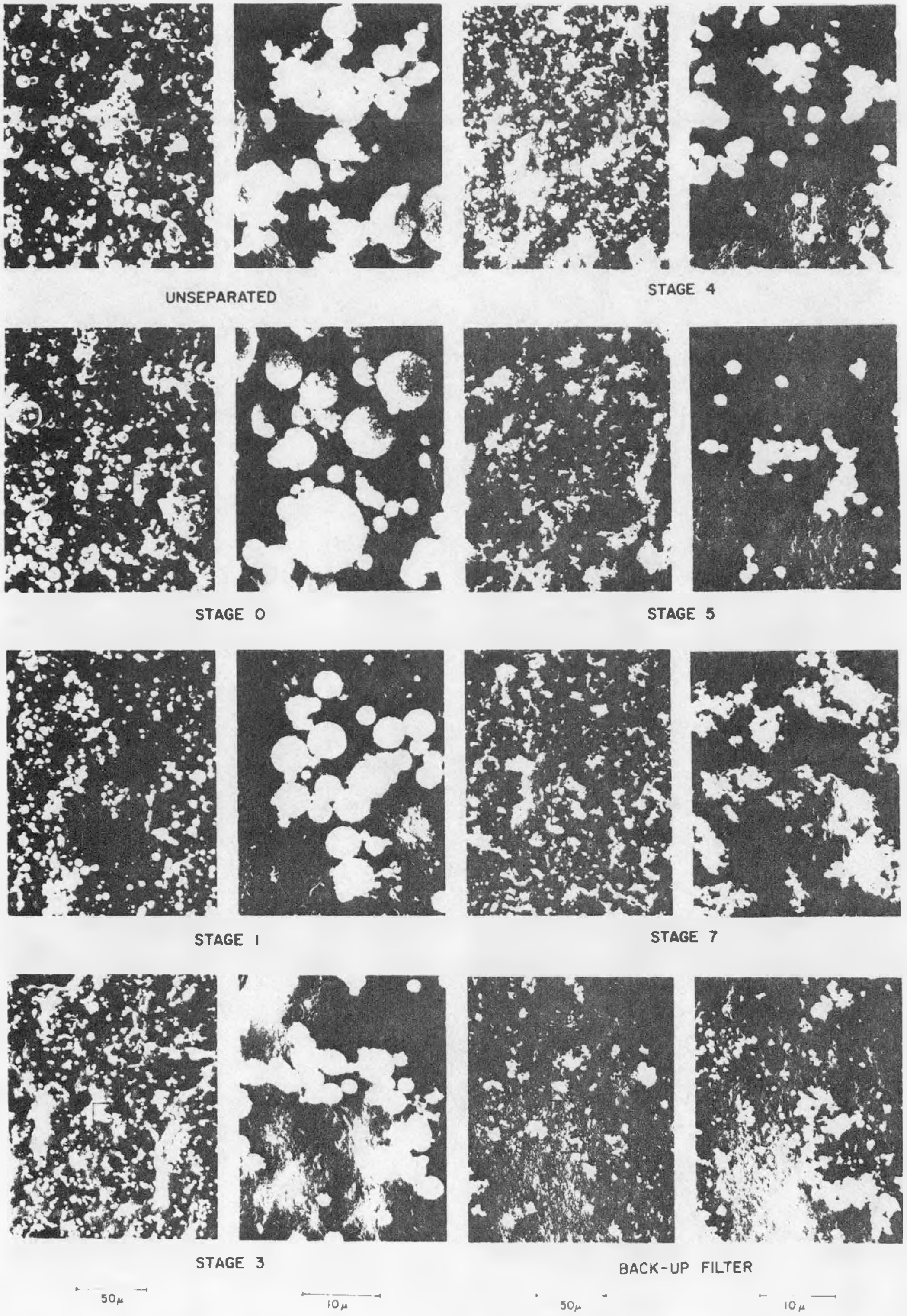

Figure 5 Scanning electron micrographs of separated fly-ash on selected stages and the filter of the impactor.

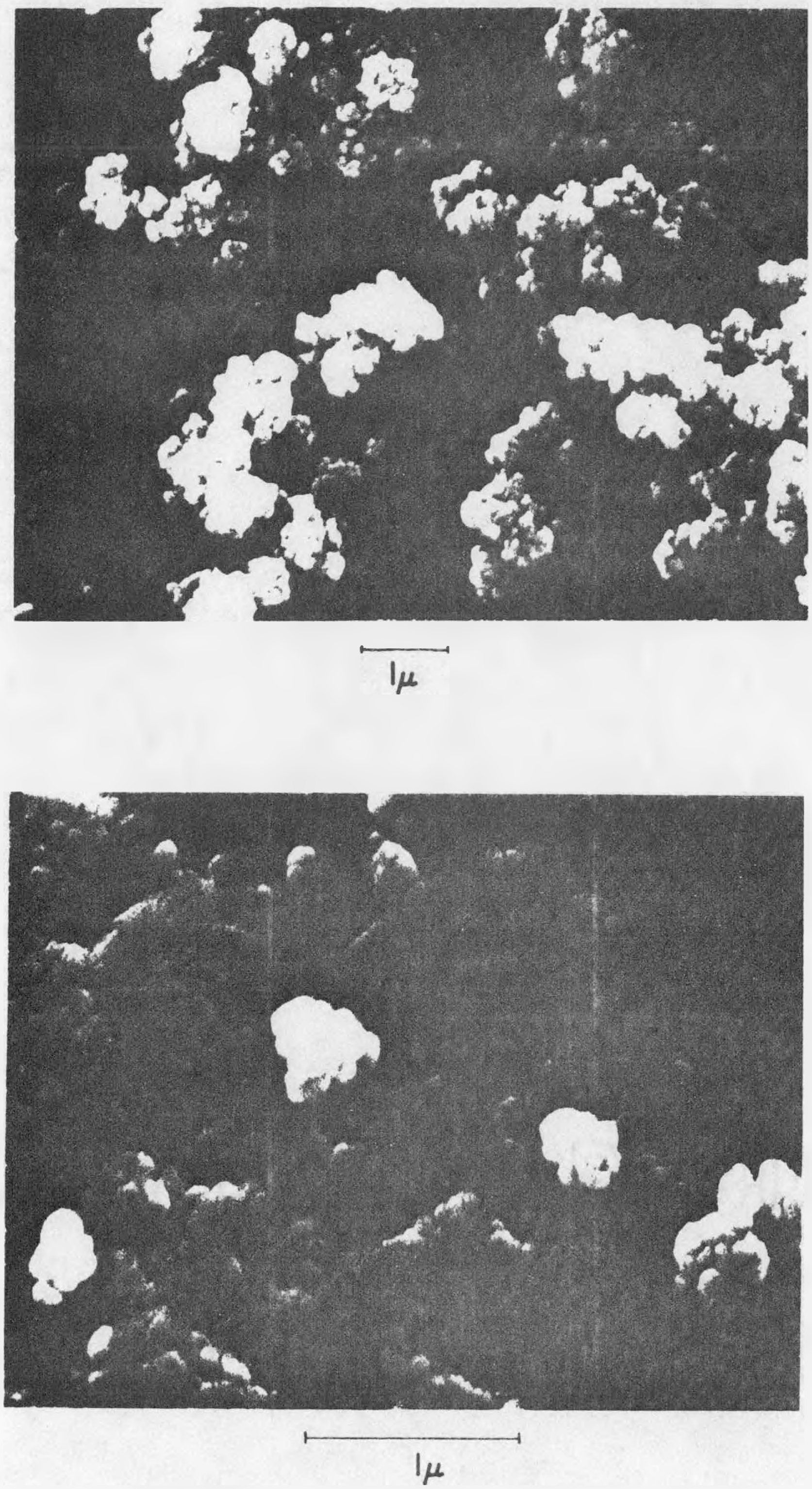

Figure 6 Scanning electron micrographs of fly-ash collected on back-up filter at the cascade impactor outlet.

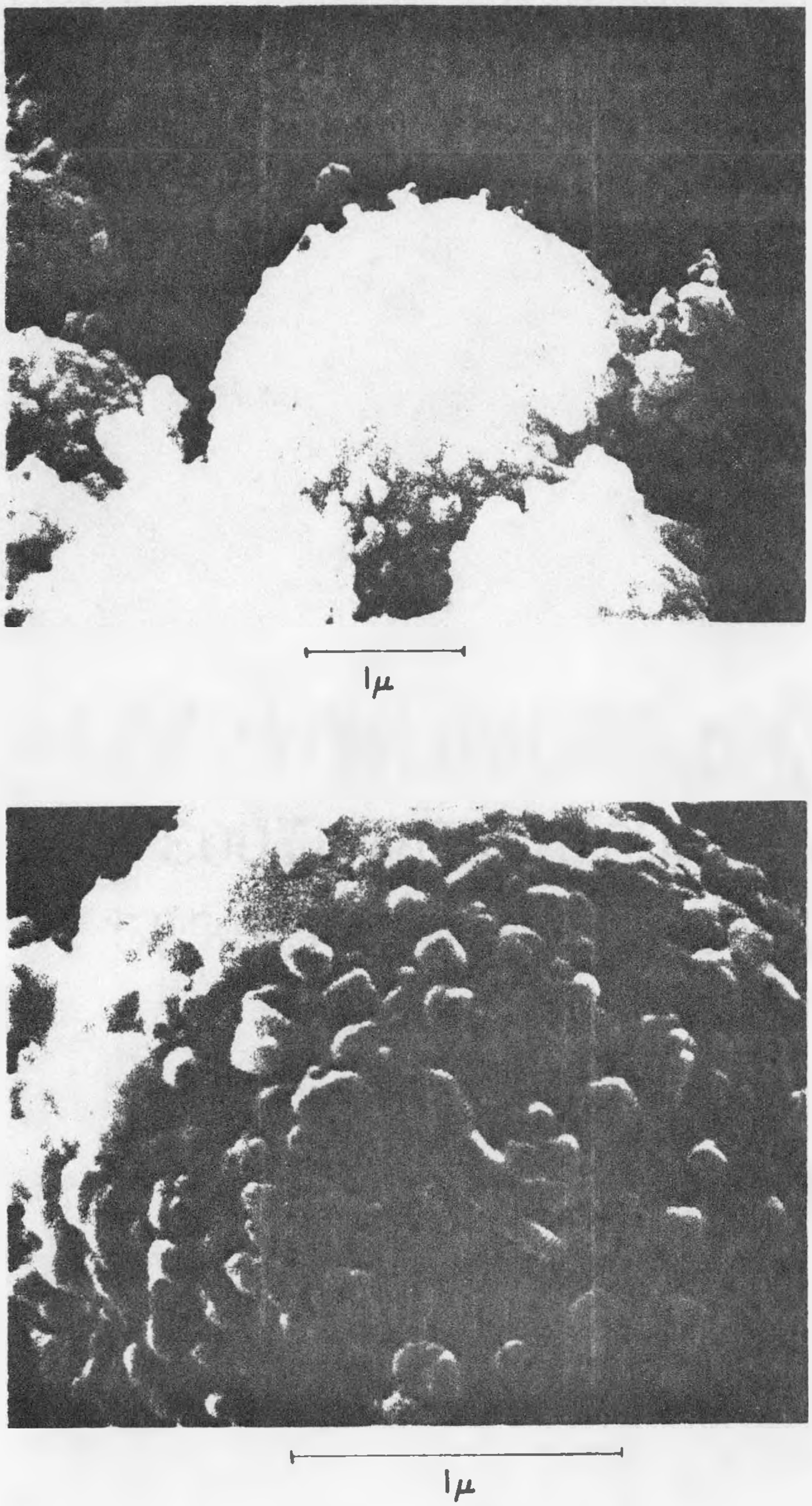

Figure 7 Scanning electron micrographs of probe sample collected at 7th floor radiant section. Center portion of top photograph is shown at a higher magnification in bottom photograph.

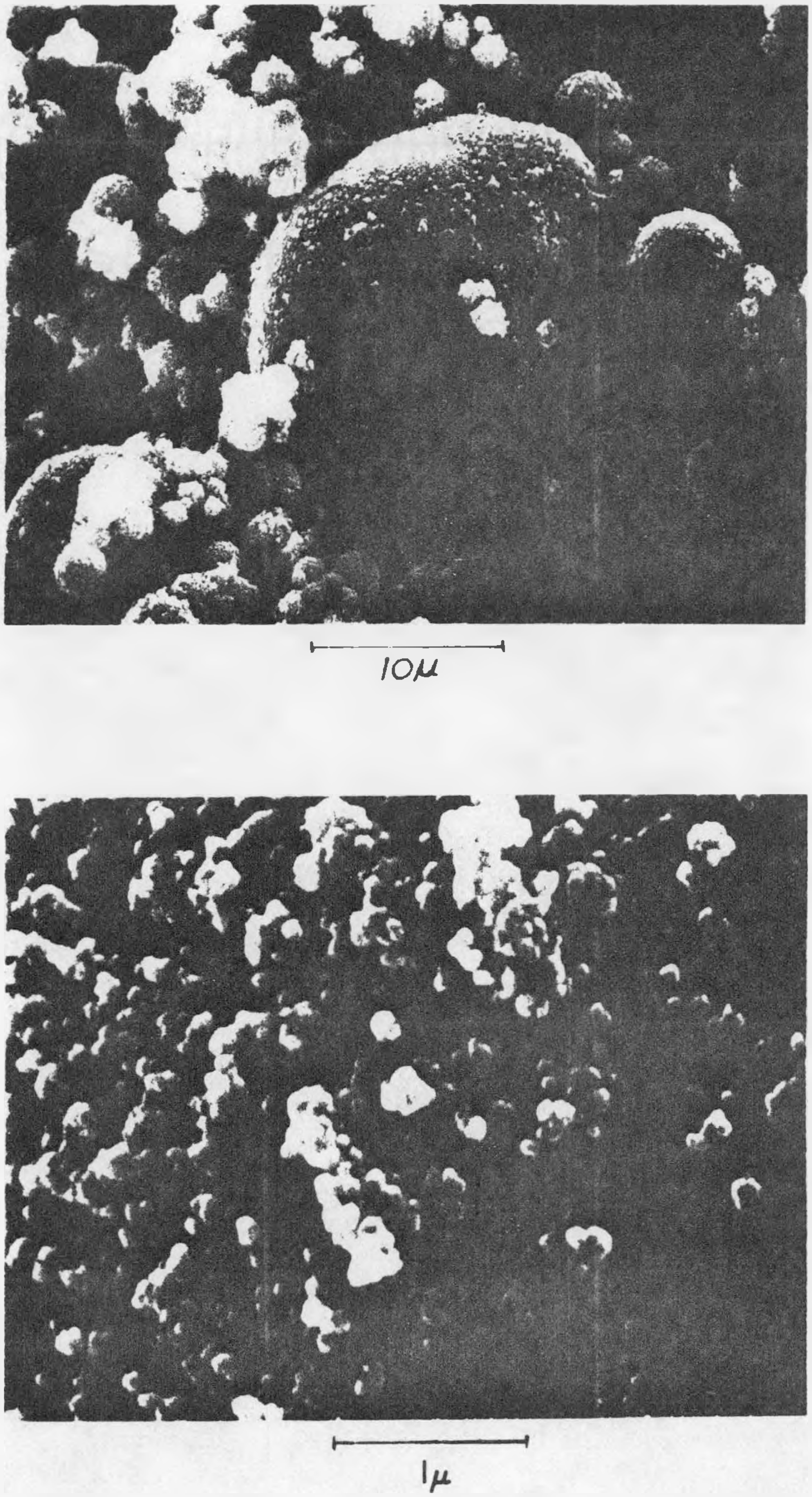

Figure 8 Scanning electron micrographs of hopper ash. Center portion of top photograph is shown at a higher magnification in bottom photograph.

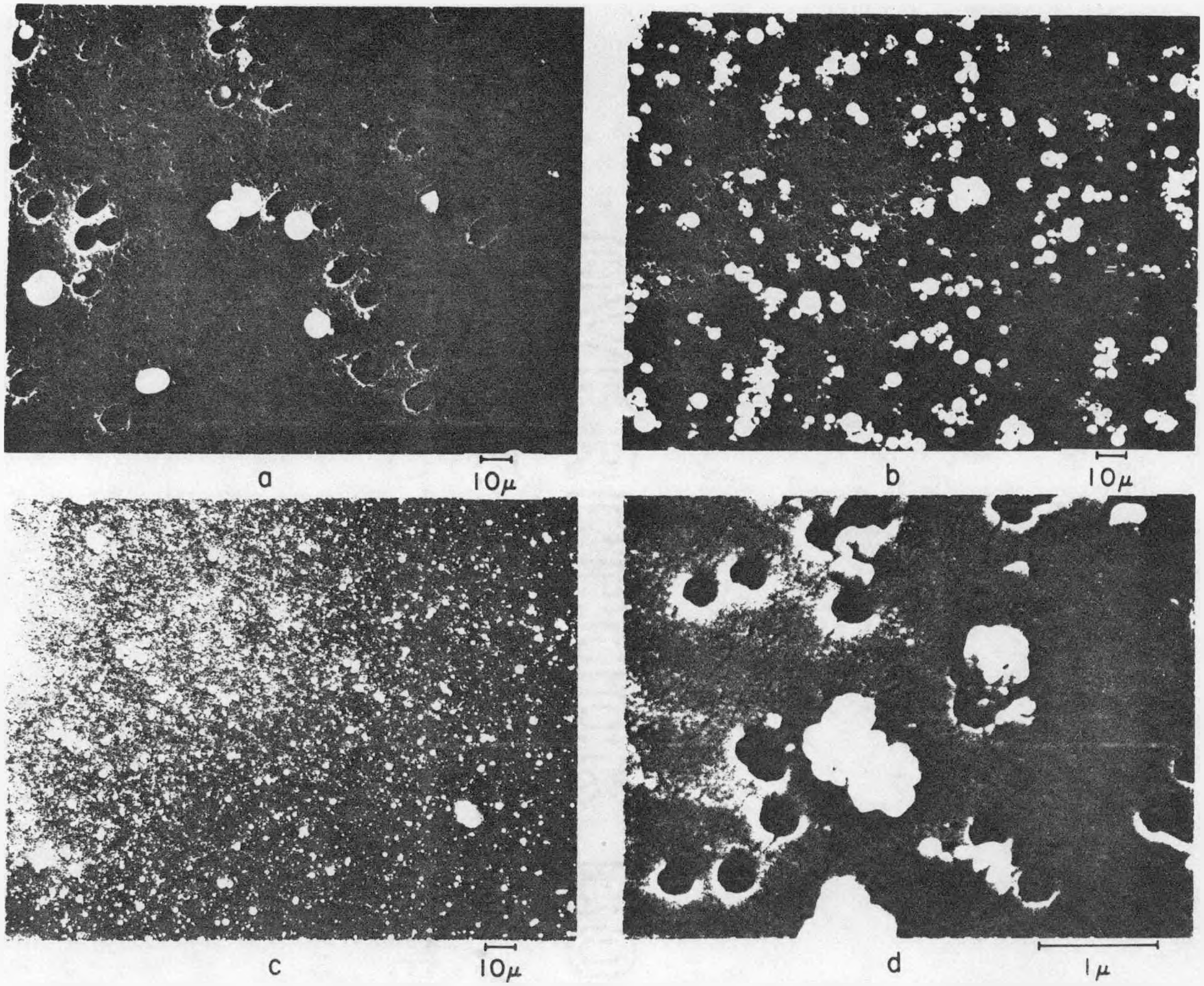

Figure 9 Scanning electron micrographs of separated fly-ash on selected Nuclepore filter, (a) 10 μm filter, 600X magnification (b) 3 μm filter, 600X magnification (c) 0.4 μm filter, 600X magnification (d) 0.4 μm filter, 23,400X magnification.

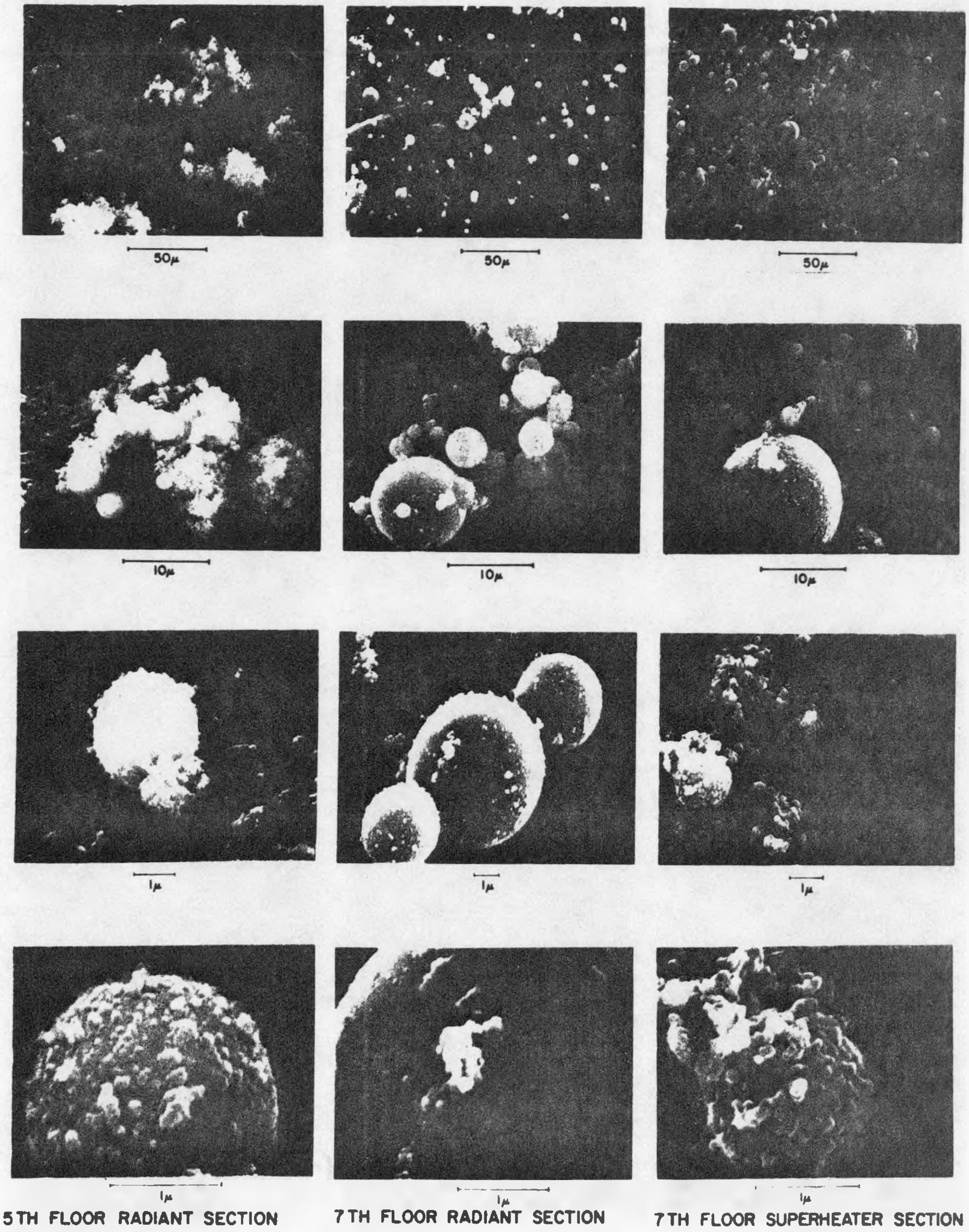

Figure 10 Scanning electron micrographs of probe samples collected at different locations in the boiler.

surfaces of larger particles have considerably less fines attached to them than impactor-separated samples. Aggregates containing fewer primary particles are also found. This demonstrates that ultrasonic energy used in sample dispersion was able to disengage submicron fines that were physically attached.

Ash samples collected at different locations in the operating boiler (representing different residence times) are shown in Figure 10. No distinguishable morphology can be identified in the three samples. All classes of particles found in each of the three probe-collected samples are also found in the hopper ash. It should be noted that relative amounts of each size fraction are not known since these samples were not subjected to the same size fractionation procedures. Numbers and quantities of probe samples are not sufficient to support quantitative conclusions. Problems of thermal deposition within the probe and inadequate quenching undermine the validity of these samples.

D. Chemical Analysis

Unseparated hopper ash samples were analyzed using atomic absorption spectroscopy (AA). Fractions separated by the cascade impactor, because of limited quantities, were examined using energy dispersive x-ray analysis (EDAX) and inductively coupled plasma analysis (ICPA). In AA analysis, 100 mg of a sample is necessary to simultaneously determine the concentrations of silicon, iron, aluminum, calcium and magnesium. Dissolution of the sample was achieved by acid digestion in a Parr bomb (22). Ammonium molybdate was used in the sample solutions to prevent the polymerization of silica and to eliminate possible flame interferences (23) (Appendix A). Nine analyses were performed on the hopper ash samples. Results reported in weight percentages are: 19.6 ± 0.71% for silicon, 12.89 ± 0.63 for iron, 9.84 ± 0.25% for aluminum, 4.36 ± 0.09% for calcium and 0.93 ± 0.02% for magnesium.

Chemical compositions of fractions from the cascade impactor were determined by EDAX. Appendix B describes the sample preparation procedure for SEM and EDAX. Qualitative analysis with EDAX had shown that silicon, iron, aluminum, calcium, magnesium, potassium, sodium and sulfur were the major elements (greater than 0.8 Wt.%). Elements with atomic numbers smaller than eleven were not identified with EDAX. Oxygen is the only major element persent in our fly-ash samples that is not identified by EDAX. Since the oxide to metal ratios of the eight elements are known, the undetected oxygen is accounted for by normalizing the total weight percentage of the total oxides to 100. Mr. John Russ, author of the data treatment computer program used in this EDAX study, indicated that the analytical procedure thus employed can cause errors of up to 20 percent. However, standard deviations of EDAX data for individual elements are generally low (within ± 2% total)(24).

A ratio of weight percentage obtained by AA to the weight percentage obtained by EDAX was calculated for each element analyzed by both methods. Table 1 shows the ratios thus obtained. The AA/EDAX ratios are noted to range from 0.65 for aluminum to 1.08 for iron, indicating that the maximum error for EDAX analysis to be well within ± 20 percent as suggested. EDAX results for impactor separated stages were corrected using these factors. The corrections thus applied are expected to significantly reduce possible errors of EDAX. It is possible that this calibration technique may not apply to the separated submicron fractions. To check this, the relatively new ICPA technique was used to analyse one

TABLE 1

EDAX and AA Analysis of Hopper Ash. (Weight Percentage).

Element	AA	EDAX	AA/EDAX Ratio
Al	9.84	15.19	0.65
Si	19.06	22.53	0.85
Fe	12.89	11.97	1.08
Ca	4.36	4.17	1.05
Mg	0.93	1.37	0.68
Na	---	0.74	---
K	---	1.11	---
S	---	1.90	---

Sample of unseparated hopper ash and three samples of cascade impactor separated submicron hopper ash. This was done by Mineralab Incorporated, Action, Massachusetts. The results are in good agreement with the AA-corrected EDAX analysis and are concluded as a valid confirmation of that technique.

The EDIT/EM computer program (25)(Appendix c) was used for EDAX data treatment. This program converts resultant x-ray intensities of elements under analysis to absolute weight percentages. Classical quantitative EDAX analysis of a bulk sample requires the specimen to have a flat surface. To fulfill this requirement, the "thin specimen" assumption was made in fly-ash samples. With this assumption, the electron beam was focused on an area consisting of a thin layer of numerous particles. The results represent an average chemical composition of all particles under the beam. This assumption was verified by analyzing a number of individual particles without the thin specimen assumption and comparing the average chemical composition of the individual particles with an overall area analysis. The results are in good agreement.

Data obtained using these various technique are shown in Figure 11.

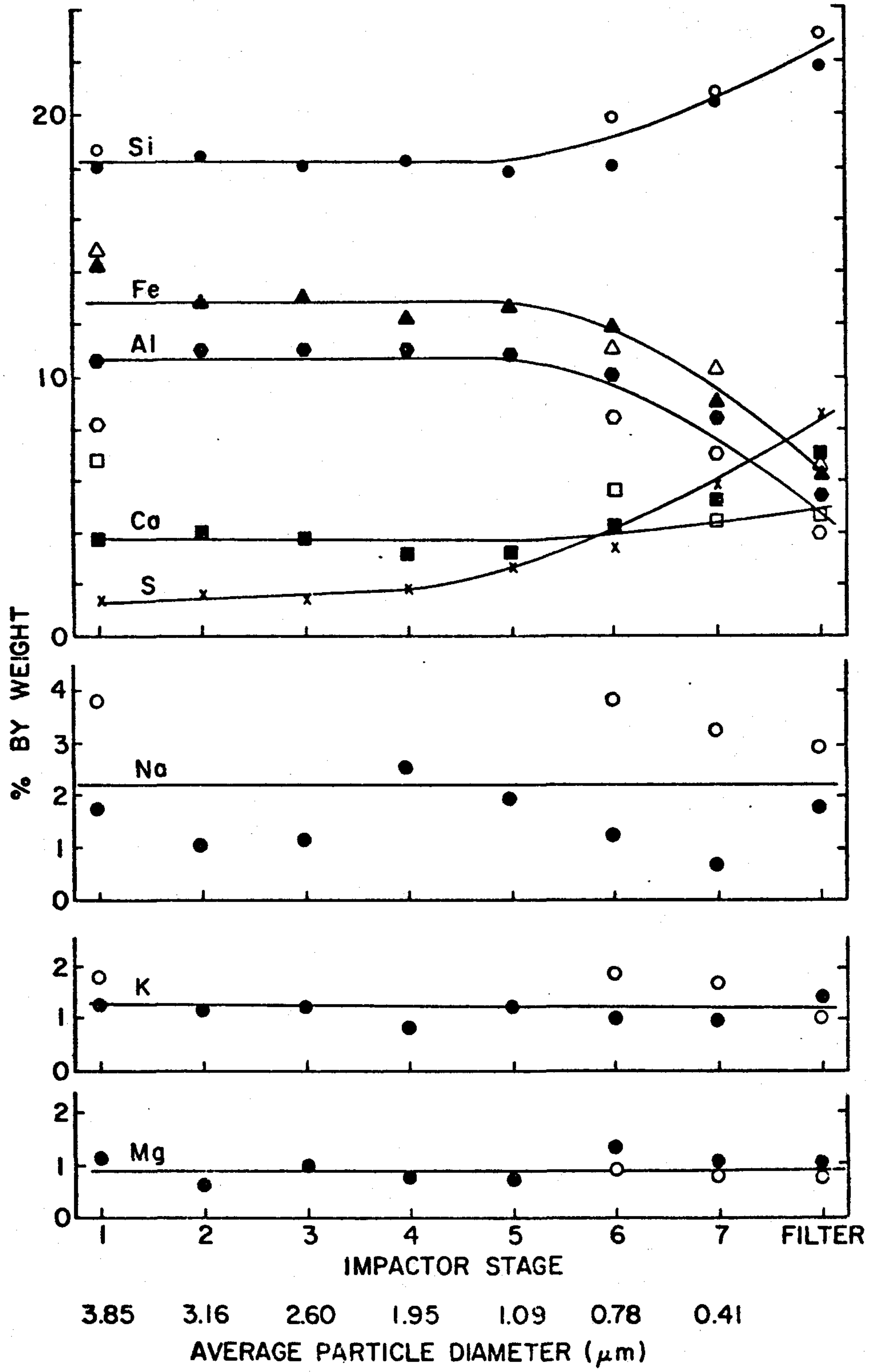

Figure 11 Composition as a function of particle size for fly-ash separated in an impactor. Filled symbols represent analysis by SEM microprobe (EDAX). Open symbols represent data obtained by inductively-coupled plasma analysis.

Chapter IV

Results

As described in preceding sections, hopper ash from Merrimack No. 2 boiler was separated by three different procedures and each size fraction was analyzed for chemical composition. Among the three separation techniques used, the combined and normalized results of Joyce-Loebl and Nuclepore techniques are believed to give more accurate size distribution data than impactor separation. This observation is consistent with the SEM photographs in Figures 5 and 9. The impactor procedure, however, has the ability to separate large quantities of bulk samples yielding size fractions large enough for subsequent chemical analyses. The percentage of ash below 0.4 micron (mostly submicron aggregates) was found to be 7 by Nuclepore filtration and only 2 by the cascade impactor. This discrepancy is mainly attributed to more extensive attachment of fine particles to the larger ones in the impactor samples.

Figure 11 shows the composition of hopper ash as a function of particle size. Most samples were taken from the cascade impactor. Enrichment is evident for elements silicon and sulfur in smaller particles while iron and aluminum are depleted. Other elemental concentrations are independent of particle size except for calcium which may be slightly enriched. It is also noted that concentrations of all metallic dements are essentially constant for particles larger than 1 micron and enrichment trends occur only in the submicron range, represented by particles on the 6th and 7th stages and the back-up filter. It is also evident from the micrographs that these stages are progressively enriched in submicron particles. The respective trends of elemental and submicron particle enrichments may suggest that elemental concentration is not a continuous function of particle size. The smooth change in concentration trends may have been more abrupt if true bimodal separation had been achieved.

Samples separated by Nuclepore filtration were also analyzed by EDAX. These analyses were carried out directly on Nuclepore filters since efficient removal of the particles from the filters and then depositing them on a carbon specimen stub was not possible. Results thus obtained showed high standard deviations and this procedure is not recommended for routine EDAX analysis. Nevertheless, within the limits of percision, chemical compositions of these samples were similar to those of the impactor samples except for sulfur which was found to represent only 0.5 weight percent in all filter-separated fractions. This suggests that sulfur was present in a water soluble state which was removed by the aqueous dispersion required for filtration.

Chapter V

Discussion

The object of this study was to characterize submicron fly-ash from a CF boiler. Information obtained from this experimental study is intended to assist in the development of a generalized fly-ash formation model.

Fly-ash, in general, consists of two distinct classes of particles. On a mass basis, the major class of ash particles contains discrete spheres with diameters ranging from approximately 0.5 to 50 microns. These larger particles originate from the residual mineral matter remaining after coal particles have undergone combustion. Their glassy, spherical appearance indicates a prior existence as molten, liquid droplets. They are termed entrainment ash. The other class of ash particles is submicron in size consisting mainly of aggregates containing even smaller primary particles. This class of particles is designated as condensation ash. It is presumably produced by the vaporization of metallic species which recondense.

Chemical composition of submicron fraction of ash is significantly different from the rest as shown in Figure 11. The slopes of these concentration trends as observed are dependent on the method of size separation. The smooth and gradual concentration changes with respect to particle size as presented in Figure 11 are probably caused by the inherent characteristics of cascade impactor separations. Assuming the changes in concentration in the submicron fraction result from an increasing population of condensation ash, step changes instead of smooth curves would be expected if pure condensation ash could be separated from entrainment ash. This supposition is qualitatively supported by scanning electron micrographs (See Figure 5) which show that stages exhibiting concentration changes are also increasingly enriched in submicron particles.

The enrichment trend of sulfur is different from other elements. The increase in sulfur concentration is observed to begin at an earlier stage. This may suggest that the enrichment of sulfur is a surface effect with the increase in specific surface area of smaller particles as the main cause of sulfur enrichment. Further support for this hypothesis comes from the EDAX analyses of particles separated by Nuclepore filtration in which ash samples were dispersed in water. The concentration of sulfur was found to be less than 0.5 percent in all filter separated fractions. The surface enriched sulfur is believed to have been washed away in the aqueous dispersions.

Figure 6 shows that ash particles collected by the absolute filter at the impactor outlet are almost pure submicron aggregates. The chemical composition of these particles is thus assumed to be approximately that of condensation ash. Results are given in the third column of Table 2. When compared with the composition of the original coal ash, silica is found to be enriched by 11 percent, alumina is depleted, iron oxides are depleted and calcium oxide is slightly enriched, concentrations of other measured elements remained essentially constant.

In CF boilers, crushed coal is blown into a cylindrical chamber and combustion air is introduced tangentially. This creates the cyclone effect and causes the larger coal particles to be accelerated to the wall of the burner chamber in the cyclone slag. The smaller coal particles,

TABLE 2

Composition (weight percent) of condensation ash in a cyclone, coal-fired boiler. (Values in parentheses are based on the experimental composition).

Constituent	Original Coal Ash	Composition of Submicron Ash Predicted*	 Experimental**
SiO_2	37	55.9	48.0
Al_2O_3	19	0.05	10.0
$FeO(Fe_2O_3)$	18 (20)	20.0	8.0
CaO	7	0.02	10.0
MgO	1.2	(1.7)	1.7
Na_2O	---	(2.4)	2.4
K_2O	---	(1.7)	1.7
Balance	15.8	(1.2)	1.2
SO_2	---	(17)	17
Total	100	100	100

*Calculated results from mathematical model developed in a separate study (11).

**Obtained by SEM Microprobe and Atomic Absorption.

instead of impinging on the slag, burn suspended in the flowing gas. These are thought to play a major role in the formation of condensation ash. During char burnout of coal combustion, the mineral inclusions of coal particles are exposed to high temperatures and a reducing atmosphere. It is worth noting that the surface temperature of char particles may be two to three hundred Kelvin degrees higher than the gas temperature. Desrosiers et al. (11) have calculated the amount of vapor phase transport of mineral matter from the surface of char particles. The major species considered in their calculation were SiO_2, FeO, AlO and CaO. Results indicate that 5 percent of the suspended ash may be vaporized at conditions in the Merrimack No. 2 boiler. About one fifth of this is thought to originate from the slag suspended coal particles, the balance comes from gas-suspended particles. Composition of condensation ash predicted from this model is presented in column two of Table 2. When compared with the original coal ash, silica is enriched, alumina and calcium oxide are depleted and iron oxides are slightly enriched according to the model.

The chemical composition of submicron ash collected at the impactor outlet can be compared with the predicted condensation ash composition. Concentrations of silica and alumina show good agreement in the sense that experimentally silica shows enrichment and alumina is depleted as predicted by the mathematical model. The predicted and experimental trends for iron and calcium are, however, contradictory. These discrepancies are noted by Desrosiers, et al. and explained as follows: Since submicron ash is usually observed as large aggregates, fine entrainment ash concealed by the aggregates may not be distinguishable by scanning electron micrographs. Ash fractions collected on the back-up filter may actually contain minute entrainment ash particles having the bulk ash composition. The discrepancy concerning iron and calcium species may be caused by doubtful thermodynamic data used in the model calculations (29).

Assuming condensation ash to be that smaller than 0.4 micron obtained by Nuclepore filter separation, it represents about 7 percent of the total fly-ash. One also has to consider that the ash under study is hopper ash and there may be an additional 1 percent or so submicron ash uncollected by the electrostatic precipitator. Also, scanning electron micrographs of Nuclepore filters used in this separation process indicate a noticeable amount of submicron fines on early filter stages. Based on experimental data, the amount of submicron ash generated in this boiler design is estimated to be about 10 percent of the total fly-ash. The theoretical prediction of 5 percent is low when compared with the experimental estimate. However, particles smaller than 0.4 micron do not necessarily represent condensation ash alone. Fine entrainment ash particles may constitute part of this function. This is consistent with the concentration trends of silica and alumina observed earlier. Possible errors in the assumed combustion temperature used in the transport calculations are another possible cause.

When the volatile metal vapors diffuse out of the particle boundary layer, rapid nucleation is assumed. The growth processes thereafter are controlled by collision frequency and rate of coalescence. Growth equations developed from silica particles in a laboratory burner were employed. Calculation procedures are given in previous work (26,27,28). In employing the equations developed for silica particles, parameters including vapor concentration, viscosity, and surface tension of condensed ash were necessary. Based on 5 percent of fly-ash being vaporized in the transport process and assuming that precipitation occurs near the combustion zone, the primary particle size of pure condensation ash was calculated to be 0.040 micron. The same calculation, based on 10 percent condensation ash present showed a primary particle size of 0.052 micron. The primary particle diameter, as measured, shows fair agreement with that calculated, assuming 10% condensation ash. The experimental estimation of 10% condensation ash is thus consistant with the growth calculations.

Aggregates are predicted to consist of 4 to 8 primary particles. Scanning electron micrographs show aggregates consist of 10 to 15 primary particles, somewhat more than the model prediction. This discrepancy may be caused by the sample preparation procedure for electron microscopy. Proper sample dispersion is hard to achieve for scanning electron microscope samples and hence aggregate size determined by this approach can be misleading. Also, a lower than actual ash viscosity, assumed in the calculations, may cause such a discrepancy.

These results indicate that vaporization-condensation is a controlling mechanism in the formation of submicron fly-ash. Though qualitative in nature, the experimental results show that the preliminary fly-ash model developed gives promising results.

Chapter VI

Conclusions

Results of this study indicate fly-ash from a CF boiler consists of two distinctly different classes of particles. Loosely defined, the larger particles are termed entrainment ash and the submicron aggregates are termed condensation ash. A vaporization-condensation mechanism is believed to be responsible for the formation of condensation ash. In general, experimental data substantiate the theoretical model development. Although results are qualitative and somewhat circumstantial, they serve as an important aid in providing physical understnading of ash formation and to substantiate and rectify mathematical predictions. More experimental and theoretical refinements in current work are clearly necessary.

Chapter VII

Recommendations

To formulate the mechanisms of fly-ash formation more precisely, better probe samples are necessary. The major obstacle for probe sample analysis is the sample size limitation. If a large enough ash sample can be collected, particle entanglement, size separation and chemical analysis problems are solvable with slightly modified laboratory techniques. These may include a powder feeder for cascade impactor separation, and a more extensive range of Nuclepore filters used in filter separation. An improved method for collections of ash samples from various locations in an operating boiler certainly deserves attention. For further refinements, the physical conditions within the boiler while sampling must also be characterized. This may include measurements of temperatures and gas velocities of relevant parts of the boiler. The effects of boiler operating variables on ash samples collected is also important. Operating variables may include frequencies of soot blowing, nature and amount of fuel additives, and possible fuel changes.

In laboratory studies, the more refined use of Nuclepore filtration is worth investigating. The proper dispersion of ash samples with ultrasonic energy will enable a more precise observation of submicron aggregates.

Extending the chemical analyses to include trace elements in submicron ash is another area for further experimental study. ICPA has potential for performing such an analysis.

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APPENDIX A

Atomic Absorption

Atomic absorption spectroscopy was used to analyze unseparated hopper ash for the elements silicon, iron, aluminum, calcium and magnesium. Sample size limitations and the elimination of chemical interferences between the elements silicon, iron and aluminum were major considerations for the choice of the following sample preparation scheme. Dissolution of ash samples without volalization was achieved by the use of Parr acid digestion bombs. Ammonium molybdate was used in an acidic solution to form a silicon-molybdate complex to prevent the polymerization of silica and other interferences.

Reagents All chemicals were analytical reagent grade. Aqueous solutions were prepared in distilled deionized water.

Sample Dissolution Parr model 4745 acid digestion bombs were used for ash dissolution. The bomb permits the use of hydrofluoric acid and aqua regia at high temperatures without the loss of silican.

Procedure: Transfer 100 mg of fly-ash sample into the Teflon decomposition vessel. Add 1 ml aqua regia as a wetting agent and make certain that the sample is thoroughly wetted. Add 5 ml hydrofluoric acid and close the Parr bomb by hand tightening the screw cap. Place the bomb into the oven for 3 hours at 140°C. Then Cool to ambient temperature. Open the bomb and transfer the decomposed sample into a Teflon beaker. Rinse the decomposition vessel with the dilution solution to obtain all traces of precipitated metal fluorides. Add 20 ml of saturated boric acid solution to dissolve the precipitated metal fluorides. Dilute the resulting solution to 100 ml. Make a 1:10 dilution of the sample solution for calcium and magnesium detections.

Preparation of Standards Standards for ion and aluminum were prepared from pure metals. Silicon standards were prepared from water soluble sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$). Calcium and magnesium standards were prepared from the nitrates. A diluting solution was used in the preparation of all sample solutions and standards. The use of this diluting solution was necessary to prevent the polymerization of silica, to control pH, to facilitate doping with alkali, and to enhance reproducibility (23).

Procedure: Dissolve 1 g sodium metasilicate in 30 ml water, 56 mg aluminum wire in 10 ml warm hydrochloric acid (1:1 dilution) and 68 mg iron wire in 10 ml nitric acid (1:1 dilution). Obtain the standard stock solution by mixing the above three solutions and then dilute to 200 ml. Prepare five 50 ml standards by diluting the standard stock solution. These constitute the standards for silicon, aluminum and iron. Prepare stock solutions for calcium and magnesium by dissolving the respective nitrates in 1:1 dilutions of hydrochloric acid. Obtain calcium and magnesim standards by mixing and dilution their standard stock solutions. Add 5 ml of the silicon, iron and aluminum stock solution to every 100 ml of calcium and magnesium standard. Dilute 25 ml of standard stock solution to 500 ml to obtain the zero solution. (The zero solution was prepared to provide a base line with proper flame temperature.)

For the diluting solution, dissolve 16 g of ammonium molybdate in about 400 ml water, 6 g sodium carbonate in 400 ml of 0.3 N nitric acid (1:50), and 15 g boric acid in 400 ml hot water. Mix and dilute the above three solutions to 2 L with 0.3 N nitric acid.

<u>Flame Used</u> The atomic absorption spectrometer was used under standard procedures. Samples and standards for silicon, aluminum, calcium and magnesium were aspirated into a nitrous oxide-acetylene flame and for iron into an air-acetylene flame.

APPENDIX B

SEM/EDAX Sample Preparations

The technique of mounting fly-ash particles for SEM studies was worked out through trial and error. Among the requirements for particle mounting were: 1) Particles of different sizes should be secured firmly on the stub. 2) The adhesive material used to secure particles on the specimen stub should be electrically conductive to prevent local charging. 3) Specimen background should be smooth, uniform and able to provide good contrast to the particles. 4) If x-ray analysis was required, the choice of conductive material (for paint, coating, and specimen stub) was restricted to carbon only. In this study, all particle mountings were done on graphite specimen stubs and a conductive carbon paint was used to secure the particles on the stub. The carbon paint used was highly viscous so that it held the particles firmly without "climbing" over them.

Carbon and/or metal coatings of the mounted fly-ash particles are necessary because of charging effects from the electron beam. The mounted specimen stubs were coated in the vacumn evaporator under standard precedures. When x-ray analysis was not required, the stub was first coated with carbon followed by metals, a combination of gold and palladium was used as a coating material in this study. When x-ray analysis was required, a single coating of carbon was applied. The carbon had a tendency to coat the underside of the particles in contact with the paint while the metal gave better emission characteristics (30). The carbon coating was about 50 ^{o}A thick. A combination of carbon and metal coating gave a 150-200 ^{o}A coating. Since the smallest particles observed in the scanning electron micrographs were at 0.09μ, the coatings contributed an average of 30-40% increase to the diameter for this class of particles.

Particle Mounting Procedure: A No. 1 bristle brush was dubbed into the ash sample until saturated with ash particles (A minimum of 3 mg ash was necessary). A graphite specimen stub was then lightly coated with the carbon paint. A glass micro slide was held about 2 cm above painted area of the specimen stub and the bristle brush was stroke against the slides's edge to disperse and deposit the ash particles on the paint. The stub was held with a tweezer and then tapped firmly several times on a solid surface with the paint and particles facing upwards, in order to set the particles into the tacky surface. The stub was then turned side ways and was tapped again on a solid surface to dislodge the loose particles. (Loose particles produce serious charging effects in the SEM even when metal coated. Also loose particles may separate from the specimen mount and deposit in the SEM column giving serious contamination problems.) The prepared stub was dried overnight in a dust free environment and then stored in a desicator. The specimen was then ready to be coated and examined.

APPENDIX C

Quantitative EDAX Analysis

In a scanning electron microscope an electron beam is focused onto the surface of the specimen. This beam is deflected by magnetic coils to perform a scanning motion by moving line after line across the specimen surface. At each location of incidence, the beam gives rise to the emission of secondary electrous, backscattered electrons and characteristic x-rays. Secondary electrons and backscattered electrons are responsible for the generation of a magnified image. Areas with high electron emission are shown bright and vice versa. Information about the elements in the sample can be collected by detection of x-ray emission. The x-rays caused by the incident electron beam have characteristic wavelength and energy spectra for each element. With EDAX one can detect all elements at one point of the specimen simultaneously.

X-rays produced by different elements have different energies. A spectrum of relative signal strength (counts) versus characteristic x-ray energy (electron volts, Ev) can be obtained from a sample of mixed elements. The characteristic x-ray energy is dependent upon the atomic number of the elements. This allows the identification of the elements. The signal strength is related to the amount of the measuring element persent and this allows the measurement of concentration.

For quantitative analysis, the resultant spectrum is subjected to the following data treatments: 1) Peak identification, 2) background subtraction and 3) correction of any non-linear relationships between x-ray intensitie and element concentrations.

In order to get the net intensity values from the spectrum, two separate steps are necessary. The first step is to separate the peaks from each other and the second step is to separate the peaks from the background. In a x-ray spectrum one element can be responsible for many lines such as the α and β lines of K, L or M (e.g.: Kα, Kβ, Lα, Lβ, ...etc). However, only the more important peaks are clearly distinguisable in the spectrum. For the purpose of this study, only major elements are considered important and the Kα line of each element was used as a basis for all calculations. In a study of trace elements, the interference of the minor lines of the major elements with the major lines of the trace elements can be serious and more sophisticated approaches will be necessary. Also, there are possibilities of the overlapping of peaks. This was confirmed not to be true for the Kα lines of the eight elements being measured. Background subtraction was done by the linear method i.e. a straight line was drawn across the spectrum and counts below this base line were subtracted from the peak heights. This simple approach was used because we were working with single isolated peaks of major elements. The errors introduced by this method are generally acceptable. More sophisticated methods are available, e.g. the EDIT/NOVA program which uses the frequency filter method.

After obtaining the net intensities the second step in doing quantitative analysis is to convert the intensity ratios to concentrations. The major correction here is the interelement effects. The model used for these corrections depends on three factors called Z, A and F factors. Z is for atomic number, A is for absorption, and F is for fluorescence. The fluorescence correction attempts to take into account that x-rays emitted from one element when they are absorbed by another element may give rise to additional x-rays from the second element. For instance, in stainless steel there are a lot of iron x-rays being generated in the sample. On their way out of the sample a reasonable percentage of tem get absorbed by chromium atoms. When that happens, the chromium atoms are excited and give out their own characteristic x-rays. When the chromium atom emits an x-ray, the detector can not distinguish that x-ray is generated by an iron x-ray from the one that was generated by incident electrons directly. Fluorescence correction takes into account the interelement fluorescence effects.

The absorption factor corrects the fact that x-rays are absorbed differently in the matrix than they are in the matrix of a pure element. This correction is important when a pure element is used as a standard for calibrations. In this study, a no standard approach was used because a pure element with the exact geometry of fly-ash particles is not possible to obtain. The absorption factor was hence neglected.

The atomic number correction accounts for the differing degrees of electron backscattering by different elements. When electrons strike samples of different compositions, different amounts of electrons may backscatter from the sample, or they may penetrate to different depths in the sample before x-rays are produced. The amount of backscattering and penetrating power of electrons are directly related to the bulk sample composition and not to the elements of interest.

In a fly-ash particulate analysis the x-ray analytical capabilities were hindered by several difficulties. Among these are: a) classical electron probe microanalysis required a flat, effectively infinite specimen placed normal to the electron beam for quantitative ZAF calculations to be valid b) the smallest particles under study might be smaller than the x-ray excitation volume for a given set of experimental conditions. This means particles with same chemical compositions but different sizes may show up as having different chemical compositions on EDAX c) the particles although mostly spherical might also be of complex shape such as highly aggregated submicron particles. Geometrical corrections are thus hard to carry out d) x-ray intensities from submicron particles might be low thus contributing to uncertanties as to change in the lower concentration elements.

Realizing the inherent errors of small particle bulk analysis, the assumption of "thin specimen" was made. Sample particles were dispersed to form a thin layer on the specimen stub and such a geometry was used for EDAX measurements. The use of thin sections yields a great simplification for quantitative analysis. The electrons lose only a small fraction of their energy in passing through the sample and so the probability of interacting with other atoms does not change. Also, electron backscattering is neglecgible and can be ignored. Data treatment of this study was accomplished by the EDIT/EM program. This program does peak identification and background subtraction by the straight line method. Relative elemental atomic calculations were calculated directly from their relative intensities by simple ratioing without Z-A-F corrections. Data treatment of an ideal sample with Z-A-F corrections gives an accuracy of ± 5 percent relative. The use of the EDIT/EM program with the "thin specimen" assumption gives an accuracy of ± 20% relative (24).

Results of the mathematical model were compared with experimental results obtained in this study.

APPENDIX D

An Abstract of the Fly-Ash Formation Model

A mathematical model has been developed by Desrosiers et al. of UNH Fly-Ash Research Group (11). The work is divided into two categories: 1) the process of transport to the bulk phase and 2) the precipitation growth process.

Transport calculations include three important elements: 1) the determination of surface temperatures and oxygen concentrations, 2) calculation of the concentrations of metal-containing gaseous species near the particle surface depending on their relative volatility under the calculated conditions, and 3) derivation and integration of expressions for the rates of diffusion of these species during burnout.

The physical model for growth is based on studies of silica behavior in premixed, flat-flame burners (21,26). Following transport of metal oxide species to the gas phase, rapid nucleation is assumed. Growth after nucleation is controlled by the combined effects of interparticle collision and fusion or coalescence. The relative rates of these two processes determine the aggregate morpholology. Collision and fusion rates can be specified by conventional kinetic expressions. Equations describing particle growth include vapor concentration, viscosity, and surface tension of the condensed ash as parameters. Concentration was taken from transport claculations described above. Equations of Rossin et al. (30), for silica-alumina mixture were used for viscosity estimations. Surface tension is much less sensitive to composition as viscosity and is essentially independent of temperature over wide ranges.