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# AN INVESTIGATION OF THE MECHANISM OF FLY-ASH FORMATION IN COAL-FIRED UTILITY BOILERS

Quarterly Report for the Period
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## I. OBJECTIVE AND SCOPE

Recent studies of fly-ash emitted from stationary combustion equipment suggest that substantial numbers of sub-micron particles are discharged even from units having electrostatic precipitators. This is the size fraction which is least efficiently collected and most damaging physiologically. Most previous work on ash formation has dealt with operating problems such as slagging and fouling caused by ash in the boiler itself. To attack both the operating and health problems in a more intelligent way, it is important to understand better the mechanism of ash formation and growth.

This group is studying the process from two directions. The first is a fundamental investigation of quench temperature, sticking coefficient, aggregate morphology, particle size distribution, electrical charge effects, and other phenomena that influence the formation and growth of pure and mixed metal oxide particles. This study is being conducted with the aid of a precision laboratory burner. Secondly, the growth of ash particles in a full-scale commercial utility boiler is being examined in an effort to determine fly-ash characteristics as a function of temperature and residence time in the unit. The cyclone-fired boilers at a nearby power plant have been made accessible for this work. Using results from the fundamental study, a model will be formulated to describe particle behavior in the commercial boilers. The ultimate aim of this three-year project is to develop a method for predicting the characteristics of ash particles produced in a coal-fired boiler based on furnace parameters and coal composition.

## II. SUMMARY OF PROGRESS TO DATE

During this quarter, most of the effort was devoted to preparation of the technical paper, "Submicron Fly-Ash Formation in Coal-Fired Boilers", (to be presented at the Seventeenth Symposium on Combustion, Leeds, England, August 1978). It is a first attempt to apply the particle-growth and ash vaporization information developed during this project to an operating boiler. In brief, model predictions regarding the quantity and size of submicron ash are reasonably accurate. Predictions of metal enrichment for silica and depletion for alumina are also confirmed in the analyses of submicron ash particles. For iron, enrichment is predicted, but depletion is observed.

Calculations indicate that cyclone-fired utility boilers may produce up to five percent (by weight) of the total fly-ash in the submicron range, whereas, because of lower combustion temperatures, about 0.05% is predicted for a pulverized-coal-fired unit. Experimental results from a CF unit reveal about ten percent ash in the submicron range. The difference appears to be entrainment of fragments of bulk ash which coagulate with the condensation ash. For a first attempt, agreement between predictions and observations is gratifying. Details are described in Appendix B which is a preprint of the paper.

Work in the laboratory has been meager. The study of titania growth, scheduled for this past quarter, was not conducted and has been rescheduled for the next quarter. The status of this and various other phases of the project are shown in Table I. Because of the lapse in laboratory activity, objectives A-4, A-6, A-8, and B-2 have been moved back three months. The manuscript mentioned above represents completion of B-3, although the model will be refined as it is employed in the future.

A thesis on characterization of submicron fly-ash by A. Chiu is near completion. It reveals the value of ash fractionation by filtration of liquid-dispersal samples through Nuclepore filters. Collection and fractionation of such samples is in progress.

The Durham Seminar on Particles in Flames was held as scheduled. The program and list of attendees are shown in Appendix A. We have experienced good communication with people in the equipment and utility industries through these seminars over the past four years. Having developed reasonable ties, the need for future seminars is questionable, and we plan to discontinue them as regular annual affairs.

Table 1. Status and Future: The Study of Fly-Ash Formation in Coal-Fired Utility Boilers At UNH. ERDA Contract No. (E49-18)-2205.

|  | Dates |  | Project Description |  |  |
|---|---|---|---|---|---|
| Objective Designation | Initiation | Estimated Completion | Laboratory Studies | Tangible Anticipated Results | Status May 1978 |
| A-3 |  |  | Particle Size Distribution. |  | Priority lessened, study postponed. |
| A-4 | February 1976 | October 1978 | Aggregate-growth rates and formulation of an aggregation model. | Durham Seminar - 1978. Technical paper with detailed analysis of aggregate behavior. (October 1978). | Paper to be prepared. |
| A-6 | September 1977 | March 1979 | Growth rates, sticking coefficients and quench temperatures of other oxides and oxide mixtures in the free-molecule regime (particles smaller than 0.05 micron). | Technical paper on growth of other oxides (April 1979). | Laboratory study in progress. |
| A-7 | December 1977 | March 1979 | Extension of growth measurements beyond the free-molecule aerosol regime through the transition and continuum regimes to a mean particle size of one micron or larger. | Technical paper on growth in the continuum regime (August 1979). | In progress. |
| A-8 | December 1978 | September 1979 | Effect of ion-producing metallic additives on growth parameters. |  | Not yet begun. |
|  |  |  | Plant Studies |  |  |
| B-2 | August 1976 | December 1978 | Evaluation of particle parameters as a function of temperature and residence time in Merrimack boiler No. 1 and continued studies of boiler No. 2. |  | In progress. |
| B-3 | May 1976 | June 1978 | Derivation of a model describing fly-ash formation in cyclone-fired boilers. | Technical paper on fly-ash in boilers. Durham Seminar - 1978. Accepted for presentation at the 17th Int. Symp. on Combustion. | Completed. |
| B-4 | June 1978 | September 1979 | Evaluation of particle-residence time characteristics of pulverized-coal utility boilers. | Durham Seminar - 1979. | In progress. |
| B-5 | June 1978 | September 1979 | Development of a model describing fly-ash formation in pulverized fuel boilers. | Technical paper on fly-ash formation in pulverized fuel boilers (Fall 1979) | Theoretical work in progress. |

# APPENDIX A

# PROGRAM

## FOURTH DURHAM SEMINAR: PARTICLES IN FLAMES

Date: Thursday, May 25, 1978 Place: New England Center, Mansfield Rm.
Durham, New Hampshire

## PROGRAM

| | | |
|---|---|---|
| 9:00 | Welcome and Introduction | Gail Ulrich, UNH |
| 9:15 | Enrichment of Certain Elements in Submicron Ash | Allen Chiu, UNH |
| 9:45 | Transport and Condensation Mechanisms in the Formation of Sub-micron Ash | Ray Desrosiers, UNH |
| 10:30 | Break | |
| 10:45 | Growth and Behavior of Sub-micron Aggregates in Flames | John Riehl, Cabot Corp. |
| 11:30 | Sub-micron Fly-Ash in Coal-Fired Boilers - an overview | Gail Ulrich, UNH |
| 12:15 | Lunch | |
| 1:30 | Slag Effects in MHD Topping Cycles | David Stickler, Avco-Everett Research |
| 2:15 | Modification of Fly-Ash via the Intro. of Vapor-Phase Additives | Shyam Dixit, Dearborn Utilities Service Company |
| 3:00 | Break | |
| 3:30 | Current Status of Dust-Control Technology in the Power Industry | Roger Trueblood, Stone and Webster Engineering |
| 4:15 | Adjournment | |

## ATTENDEES

Sushil Batra, New England Electric
Raymond Carignan, Public Service Co. of N.H.
Allen Chiu, UNH
Ray Desrosiers, UNH
Shyam Dixit, Dearborn Co.
Thomas Fowke, Public Service Co. of N.H.
Bruce French, Public Service Co. of N.H.
Shu-Mu Hsieh, UNH
Steven Joy, UNH
Alfred Kober, Apollo Chemical Corp.
Nino Molino, New England Electric
James Noble, Cabot Corp.
John Riehl, Cabot Corp.
David Stickler, Avco Everett Research
Roger Trueblood, Stone & Webster
Gail Ulrich, UNH

# APPENDIX B

# SUBMICRON FLY-ASH FORMATION IN COAL-FIRED BOILERS

BY

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## SUMMARY

The submicron fraction of coal fly-ash, though comprising a minor fraction of the total mass, has become increasingly recognized as a health hazard and a possible link in irreversible boiler fouling. An outgrowth of continuing research on submicron particle behavior, this document describes efforts to predict the composition and morphology of condensation ash. A model based on a process of metal oxide vaporization from a burning char particle, diffusion and recondensation has been constructed and employed. A submicron particle concentration equaling five percent by weight of the fly-ash from a cyclone-fired boiler is predicted. Because of lower combustion temperatures in pulverized-fuel-fired boilers, less than one tenth of one percent of the total fly-ash is attributed to vapor transport. Enrichment of silicon and iron is predicted in the submicron fraction. This is verified experimentally for silicon but not for iron. Experimental examination reveals aggregates containing primary particles, of about 60 nm in diameter. Particles of this size are evidence that the submicron ash precipitates in the combustion zone of the boiler to grow by coagulation for several seconds before quenching.

## INTRODUCTION

The particle size distribution of coal-generated fly-ash is bimodal, the major mass mode consisting of spherical particles which vary from about one to fifty microns in diameter. This so-called residual or entrainment ash is the remains of burned-out, suspended coal particles. Prior studies[1,2] indicate that, through fracturing or bursting of cenospheres, one such coal particle produces from three to five residual ash particles. Their spherical, glassy appearance testifies to prior existence as molten, liquid droplets.

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The other type of ash particle, which comprises the minor mass mode, is termed condensation ash. As the name implies, it is allegedly produced by condensation of metal-containing species that evaporate from the coal particle and diffuse to the bulk gas stream where they recondense. Even though its mass comprises less than ten percent of the composite ash, it frequently represents more than ninety percent of the total by number. These submicron particles, as seen under the electron microscope, are not discrete species but aggregated clusters or flocs of smaller primary or proto-particles.

The environmental impact of submicron ash is markedly more significant than is suggested by its small mass fraction. These smaller particles, because of larger external surface areas, adsorb higher mass concentrations of gaseous toxins and penetrate more deeply into the respiratory system where absorption in the blood stream is rapid and complete. To make matters worse, recent observations reveal that the more volatile toxic metallic elements, are concentrated in the submicron ash fraction[3, 4, 5].

Ultra-fine particles are effective scatterers of light, causing an inordinate impact on visibility and terrestrial energy transfer. Since atmospheric condensation is essentially a function of nuclei number rather than size, smaller particles exert a more profound effect on climate than would the same mass concentration of larger particles.

The installation of dust-control equipment on power plants does not necessarily resolve the problem. Electrostatic precipitators, for example, are less efficient in the submicron range. Thus, a collector may pass a substantial fraction of the submicron ash and still be rated as greater than 99 percent efficient on a total mass basis. As stated by Friedlander[6], it is possible that total particulate mass may be decreasing in some geographic areas while air quality deteriorates because of increasing numbers of particles in the submicron range.

Condensation ash particles may also play a key role in irreversible slag accumulation[7]. Their thermophoretic velocities, in the presence of a cooled surface, are expected to be up to five times greater than those of larger particles. Fouling may also be a strong function of adhesion/cohesion strength, which is pronounced for these high-surface materials. Although the total and exact process is not clear, deposition is a well-known problem in the cooling of gas streams containing submicron aerosols.

There are two additional reasons why condensation-ash deposits may pose a barrier to successful tube cleaning by conventional 'soot-blowing' techniques. First they contain the more volatile elements and will, correspondingly, exhibit a lower melting point. Second, these particles deposit as bulky, low-density aggregates having large void volumes. The composite thermal conductivity is, therefore, much lower than that of the ash. This combination of properties will tend to convert a cool, non-adherent metal surface to a hot, sticky oxide surface resulting in a rapidly-growing slag or crust.

For these reasons, a program has been underway in our laboratory to study condensation ash and similar flame-generated aerosols. The work is divided into two categories: (1) the process of transport to the bulk phase and (2) the precipitation-growth sequence. Each is considered separately below.

## TRANSPORT PROCESSES

Previous work suggests that a substantial fraction of submicron fly-ash is formed by condensation of the mineral matter which vaporizes during coal combustion. The temporal regimes of combustion are devolatilization, ignition, and char burnout. Devolatilization of suspended coal particles is usually complete in 60 msec or less under the rapid heating conditions experienced in commercial boilers[8]. The amount of material lost may be considerably greater than that determined under standard ASTM conditions, leaving a char whose density may be half that of the original coal[9]. Because of the low temperatures characteristic of devolatilization, little ash is likely to be vaporized during this process. Major vapor-phase ash transport is thought to occur during char burnout when temperatures are considerably higher. The initial ash is distributed as small inclusions throughout the char. As the carbonaceous matrix recedes, this mineral matter is exposed and melted, forming spherical ash droplets which adhere to the char surface. The molten ash is exposed to a high-temperature, reducing atmosphere in which some ash components are transformed to volatile species and diffuse away from the surface, condensing at some distance from the particle where the temperature is lower and the oxygen pressure is higher. Char combustion determines the temperature and oxygen profiles surrounding the coal particle, and diffusive driving forces must be evaluated at these conditions.

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, and (3) derivation and integration of expressions for the rates of diffusion of these species during burnout. The total amount of material transported is a function of several parameters. Experimentally one would like to examine a wide range of these variables. Our sampling was performed on utility boilers, however, which cannot be manipulated for experimental purposes. The best alternative, under these conditions, is to sample from different boilers. The widest range of variables, particularly with regard to temperature and particle size, is probably realized by comparing pulverized-fuel (PF) and cyclone-fired (CF) boilers. Therefore, both types of combustion have been modeled.

The reaction rate of a char particle as a function of gas temperature, particle size, oxygen pressure, and gas velocity was estimated from published rate data for typical low rank coals. Details of the combustion model are presented in the appendix. The instantaneous, steady state particle temperature was obtained from an enthalpy balance.

Partial pressures of gaseous species containing Si, Al, Fe, and Ca, were estimated by their equilibrium values. The computer program used for these calculations is described elsewhere[10]. The major components were SiO, $SiO_2$, FeO, AlO, and CaO. Diffusivities for these species estimated from molecular parameters, were used to derive an expression for the rate of vapor transport. This equation was integrated numerically from devolatilization to burnout of the char to predict the amounts of silicon, aluminum, iron and calcium that evaporate and diffuse away from the particle. Once transported to the oxygen-rich bulk phase, each metal species is presumably oxidized to its most stable form, subject to subsequent precipitation and coagulation.

The major differences between PF and CF boilers are the higher particle concentrations in the former and the higher combustion temperatures in the latter. For PF boilers, a Rossin-Rammler correlation was used to describe the coal size-distribution. The bulk oxygen pressure was based on the fractional burnout of each size fraction. This type of calculation has been described elsewhere[11]. The predicted quantities of condensation ash generated in PF boilers are shown in Table I.

The coal feed used in cyclone firing has a broad spread of particle sizes. The largest, averaging about 0.15 cm in diameter is the crushed fraction that burns in the cyclone slag. A smaller fraction, which represents about 15 percent of the total, is inevitably produced during crushing. These particles do not impinge on the slag but burn, rather, suspended in the flowing gas stream. To estimate ash transport, the suspended coal particles were assumed uniform in diameter (100 μm) and were viewed as burning in a constant temperature environment. Predicted quantities of condensation ash emitted by the suspended coal are also presented in Table I for several different cyclone temperatures. These values include an amount of ash evaporation from crushed coal in the slag that is estimated to be 0.16 percent of the total based on a typical slag temperature of 1600K. Since only 15 percent of the ash enters the gas stream of the cyclone boiler, the ratio of condensation ash to fly-ash is considerably larger than its ratio to the total feed ash.

Values shown in Table I reveal that approximately five percent of the fly-ash in a cyclone-fired boiler may pass through the vapor phase. Approximately one-fifth of this originates from the slag-suspended coal with the balance coming from gas-suspended particles. The predicted composition of condensation ash is considerably enriched in some constituents, notably $SiO_2$ and FeO. The ratio of these dominant species is relatively insensitive to temperature. The average ash composition is thus reasonably constant and is shown in Table II. Since predictions were limited to major constituents ($SiO_2$, $Al_2O_3$, FeO and CaO), an experimental composition was employed to provide estimates for the minor compounds (MgO, $Na_2O$, $K_2O$ and balance).

We must emphasize that the predictions are, at this stage, only tentative. The most significant influence on loading is temperature. A two-or more-fold change in the predicted condensation ash loading is created by a plausible error of 100 degrees in temperature. A second major source of uncertainty is the assumption of vapor-liquid equilibrium between molten ash and metal-containing gases at the particle surface. General departure from equilibrium will reduce the quantity of predicted transport. Deviation by individual constituents will affect the composition. Another possible cause of error lies with thermodynamic data used in the equilibrium computations. Another significant uncertainty lies with the surface area of exposed ash which directly influences the predicted transport rate.

Raask and Wilkins[12] calculated the conditions under which volatilization of silica could be expected in gasification and combustion processes. They predicted that significant silica vaporization would occur only above 2300K for stoichiometric combustion at atmospheric pressure. This is in agreement with our calculations. They conclude however, that this rules out silica vaporization in a cyclone since combustion temperatures seldom reach this level. It is important, however, to distinguish between the gas temperature and the particle temperature. The latter may exceed the former by two to three hundred degrees, allowing significant vaporization as noted in Table I.

In preliminary work done in this laboratory and published elsewhere[7], the potential for transport was estimated on the basis of simulated reducing conditions at the char surface. Equilibrium was determined at oxygen levels representing 6 and 35 percent of stoichiometric. Those results revealed much larger quantities of vaporized ash than are found here. In reality, becuase oxygen diffusion is rapid relative to surface reaction, oxygen concentrations at the char surface do not drop to levels as low as the 6 to 35 percent stoichiometric assumed earlier. Rather than reduction-assisted vaporization which was proposed, it appears that direct vaporization of metal oxides is the major source of condensation ash.

Most ash-enrichment data in the literature apply to trace metals. General trends which show enrichment of volatile elements in submicron ash are consistent with similar behavior among the major species[13].

## PRECIPITATION AND GROWTH

Following transport of metal oxide species to the gas phase, rapid nucleation at some point in the boiler is assumed. This yields particles which grow both by collision between primary particles or monomers and by fusion of the aggregates formed thereby. The physical model for such growth is based on studies of silica behavior in pre-mixed, flat-flame burners. In these systems, nucleation is an integral part of the chemical reaction[14], a process which occurs within a few milliseconds.

Subsequent growth, therefore, is controlled solely by the combined effects of interparticle collision and fusion or coalescence[15]. The aggregate morphology or "structure" is determined by relative rates of these two processes. If collision frequencies are low and viscosity is small, particles will be single, spherical droplets, growing at a rate equal to the collision rate. If viscosity is high, particles collide and adhere, but do not fuse, thus forming clusters or aggregates containing numerous smaller primary or proto-units.

Collision and fusion rates can be specified by conventional kinetic expressions. Details of the calculation are provided elsewhere[7,15,16]. Aggregate mass, so computed, grows at a rate illustrated in Fig. 1. The three solid lines represent collision characteristics of free-molecule and continuum Brownian behavior as well as a prominent extrapolation. Data from a silica-producing flame are shown for comparison. They were obtained by a laser light-scattering technique[7, 16]. These results reflect growth in a rather concentrated flame (2.6 mole percent silica). Data for lower concentrations show similar close adherence to the free-molecule and continuum limiting curves and poor agreement with the Fuchs extrapolation. The most noteworthy aspect of Fig. 1 is an abrupt decrease in particle growth when motion shifts to the continuum type. This occurs when aggregate or particle diameter (as the case may be) approaches the size of the gas mean-free path. In more dilute flames, the period of free-molecule growth is longer, but the transition mass is the same.

Changes in primary particle size and aggregate structure are well characterized by the classical Frenkel fusion model. In the case of silica, with its large viscosity, an aggregate or floc may contain several thousand primary particles. Theoretical predictions are limited, however, by a viscosity that has extremely sensitive temperature to the presence of impurities. In contrast, titania which has a viscosity, an order of magnitude smaller and a surface tension about five times larger, is less prone to form aggregates[17].

Equations describing particle growth include vapor concentration, viscosity, and surface tension of the condensed ash as parameters. Concentration was taken directly from transport calculations described above. Viscosity and surface tension, however, depend strongly on the composition. The estimation of viscosity is a particularly difficult problem, since silica, at a given temperature, is approximately 10,000 times more viscous than the ionic oxides formed from aluminum, calcium, magnesium and iron. Fortuitously, for binary systems containing silica, viscosities at the same molar compositions are similar (within plus or minus 50 percent) whether the other oxide is alumina, calcia or magnesia. This generalization is valid over most of the temperature-composition field[18, 19]. Though these variations seem broad, they are not significantly worse than those within the literature for pure silica itself. Thus, to estimate fusion rates, we have assumed that ash is a binary mixture of silica with a non-specific oxide. The viscosity equation of Rossin _et al._,[18] for silica-alumina mixtures was used.

Surface tension is much less sensitive to composition and is essentially independent of temperature over wide ranges. Regardless of the composition of the remaining oxides, the surface tension of coal ash appears to be approximately 350 ± 50 dyne $cm^{-1}$ for silica concentrations of 40 weight percent and above. For concentrations below 40 percent silica, surface tensions will approach the limiting value of 620 dyne $cm^{-1}$ which is within plus or minus ten percent of values for calcia, ferrous oxide, alumina and their mixtures[20].

## RESULTS

Based on the vapor transport mechanism presented earlier and the assumptions described above, it is possible to predict the nature of submicron ash generated in the CF boiler. Despite differences between measured and predicted ash compositions the average silica content is little affected, being approximately 62 ± 5 weight percent or 66 ± 5 mole percent, on a sulfur-free basis, regardless of which composition is used. The predicted quantity of condensation ash is 5.1 percent of the total fly-ash and about 0.8 percent of total ash in the coal. This is equivalent, under normal firing conditions, to a loading of 60 ng condensation ash per standard $cm^3$ of combustion products. At this loading, growth is totally within the free-molecule regime of Brownian motion. The calculated population of particles in number per standard $cm^3$ of gas volume is shown in Fig. 2 as a function of growth time. Other curves are shown for higher ash concentrations. The corresponding average equivalent spherical particle diameter is shown as a function of the same variables in Fig. 3.

Dilution of the stream is such that fusion rates are substantially more rapid than collision rates at temperatures above 1000K. Thus, particles are predicted to grow essentially as monomers. Since the collision frequency is approximately one per second, the predicted number of primary particles per aggregate is about four to eight based on the number of collisions that can occur in the time after the gases drop below 1000K. Physical agglomeration that may occur during collection is, of course, disregarded. This however, should result in low strength aggregates held together only by surface forces.

Interaction between condensation and residual ash is minimal in the absence of external fields or forces since the probability of Brownian collisions among submicron ash particles is one hundred times larger than that between sub and supermicron particles.

## EXPERIMENTAL RESULTS

Precipitator hopper ash from a cyclone-fired boiler was analyzed for size and chemical composition. Similar procedures for a PF-fired boiler are in progress. Samples were size-separated by three different techniques. First a fluid bed feeder was used to disperse particles into a gas stream with subsequent separation and collection occuring in an impactor followed by an absolute filter. Secondly, samples were dispersed in water using ultrasonic energy and then fractionated through a series of Nuclepore filters. A third technique, separation in the Joyce-Loebl disc centrifuge, was examined briefly with limited success. To characterize the separated fractions, scanning electron micrographs were obtained, and microprobe analyses combined with standard atomic absorption and induction-coupled plasma analysis were employed to determine chemical composition. The result is a series of chemical compositions, one for each of the separated ash fractions.

The percentage of ash below 0.4 μm was found to be 7 by Nuclepore filtration and only 2 by impactor separation. These are to be compared with the theoretical value of 5 percent in Table I. The impaction result is understandably low because many submicron particles in the bulk feed will remain attached to the surfaces of larger particles. In the nuclepore separation, on the other hand, disengagement is promoted by ultrasonic energy applied to the aqueous suspension. However, sample quantities are small, difficult to analyze and subject to poor precision. Separation efficiencies can be judged qualitatively from Figs. 4 and 5 which are scanning electron micrographs of fractions on the impactor stages and on the filters. In Fig. 4, there is little evidence of carry-over of larger particles, but significant numbers of smaller species are found with the large ones on the early stages. In Fig. 5, showing particles on three Nuclepore filters, the separation appears to be considerably "cleaner" than in Fig. 4. Frames a, b and c graphically illustrate the relationship between population and particle diameter, with mass concentrations actually decreasing from 50% to 30% to 7% respectively while the number-population increases. Frame d is a higher magnification of smaller particles and aggregates retained on the 0.4 μm filter.

Though the distinction between condensation ash and smaller sizes of entrainment ash is somewhat arbitrary and subjective, we note numerous aggregates containing up to ten or so primary particles, each approximately 100 nm in diameter. When corrected for the conductive coating required for SEM microscopy, the primary particle diameter is approximately 60 nm.

Composition trends for impactor separation are exhibited in Fig. 6. Enrichment is clearly evident for silicon and sulfur in the submicron fractions while concentrations of iron and aluminum decrease. Other concentrations are independent of size except for calcium which is possibly enriched slightly in the smaller particles. Analyses of the samples separated by Nuclepore filtration are similar except for the case of sulfur which was less than 0.5 percent in all fractions.

## DISCUSSION

Ash transport calculations, based on the time-temperature history of burning coal particles, indicate that as much as five percent of the fly-ash in a cyclone-fired boiler will pass through the gas phase, appearing as submicron particles in the gas stream. By comparison, because of the lower combustion temperature, less than one tenth of one percent, of the total ash is predicted to pass through the vapor state in a boiler fired with pulverized coal in suspension. Separated fractions of cyclone boiler fly-ash yield from 2 to 7 percent in the fraction less than 0.4 µm. The former number, obtained using an impactor, is undoubtedly low because of smaller particles which adhere to larger material retained on previous stages. The same is true to a lesser extent in Nuclepore fractionation where even the 7 percent value must be considered on the low side. The actual amount, considering retention on larger particles and the fact that about 1% of the ash, presumably submicron, was not collected in the electrostatic precipitator, is probably near 10 percent. The difference between predicted and measured values may reflect an error in the estimated combustion temperature. Submicron fragments generated during disintegration of the burning coal particles are a second possible cause. This is consistent, as well, with composition trends for alumina. For example, the amount of alumina vaporized should be neglegible. Although reduced substantially from the bulk value of 19 percent, its concentration in the smaller ash fraction is still 10 percent. This could be expected if half of the submicron fraction originated as fragments having the bulk composition.

The composition trends for iron and calcium are anomalous. Predictions indicate slight enrichment for iron and depletion for calcium in the condensation ash. Based on the sample analysis, iron is actually depleted as severely as alumina whereas calcium shows little change. The iron discrepancy is attributed to poor equilibrium data which, according to the JANAF tabulation of sources[21], appears possible.

Sulfur shows a substantial concentration increase in smaller ash particles separated by impaction. The lack of enrichment in filtered samples suggests that sulfur is adsorbed on the surface in a form that is readily dissolved in water. Since water dispersion has no effect on the metal concentrations, sulfate compounds are unlikely.

The observed primary particle size of 60 nm is somewhat larger than the value of 40 nm predicted from Figure 3 based on 5% of total ash passing through the vapor phase and a total residence time of 3.6 seconds. If precipitation occurs in the boiler tube section, the maximum predicted equivalent diameter is somewhat less, 32 nm, because growth can occur for no more than 2.5 seconds. One could argue that the ash is actually precipitated in concentrated zones surrounding the burning char and grows at a more rapid rate corresponding to a higher concentration. This, however, requires growth to 60 nm prior to any significant dilution which is unlikely. Otherwise, growth converges to a slower rate corresponding to the average concentration. If, as suggested above, entrained fragments coagulate with condensation ash, growth will occur at a faster rate. For an equal mass mixture of submicron entrainment fragments and condensation ash, a primary particle diameter of 52 nm is possible in a residence time of 3.6 seconds. This is reasonably near the measured value.

Aggregates are predicted to contain from four to eight discrete primary particles. In fact, each primary particle in a four-unit aggregate should be only 32 nm in diameter to have the same mass as a 52 nm sphere which is the basis of Figure 3. Micrographs indicate that most aggregates are slightly larger, containing ten or so 60 nm units. Several causes are plausible. First, actual ash viscosity may be somewhat higher than the theoretical value used for predictions. This is an explanation for the larger number of primary particles but not for the larger diameter. Some agglomeration may be promoted in the precipitation. This would be difficult to distinguish in electron micrographs of coated samples. Similarly, some of the aggregation may actually be physical entanglement that has not been eliminated during sample preparation. Flaws in the theoretical model are also possible. Perhaps, because of electrical or other effects, collision frequencies are larger than predicted. Further work is needed to clarify this discrepancy.

## CONCLUSIONS

A preliminary model for predicting concentration, composition, size and morphology of submicron coal ash has been developed. While promising, several areas of further refinement can be noted.

Vapor-phase transport of fly-ash in a cyclone-fired boiler burning bituminous coal is estimated to be five percent of the total. Approximately ten percent is actually found as submicron ash. This difference combined with observed composition trends indicates that half of this ash originates as minute entrained ash fragments which has coagulated with the vapor-transported material.

Enrichment of silicon and iron is predicted in the submicron ash. Similar behavior would be expected of volatile trace elements which were not considered in this study. Experimental studies by others confirm trace element trends, and silica enrichment is found in this work, but iron is actually depleted in the smaller particles. At the present time, we suspect erroneous thermodynamic data as a cause of the iron discrepancy.

Condensation ash, as separated and examined by electron microscopy, is comprised of aggregates containing approximately ten primary particles which are about 60 nm in diameter. Assuming precipitation occurs in the combustion zone of the boiler, coagulation, according to this model, would yield smaller aggregates containing somewhat smaller primary particles. Refinements in theory and experiment are clearly needed and will continue in the future as we obtain additional samples at intermediate residence times, with different coal compositions, in different boilers and with additives present.

## ACKNOWLEDGEMENTS

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# ADDENDUM

Combustion of suspended coal particles occurs in both pulverized fuel (PF) and cyclone-fired (CF) boilers, though only about 15 to 20 percent of the fuel is burned in suspension in the latter. In both systems, following devolatilization, the suspended particle is ignited by recirculated flue gas and reacts heterogeneously with oxygen to produce carbon monoxide. The latter is assumed to burn to $CO_2$ at some distance from the particle, having no direct effect on the particle temperature, $T_p$, but serving to raise the gas temperature, $T_g$, along the particle path.

The reaction rate of the char at steady-state, q (g $cm^{-2}s^{-1}$), is expressed by

$$q = K_d \, (p_g - p_s) = K_s p_s \equiv K \, p_g \qquad (1)$$

where

$$K^{-1} = K_s^{-1} + K_d \qquad (2)$$

$K_d$ is a diffusion rate coefficient, $K_s$ a surface reaction rate coefficient, and $p_g$, $p_s$ are the oxygen pressures in the bulk gas and at the particle surface respectively.

Since the diffusivities of CO and $O_2$ are nearly identical, and the relative velocity between the particle and gas stream is very low, it may readily be shown that[22]

$$K_d = 48 D_{CO} / R T_g d \qquad (3)$$

where R is the gas constant and d is the particle diameter. The diffusivity of CO in $N_2$ is very closely approximated by the expression $D_{CO} = 1.6 \, \theta^{1.66}$ where $\theta$ is temperature in thousands of degrees Kelvin. Thus, with particle diameter expressed in microns

$$K_d = 9.35 \, \theta^{.66} / d_{\mu} \qquad (4)$$

This expression accurately predicts combustion rates under conditions which are known to be diffusion controlled.

The surface reaction rate is usually expressed in grams per second per unit of external surface area. Oxidation occurs internally, as well, in pores and voids created by the devolatilization process. Catalysis by mineral matter has also been observed. The detailed extraction of adsorption, desorption and intrinsic rate parameters has never been accomplished for this complex system. Instead, rate data for a wide range of carefully controlled combustion conditions have been obtained. These rates, usually falling substantially below the diffusion limiting rate, have been interpreted in terms of Eqs. (1) and (2) and expressed empirically. For example, Field[23] has proposed the following expressions for low rank, non-swelling coal:

$$K_s = 8710 \exp(-7.976\,\theta_s); \qquad \theta_s < 1.3 \qquad (5)$$

$$K_s = \theta_s\,(0.158\,\theta_s - 0.126) - 0.09; \qquad 1.3 < \theta_s < 2.0 \qquad (6)$$

where $\theta_s$ is a reduced surface temperature.

In a refined model, the temperature profile in the boiler would be calculated from the reaction rate expression and detailed energy balances, or an experimental profile could be used. In these exploratory calculations however, plug flow and a one-dimensional gas temperature profile are assumed. Gas temperature $T_g$ is thus a simple function of residence time. Surface temperature $T_s$ may be calculated at any time if the particle is assumed to have a uniform temperature which adjusts itself instantaneously to $T_g$ to maintain a steady state enthalpy balance. The agreement between temperatures calculated in this way and measured surface temperatures is remarkably good[22].

Carbon monoxide and carbon dioxide concentrations surrounding a burning char are not at their local equilibrium values since rates for chemical equilibration of these species are slower than the related diffusive processes. The oxygen concentration at the surface may be calculated from the combustion rate. Thus for a given surface temperature and oxygen partial pressure, partial pressures of metal-containing species such as AlO and SiO are calculated under conditions where $CO_2$ formation is suppressed. The computer program used for these calculations is described elsewhere[10]. The assumption that actual partial pressures are near the equilibrium values is one that seems reasonable for the elevated temperatures under consideration. If in error, it at least provides limiting values for maximum diffusion rates.

Diffusivities were obtained using the usual kinetic theory expression with estimated molecular parameters. For example, values for SiO and $SiO_2$ were evaluated using the molecular constants for CO and $CO_2$.

During burnout, the char surface is not uniformly coated with ash but rather droplets form and agglomerate to form larger droplets as the char surface recedes. Sarofim et al.[2] expressed this process mathematically as a function of char burnout, $f_b$. Their results were used to develop the following relationship between the ratio of ash surface to external char surface $F_a$ and fractioned burnout.

$$F_a = c_1 f_b + c_2/(1.05 - f_b) - c_3 \qquad (7)$$

where the constants are dependent on the initial-char diameter (μm) as follows:

$$c_1 = 0.24\ (d_o - 18)^{1/2}$$

$$c_2 = 0.035 + .0055\ d_o \tag{8}$$

$$c_3 = 0.1 + .005\ d_o$$

The burnout parameter can be expressed as

$$f_b = \int_o^{\tau} (6\pi d^2\ q/\pi d_o^3\ \rho_{char})dt \tag{9}$$

or

$$\dot{f}_b = 6qd^2/d_o^3\ \rho_{char} \tag{10}$$

where $d_o$ and d are the char diameters initially and after time τ, and $\rho_{char}$ is the density.

Once vaporized at the char surface, metal-containing species will diffuse through the boundary layer which surrounds the particle at the following rate:

$$\dot{m}_i = \pi d^2 M_i\ (N_{Sh}\ D_i/RTd)\ (p_{i,s} - p_{i,g})\ F_a \tag{11}$$

where $m_i$ is the diffusion rate, $M_i$ is the molecular weight and $N_{Sh}$ is the Sherwood number. Partial pressures of the migrating species are $p_{i,s}$ at the particle surface and $p_{i,g}$ in the bulk gas phase. This can be rearranged and simplified through use of the diffusivity-temperature dependence, $D_i = D_i^o\ \theta^{1.7}$, to yield

$$\dot{m}_i = (\pi N_{Sh}/1000\ R)\ D_i^o\ M_i\ \theta^{0.7}\ F_a d\ (p_{i,s} - p_{i,g}) \tag{12}$$

Equation (12) was integrated numerically in connection with Eqs. (1), (7) and (9) to yield the transported composition and quantities shown in Tables I and II.

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# TABLE I

Predicted amounts of condensation ash produced in utility boilers at selected combustion conditions. The fuel is a medium-volatile, West Virginia, bituminous coal (Loveridge Mine, 36.9 percent volatile matter, 7 percent ash).

| Maximum Flame Temperature (deg-K) | Excess Air (percent) | Percent of Total Coal Ash Evaporated | Condensation Ash as Percent of Total Fly-Ash |
|---|---|---|---|
| | Pulverized Fuel Boiler | | |
| 1960 | 13 | 0.052 | 0.052 |
| 1880 | 13 | 0.017 | 0.017 |
| 1800 | 13 | 0.005 | 0.005 |
| 1720 | 13 | 0.001 | 0.001 |
| 1880 | 17 | 0.019 | 0.019 |
| 1880 | 11 | 0.017 | 0.017 |
| | Cyclone Boiler | | |
| 2200 | 17 | 0.77* | 5.1 |
| 2100 | 17 | 0.37* | 2.5 |
| 2000 | 17 | 0.22* | 1.5 |

*Includes 0.16% from crushed coal in the cyclone at 1600K.

## TABLE II

Composition (weight percent) of condensation ash in a cyclone, coal-fired boiler. The fuel is the same as that described in Table I. (Values in parentheses are based on the experimental composition).

| | | Composition of Submicron Ash | |
|---|---|---|---|
| Constituent | Original Coal 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 |
| $Na_2O$ | 15.8 | (2.4) | 2.4 |
| $K_2O$ | | (1.7) | 1.7 |
| Balance | | (1.2) | 1.2 |
| $SO_2$ | | (17) | 17 |

*Obtained by SEM Microprobe and Atomic Absorption.

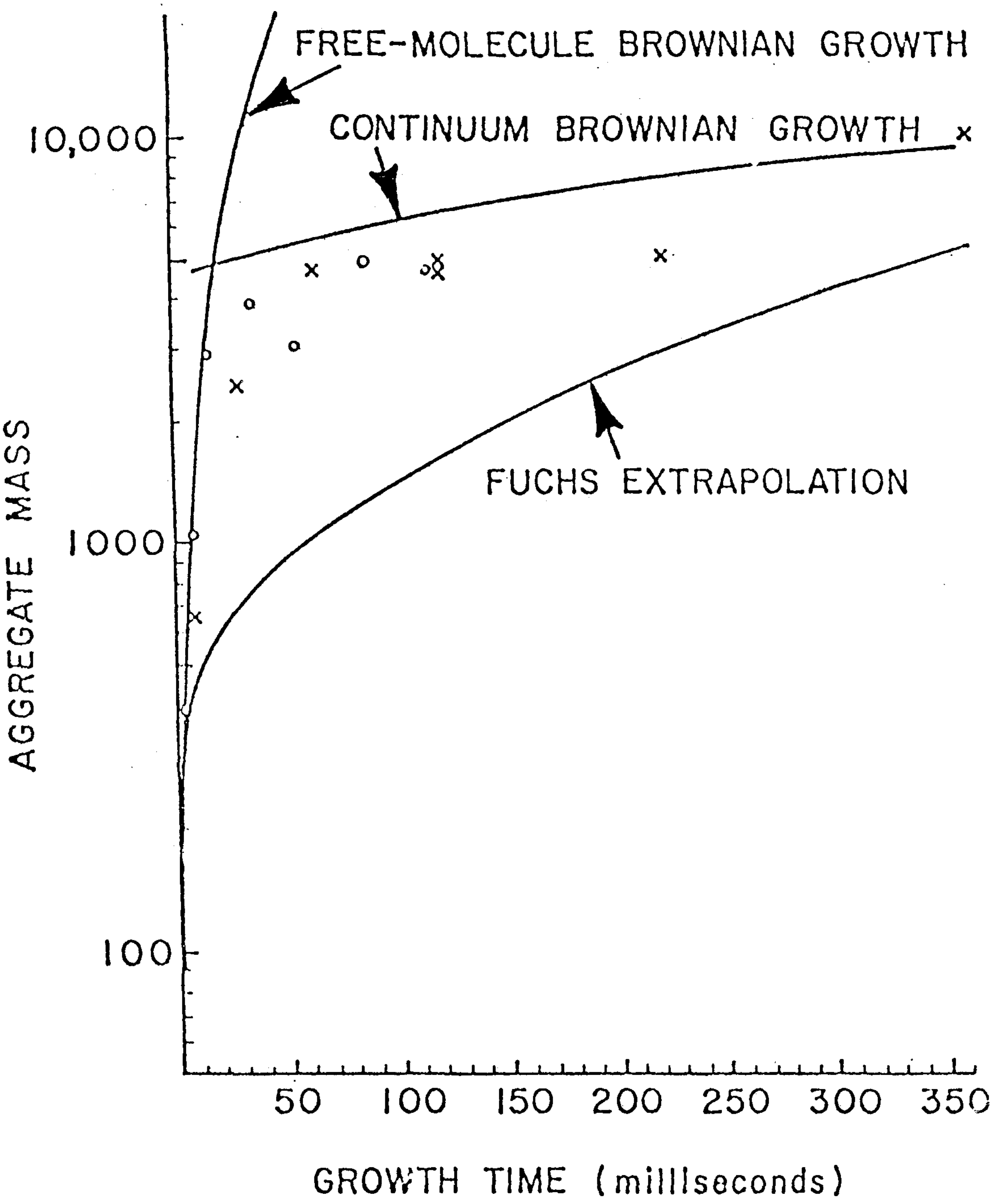


Figure 1. Aggregate mass (millions of atomic weight units) as a function of residence time for growing silica particles. Solid lines represent theoretical predictions for free-molecule and continuum Brownian behavior plus the Fuchs theoretical interpolation. Data points represent measurements taken at different flame conditions but the same silica concentration of 2.6 mole percent.

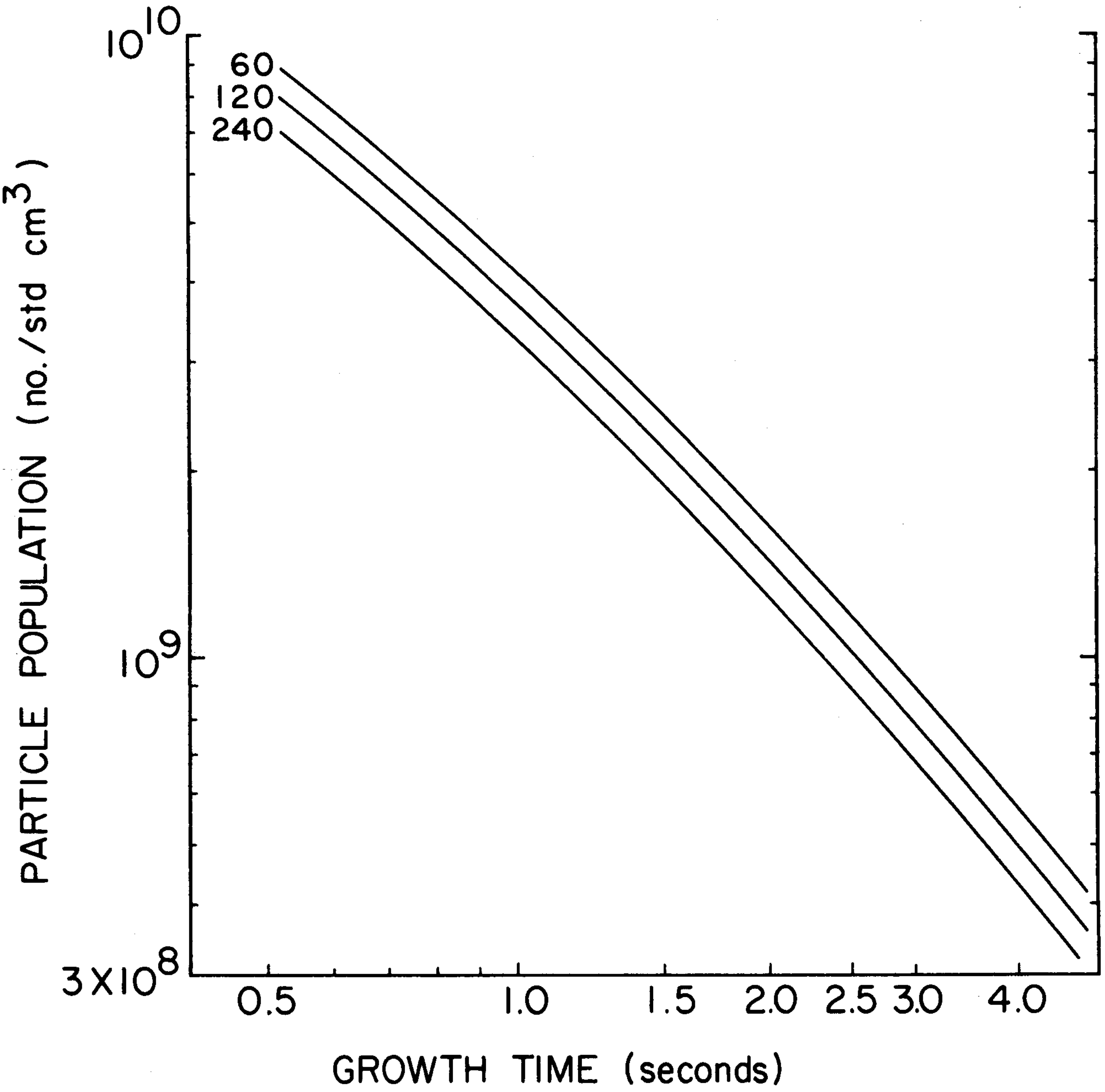


Figure 2. Predicted particle populations as a function of time during coagulation of submicron fly-ash. Parameter represents ash concentration in ng/std.cm$^3$.

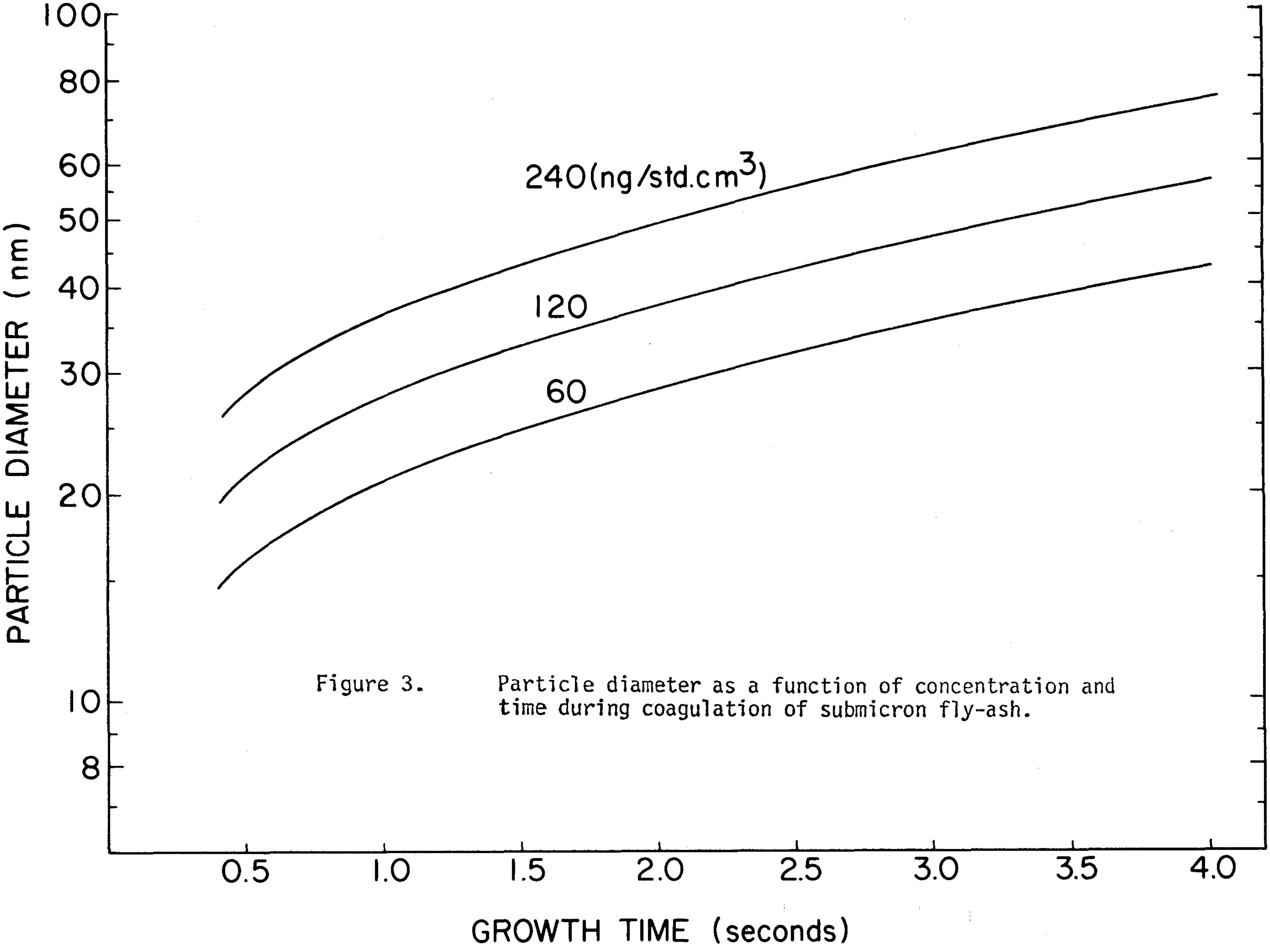
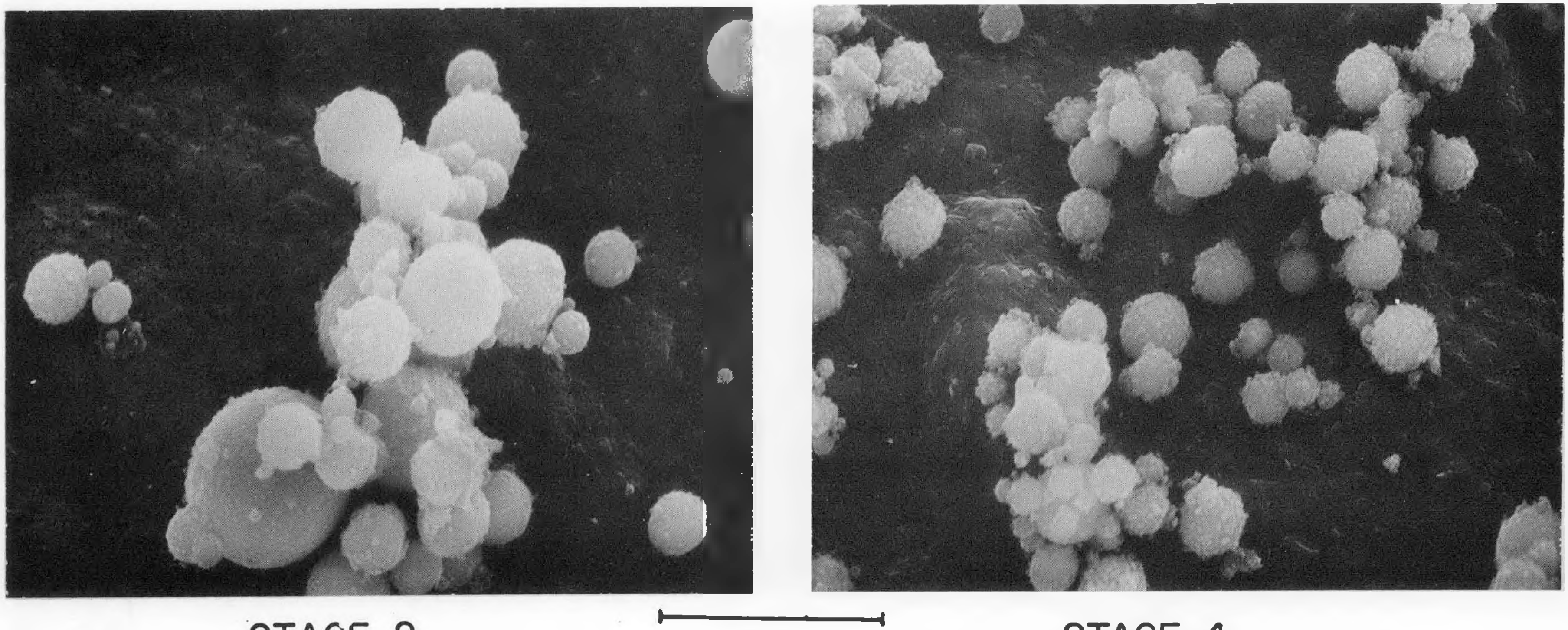
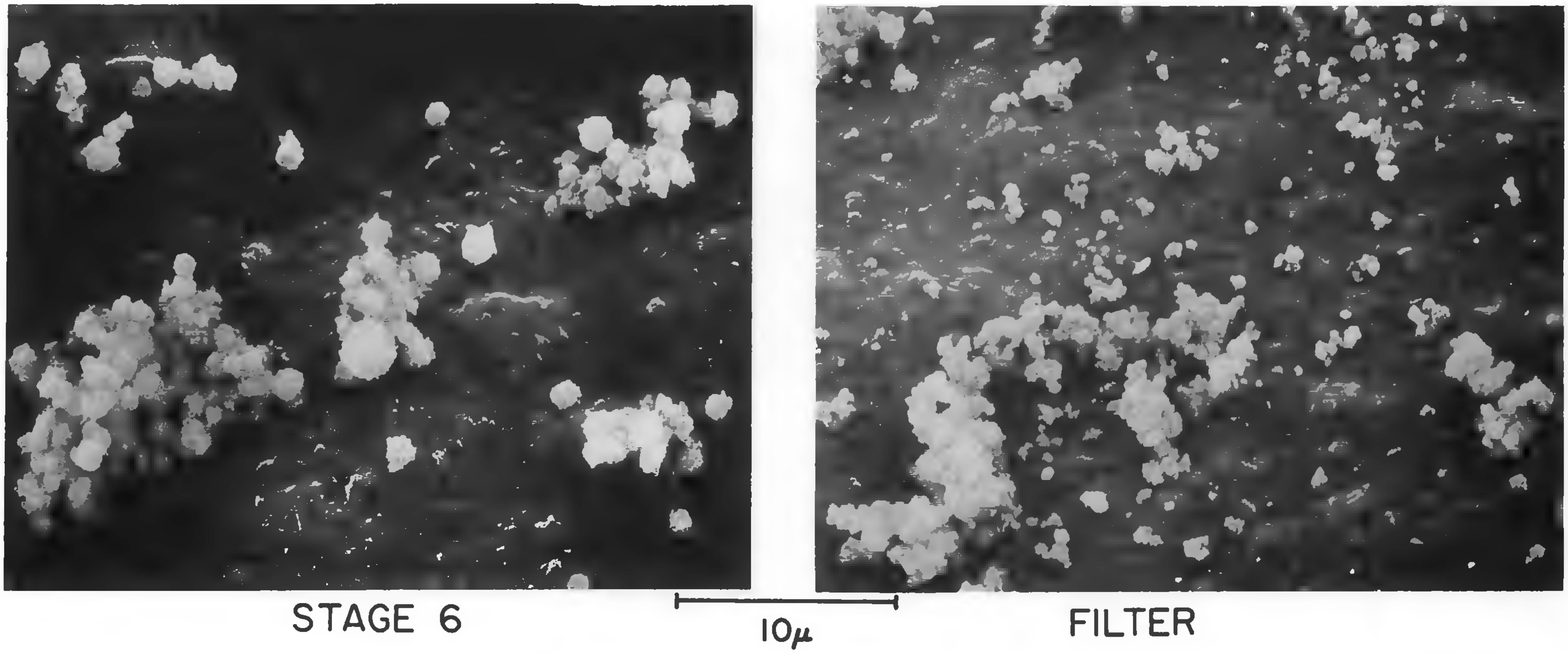


Figure 3. Particle diameter as a function of concentration and time during coagulation of submicron fly-ash.



STAGE 2

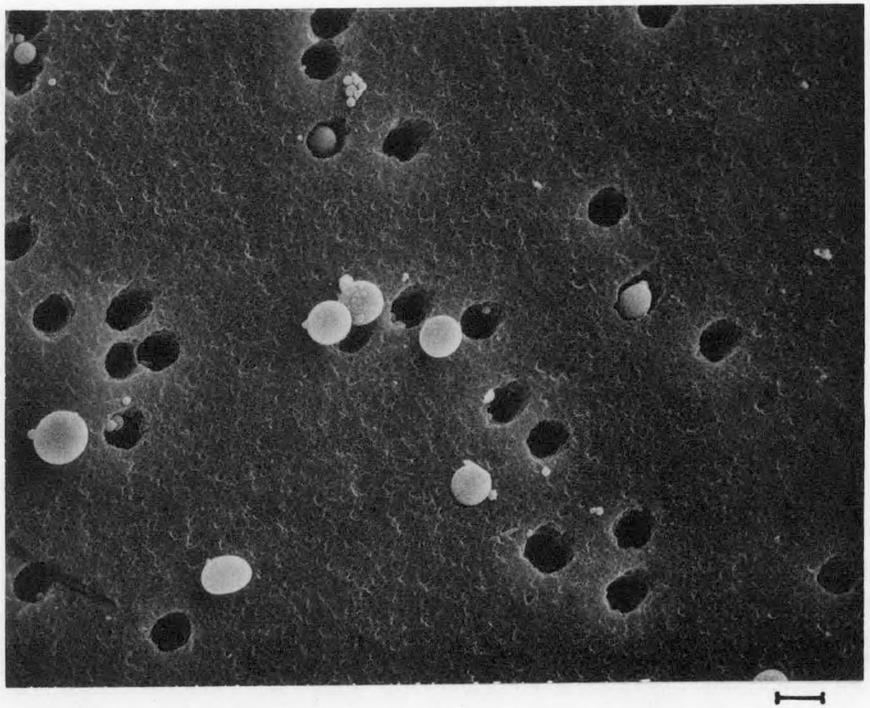
STAGE 4



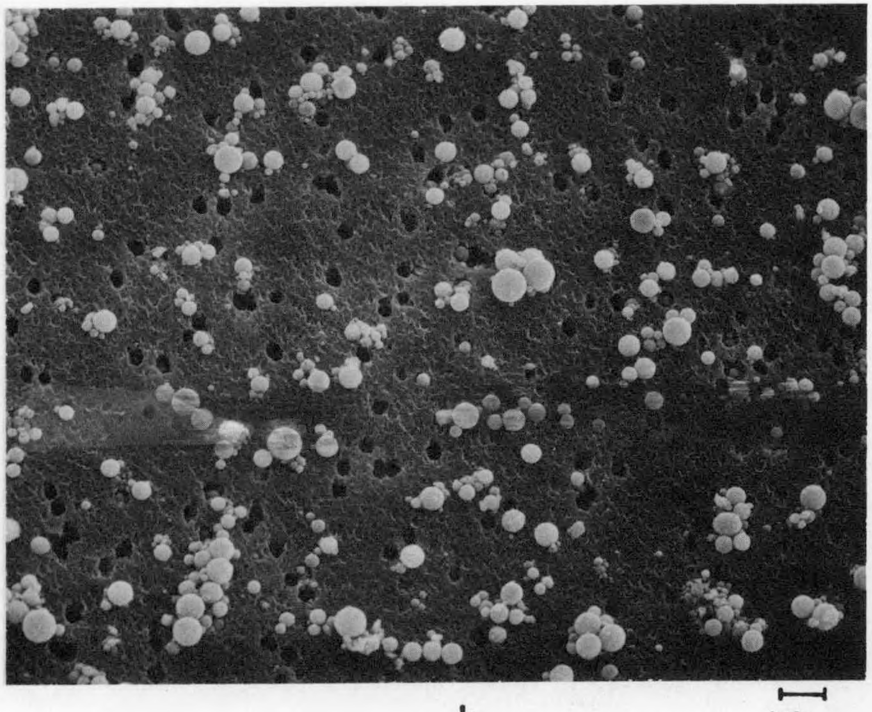
STAGE 6

FILTER

Figure 4. Scanning electron micrographs of separated fly-ash on selected stages and the filter of the impactor.



a



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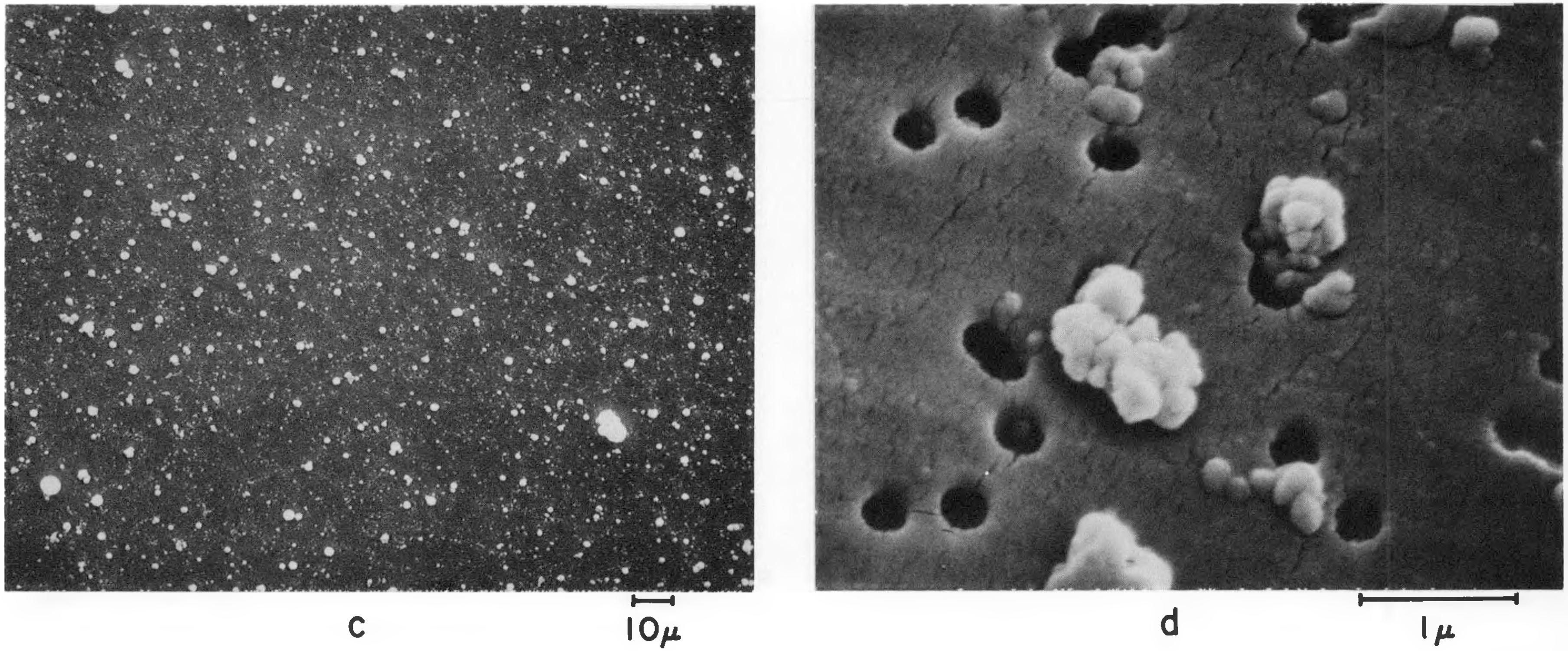

Figure 5. Scanning electron micrographs of separated fly-ash on selected Nuclepore filters. (a) 10 μm filter, 600X magnification (b) 3 μm filter, 600X magnification (c) 0.4 μm filter, 600X magnification (d) 0.4 μm filter, 23,400 magnification.

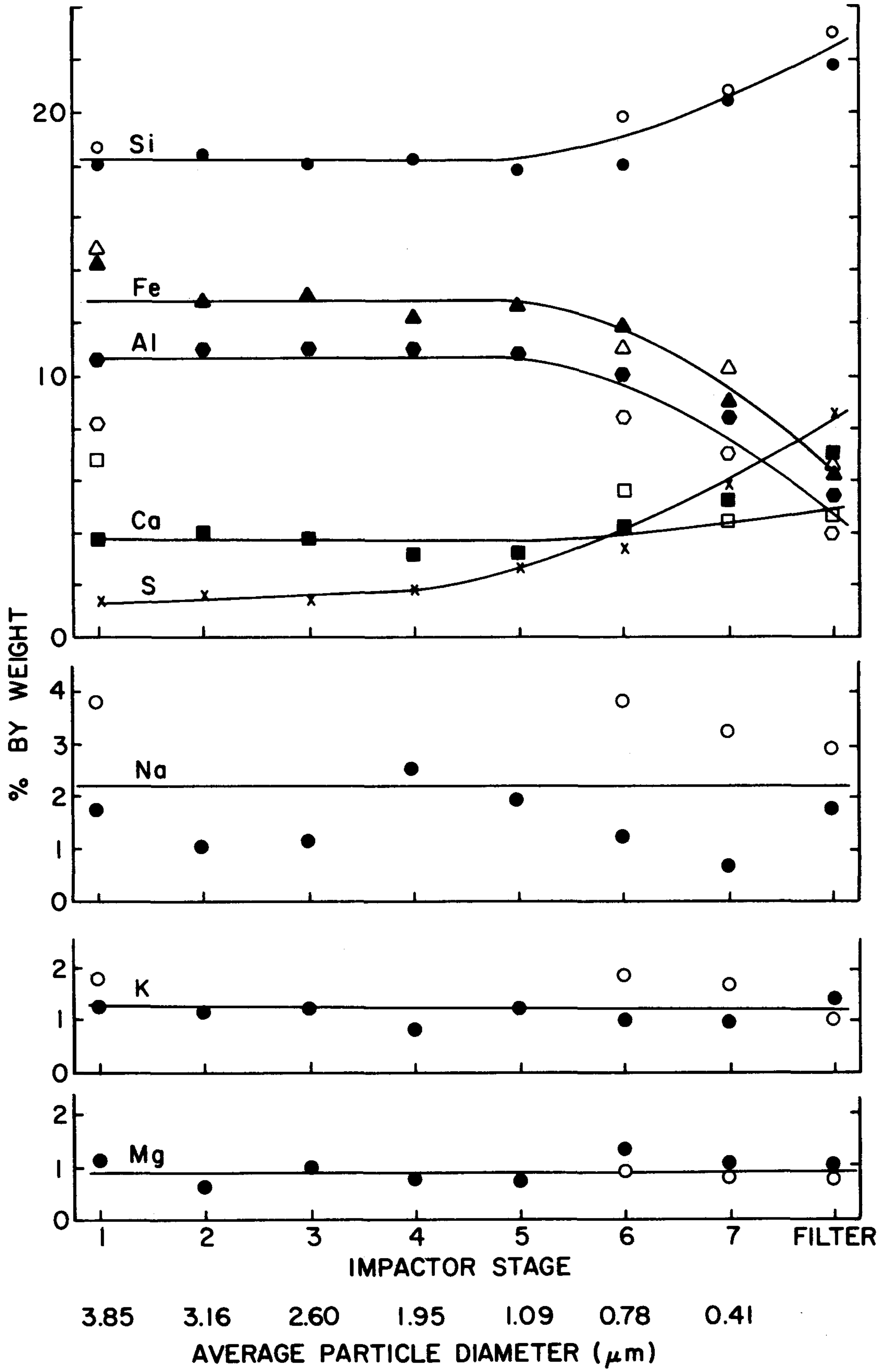

Figure 6. Composition as a function of particle size for fly-ash separated in an impactor. Filled symbols represent analysis by SEM microprobe (EDAX). Open symbols represent data obtained by inductively-coupled plasma analysis.