Evaluation of Flyash Surface Phenomena and the Application of Surface Analysis Technology

Summary Report - Phase I

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May 1981

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EVALUATION OF FLYASH SURFACE PHENOMENA
AND THE APPLICATION OF SURFACE ANALYSIS
TECHNOLOGY

SUMMARY REPORT - PHASE 1

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SUMMARY

The factors governing the formation of flyash surfaces during and following coal combustion are reviewed. The competing chemical and physical processes during the evolution of inorganic material in coal during combustion into flyash are described with respect to various surface segregation processes. Two mechanisms leading to surface enrichment are volatilization-condensation processes and diffusion processes within individual flyash particles. The experimental evidence for each of these processes is reviewed. It is shown that the volatilization-condensation process is the major factor leading to trace element enrichment in smaller flyash particles. Evidence also exists from surface analyses of flyash and representative mineral matter that diffusion processes may lead to surface enrichment of elements not volatilized or cause transport of surface-condensed elements into the flyash matrix. The semiquantitative determination of the relative importance of these two processes can be determined by comparison of concentration versus particle size profiles with surface-depth profiles obtained using surface analysis techniques. A brief description of organic transformations on flyash surfaces is also presented. The various surface analytical techniques are reviewed and the relatively new technique of Static-Secondary Ion Mass Spectrometry is suggested as having significant advantages in studies of surfaces and diffusion processes in model systems. Several recommendations are made for research relevant to flyash formation and processes occurring on flyash surfaces.

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1.0 INTRODUCTION

The use of coal as an energy source by direct combustion will probably continue to grow during the next few decades. The combustion of coal in large coal-fired plants (often with generating capacities exceeding 600 MW) is economically efficient and offers practical advantages for meeting environmental regulations. These plants may utilize the most modern and efficient pollution control devices, may be situated in remote locations (often near the coal supply), and, by high combustion efficiency, may produce reduced amounts of some pollutants. Thus, there is increasing concern and regulatory activity with the environmental impact of the effluents and waste products from coal combustion.

While the chemistry associated with the formation and ultimate fate of organically-bound coal sulfur and nitrogen has been fairly well-defined, until recently the chemical nature and fates of the elements associated initially with the mineral matter in coal during and following combustion have attracted considerably less interest. A similar situation exists regarding the formation and fate of organic pollutants. The control of particulate emissions has been of concern for many years, but with emphasis being placed primarily on the visible stack emissions from the combustion facilities. Recent research into the nature of the inorganic emissions from coal-fired plants, however, has given reason for renewed concern. These results indicate that particulate emissions may be greatly enriched in certain trace elements, and that these trace elements may be in chemical and/or physical forms which have an enhanced impact upon man. Since the chemical and physical

characteristics of the surfaces of these particles determine their role in the combustion and postcombustion processes, as well as the ultimate environmental impact, an understanding of these surfaces is required if one is to ultimately model these processes or predict their impact.

The potential impact of coal combustion as a source of atmospheric pollutants is significant. Coal production amounted to approximately 7×10^8 tons in the U.S. in 1978. World production of coal presently amounts to approximately 4×10^9 tons/yr. In 1970, approximately 60% of the coal mined in the U.S. was used by electrical utilities, which produced half the total particulate emissions from coal use. In 1977, electrical utilities accounted for 77% of the coal consumed in the U.S. The conversion of existing oil-fired plants to coal, construction of new coal-fired plants, and the slowdown in nuclear construction are also important factors in the projected increase in coal combustion in the near future.

The trace elements in coal may produce a significant fraction of the environmental impact of the emissions from coal combustion due to the large enrichments often observed in the particulate emissions. The enrichment processes may result in greatly enhanced effects on biological systems not adequately assessed as part of the impact of coal combustion. Flyash surface species may play an important role in both high temperature transformations during combustion and in the ambient temperature chemistry related to the transformations of organic species on flyash surfaces. In terms of the factors more directly related to power plant performance, there may be important relationships with slag and corrosive formation and their surface characteristics, the formation and transport of chemical species relevant to

corrosion, and factors which determine flyash resistivity (and, hence, the collection efficiency of electrostatic precipitators). Many of these processes are directly related to the presence or formation of surface concentrations on flyash of particular chemical species. Thus, there is a need to understand the nature of the surface enrichment processes which occur during coal combustion and to develop adequate techniques for their study.

The events leading to surface enrichment during combustion and in the postcombustion region have only been studied indirectly and the relative importance of various postulated processes remains undetermined. For pulverized coal combustors, pulverized coal is injected into the furnace and ignited while in suspension, producing a diffusion flame typical of solid or liquid fuels. The coal particle size distribution is typically quite broad and often has a mass median diameter in the 30 to 75 μm size range. The coal is heated both radiatively and by mixing with the combustion products. As the coal particles are heated, volatile matter (including devolatilized and pyrolyzed organic species) is vaporized and combustion occurs as either attached or detached flames, depending on the physical constraints of the system and the thermal properties of the coal. The conditions at the coal particle surface are initially reducing. A portion of the pulverized coal may actually be composed of free mineral matter, leading to quite different local conditions. The reaction is at least partially internal and activation energies typically quoted are in the range of 20 to 60 kcal/mole^(1,2).

The physics and chemistry of the transformations related to the organic matter in coal during rapid heating and combustion have been relatively well studied and a number of reviews are available (see references 1 and 2, and

references therein). The rate of combustion of the smaller coal particles (<100 μm) is essentially kinetically-limited, whereas burning of larger particles is diffusion-limited⁽²⁾. It has been suggested that at high flame temperatures diffusion of oxygen through the boundary layer becomes the controlling mechanism for combustion, limiting fragmentation of the burning char⁽¹⁾. As combustion proceeds, relatively nonvolatile trace elements which are trapped in an organic matrix or bonded in organic compounds (organometallic species including chelates, metal carbonyls, etc.) may be transferred to the gas phase⁽³⁾. The fate of organically associated elements during coal combustion may be particularly important in determining the ultimate trace element emissions, as postulated previously^(3,4). Additionally, elements present in the mineral matter in their more volatile forms may also be vaporized in either their original or reduced state. By the time most of the volatile organic matter has been liberated and the flame has become attached (probably necessary for consumption of the remaining organic matter, other than a few percent of carbon char), the ultimate flyash matrix materials (aluminosilicates, SiO_2 , etc.) will often have melted to form the spherical particles characteristic of flyash^(5,6,7). The precise heating rate is determined primarily by the furnace temperature profile, the thermal conductivity of the particle, and the particle's size and path through the furnace.

The most likely mechanism^(8,9) for the evolution of a coal particle to flyash particles envisions the melting of the mineral inclusions concurrent with consumption of the organic matrix. The receding carbon surface allows the molten mineral inclusions (which do not appreciably wet the carbon

surface) to coalesce and form increasingly large ash droplets. As combustion nears completion the coal particle may break up, in part due to internal burning. The final products are usually spherical ash particles, which may undergo other processes such as coalescence with other particles or expansion due to internal gas release, to form the hollow particles which are a common feature of flyash. This process is illustrated in Figure 1.

With the formation of the liquid spheres, the flyash matrix material is probably at its highest temperature (possibly as high as 1500 to 1600°C for pulverized coal combustion), and a significant fraction of the volatile forms of elements may exist in the gas phase. It is possible that in the limited amount of time particles spend in the high temperature zone (less than a few seconds), that the larger particles are not completely melted. This may account for the qualitatively different nature of the largest flyash particles, which may often be nonspherical, or even crystalline, in structure. Other particles with higher melting points, such as those composed of nearly pure silica, may not melt regardless of size and are often observed as minor flyash components.

It is important to recognize that not all of the trace elements in coal which may possibly volatilize during combustion will do so. A sizeable portion of these elements may well be trapped in the liquid or solid matrix. Volatilization of these species may depend on the rates of diffusion processes, which may be restricted by the brief exposure to the high temperature region⁽³⁾. Diffusion of various elements to and away from the surface of ash particles may also occur at presently undetermined rates. (Evidence does exist to support surface enrichment by diffusion under some conditions⁽¹⁰⁾; bulk or grain boundary mechanisms have been suggested.)

FIGURE 1. The most widely accepted model for flyash formation, based upon the work of Padia . The progression from left to right represents increased burning of a coal particle. As the particle fractures liquid ash droplets agglomerate. At complete burning only the liquid ash particles remain. A portion of the ash particles may expand by internal gas release to form hollow spheres.

These arguments emphasize the complexity of the situation; not only may involatile species be transferred to the vapor phase (due to their intimate association with the organic matter), but a significant fraction of the potentially volatile species may be trapped within the matrix material. Tentative evidence to support such mechanisms includes ion microprobe, ESCA and Auger studies^(11,12,13,14) which show enhanced surface concentrations of several species which might be expected to volatilize completely during combustion (e.g., P, Pb), but still appreciable concentrations in the bulk material. Alternate rationalizations of these results, such as the existence of an involatile form of these elements, or a diffusion process into the bulk material following condensation of volatilized components are possible; unless equilibrium distributions are obtained, the mechanism leading to surface enrichment cannot be determined solely from depth profiles of flyash particles. Diffusion processes within the condensed phase will be most important at high temperatures but may be significant even at ambient temperature for the glass-like flyash material. In this regard, Fischer et al. have noted crystal growth on flyash particles stored for several weeks in closed containers after collection⁽⁵⁾. Hulett and Weinberger have also noted significant crystalline phases in flyash particles, composed primarily of mullite and quartz residues⁽¹⁵⁾. The rate of formation of such crystalline phases remains undetermined.

When the last of the combustible volatile matter in the coal particles has been consumed, the conditions at the particle surfaces will change from strongly reducing to perhaps mildly oxidizing. In the postcombustion region of a stoichiometric coal-air turbulent flame, the oxygen content of the gas is

approximately 2 mole %; however, often a considerable excess of air (~20%) is also used during combustion. Mineral matter originally injected into the combustion region as free mineral matter will have been subjected to more strongly oxidizing conditions through the entire combustion process.

As the combustion products leave the furnace and begin to cool over a period of several seconds in the economizer and the series of heat exchangers, condensation of the volatilized trace elements will occur. For the higher boiling compounds, this will be a rapid diffusion-limited process. Assuming that these condensation processes are diffusion-limited below their boiling points, condensation will occur rapidly and be essentially complete for most elements before the flue gas reaches the electrostatic precipitators (at a temperature of ~350°C for hot-side precipitators located before the air preheaters). For elements in which condensation is delayed, flyash sampled from high temperature regions before the electrostatic precipitators may show quite different trace element concentrations than samples obtained from the cooler regions. This may result from delayed condensation of volatilized species with low boiling points (relatively high vapor pressures) and, perhaps, the slower cooling of the flyash particles compared to the flue gas. Elements forming chemical compounds with particularly high vapor pressures (e.g., Hg, Se) may be initially emitted from the stack partially or completely in the gas phase, as is often the case for organic pollutants. The mechanism for association of these species with flyash may be quite different; however, each of these must be considered to have the potential for enhanced surface concentrations.

The organic pollutants (ubiquitous products of nearly all combustion processes) probably become associated with the flyash by adsorption or absorption processes rather than condensation. Most concern has been centered upon the emissions of known mutagens such as polycyclic aromatic hydrocarbons. However, increasing emphasis will undoubtedly arise concerning the more polar organic products including the nitrogen heterocyclic compounds, aromatic amines, and other combustion products recently identified as potent mutagens in other combustion processes. The chemistry involved in the surface enrichment of these compounds and the transformations which may occur on the surfaces have only been studied indirectly. There is a need to study these transformations with respect to the surface and particularly to the role of the surface. Fortunately, newly developed analytical techniques offer the potential of studying complex organic interactions on surfaces. The role of these interactions and their relationship to the concentration of particular organic pollutants emitted into the atmosphere remains to be explored.

The purpose of this report is to review and evaluate the present level of understanding regarding the nature of flyash surfaces, possible enrichment mechanisms, and the application of various established and new surface analysis techniques to these problems. The section which follows will review the existing data relative to enrichment of flyash as a function of particle size (i.e., enrichment in the smallest particles). Section 3.0 will review the existing data on flyash surfaces and related studies obtained using modern surface analysis technology. This will be followed by a brief consideration of organic transformations on flyash surfaces. Next, the various established

and new or proposed surface analysis technologies will be described and evaluated in terms of addressing the various questions concerning flyash surfaces. Finally, recommendations for experimental studies to resolve unanswered questions concerning flyash surface formation will be presented.

2.0 FLYASH ENRICHMENT BY CONDENSATION AND SIZE- DEPENDENT PROPERTIES OF FLYASH

There are two pathways which have been identified as potentially leading to enrichment of flyash surfaces in certain elements. One process involves condensation or adsorption on flyash surfaces in the combustion or postcombustion region, where high concentrations of volatilized inorganic elements are present. (Similar enrichments also may be expected from coagulation of very fine particles on the larger molten mineral matter particles.) This process leads to enrichment of the volatilized species in the smallest flyash particles but does not necessarily result in ultimate surface enrichment of the emitted particles due to the possibility of subsequent diffusion within the particle. A second distinct mechanism involves only the transport of species to or away from surfaces within a flyash particle. To a first approximation, this mechanism might be considered to only alter the distribution of an element within a particle and not the average concentration as a function of particle size. However, more complex processes may also be anticipated, resulting from volatilization of elements which diffuse rapidly to the surface, that also result in concentration variation with particle size (a simple treatment of this case is discussed later in this section). In this section, the experimental evidence for the condensation or adsorption mechanism resulting in surface enrichment will be examined and simple models for these processes will be reviewed.

It is now generally recognized that elements volatilized during coal combustion ultimately become enriched in the smaller flyash particles⁽¹⁶⁻⁴⁸⁾.

Studies in this and other laboratories have shown that the shape of the trace element concentration versus particle size profile varies from plant to plant, as well as with time for a given plant^(17-19,23,24,26,31,46). This variability is related to both the combustion conditions (type of coal burned, excess oxygen, residence time, etc.) and the chemical and physical nature of the coal. Within these limitations, however, it is possible to make generalizations regarding the concentration profiles. It is clear that while the extent of enrichment may vary considerably, a number of elements are known to consistently exhibit sizeable enrichments in the smaller particles as opposed to the larger flyash particles (see Table 1).

Prior to direct measurement of the concentration dependence of trace elements upon particle size, measurements had shown that the particles emitted from the stack in coal-fired plants were enriched over those collected in the precipitators. Earlier, it had been postulated that selective volatilization of trace elements would lead to increased emissions of the volatilized elements⁽⁴⁹⁾. Zoller and coworkers have shown that flyash collected in the stack is considerably enriched in certain trace elements compared to the input coal. Zoller et al. have reported enrichment factors of 10^3 to 10^4 for the elements Se, Pb, Br, and Sb relative to their crustal abundance^(49,50).

Kaakinen et al. have conducted an extensive study documenting the flyash enrichment at a number of locations through a coal-fired plant⁽⁷⁾. The plant studied burned a low-sulfur, low-ash, western coal, and had a particulate collection scheme which utilized a high efficiency mechanical dust collector, followed by an electrostatic precipitator and a wet scrubber in parallel. Samples were collected and analyzed from the coal, bottom ash,

TABLE 1
Oxide Boiling Points^(a) and Comparison with Elemental Enrichment
on Flyash Surfaces and Smaller Particles

Element ^(b)	B. P. of Oxide ^(c)	Surface Enrichment ^(d)	Enrichment in Smaller Particles		
			Previous ^(e)	Plant A ^(f)	Plant B ^(f)
Br	59			>10	
Hg	~ 500 decomp			> 5	
Se	~ 500 sub		major	14	>5
P	~ 500 sub	3.8			>1.6
Cs	~ 600		major	2	
As	1000		major	19	11
Li	1000 sub	3.8			
Rb	1100		no-minor	2	1.2
Na	1275 sub	15.2	minor	3	
Sb	1425		major	12	
Pb	1472	11.0	major	15	6.6
Sn	1510		no-minor	6	1.3
K	1527	7.6	minor	2	1.2
Cd	1559		major		
V	1750 decomp	2.0	no-minor	5	2.6
Cu	1800		minor	7	2.5
B	~1800		minor		
Tl	1890	10.0	major		
Bi	1900		no		
Ni	~1900		no-minor	5	2.5
Mo	1927		minor	10	4.9
Zn	~1950 decomp	7.2	no-major	21	7.3
W	2000		no		
Ba	2200		minor	5	1.0
Ti	2227 decomp	0.9	no-minor	1.7	1.2
Fe	2527	0.8	no	1.2	1.2
Ga	2727		no-minor	20	5.4
Co	2627		no-minor	3	
Mg	2825	0.9	negative	4	
Ca	2850	1.6 ^(g)	no-minor	3	1.1
Si	2950	1.1	no	0.6	1.1
Al	2980	1.1	negative	1.5	1.2
Cr	3000	3.3	no-minor	4	4.7
Sr	3000		no	2	0.8
Ce	3227		no-minor	2	0.9
In	3327		no		
Nb	3527		no	5	1.4
Sm	3527		no	1-2	
Mn	4050	6.4	no-minor	6	1.6
U	4100		no-minor	7	
La	4200		no	1.7	0.9
Be	4260	6.0			
Zr	4300		no	1-2	1.2
Th	4400		no	1-2	

a The boiling points of oxides of the following elements are uncertain: Dy, Eu, Au, Hg, Ho, Nd, Np, Os, Pd, Pt, Ra, Sc, Ag, Ta, Tb, Yb, Y, Ru, Rh, and Lu.

b Listed in order of increasing boiling point of the most stable oxide.

c Decomp = temperature of decomposition, sub = sublimes.

d Signal intensity at the particle surface divided by the signal intensity at an estimated depth of 500A.

e A qualitative evaluation (negative, none, minor, major) due to the uncertainty in comparing results from different furnaces and different particle size distributions.

f Enrichment as concentration in the 0.5 μ m flyash fraction divided by the concentration of the 50 μ m flyash fraction.

g Enrichment observed only in a few samples.

mechanical collector hopper, electrostatic precipitator hopper, flyash from the flue gas at the scrubber inlet, scrubber outlet, electrostatic precipitator outlet, scrubber slurry, and the scrubber make-up water.

These measurements showed that the enrichment factors for the presumably more volatile trace elements increased through the plant from the bottom ash to the precipitator outlet. These results are consistent with the decrease in the average particle size expected through the plant. These results showed a decrease in available flyash surface area through the plant. Ulrich et al. have also noted a decrease in specific surface areas from the combustion region ($7.0 \text{ m}^2/\text{g}$) to sampling ports on the fifth floor of a cyclone boiler ($0.5 \text{ m}^2/\text{g}$). A model based on a volatilization-condensation mechanism, similar to the model proposed by Natusch and coworkers, was used by Kaakinen et al. to qualitatively explain the variation of concentration with the surface area measurements.

Klein et al.⁽³⁰⁾ have made similar measurements and, consistent with the observations of Kaakinen et al., enrichments of volatile elements are found on progression from the slag, precipitator inlet flyash, to the precipitator outlet flyash. Large negative imbalances are observed for Br and Cl, and these elements are therefore assumed to be present in the gas phase at precipitator temperatures. All the Hg, and a fraction of the Se, were also observed to be present in the gas phase at the precipitators.

Natusch and coworkers first investigated directly the detailed concentration versus particle size dependence for trace elements in flyash⁽⁴⁸⁾. Their results quite clearly showed an inverse dependence of concentration for several elements (e.g., As, Ni, Cd, Pb, etc.) upon particle

size. These workers assumed that volatilized material condensed evenly over the surfaces of all particles (i.e., a surface layer thickness independent of particle size). They were able to obtain reasonable fits to their data using eq. 1

$$C = C_m + \frac{6C_L}{\rho D} \quad (1)$$

where C_m is the concentration in the matrix upon which the volatiles condense, C_L is the concentration of the surface layer in g/cm^2 , ρ is the density, and D is the particle diameter. Assuming a separate layer of each condensed element, average surface layers of 0.1 to 20 Å were calculated for most elements, using the relationship

$$L = C_L / \rho \quad (2)$$

where L is the surface layer thickness. Later results by Natusch and coworkers and other workers show that a distinct layering of individual elements in an order determined by boiling points probably does not occur^(3,51,52). As discussed later, any sequential condensation processes may be followed by diffusion which may significantly alter surface concentrations.

Flagan and Friedlander⁽⁹⁾ later suggested that a direct dependence of C on D^{-1} should exist only in the free molecule regime where the Knudsen number (K_n) is greater than 1. At lower values of K_n , in the continuum regime, they suggest that the total concentration will be proportional to D^{-2} . Physically this model is essentially the same volatilization-condensation model proposed by Davison et al. but is quantitatively quite

different, predicting much greater concentration increases for volatilized elements in the smaller size fractions. Examples of concentration versus particle size profiles obtained in this laboratory are given in Figure 2. These results clearly demonstrate that significant enrichments are obtained in the smallest flyash particles.

In the simplest case, elements may be divided into two groups on the basis of their concentration dependence upon particle size: those which show no enrichment in the smallest particles, and those which are enriched. The primary interest is with the enriched elements, since they are most likely to have a significant environmental impact. Results of analyses of flyash as a function of particle size at this laboratory indicate that the elements Mn, Ba, V, Cr, Co, Ni, Cu, Ga, Nd, As, Sb, Sn, Br, Zn, Se, Pb, Hg, and S are usually volatilized to a significant extent in the combustion process. The elements Ti, Mg, Na, K, Mo, Ce, Rb, Cs, and Nb appear to have a smaller fraction volatilized during coal combustion, or have significant variations in behavior between plants. The remaining elements, Si, Al, Fe, Ca, Sr, La, Sm, Eu, Tb, Dy, Yb, Y, Sc, Zr, Ta, Na, Th, Ag, and In, are either not volatilized, or may show minor trends which might be related to the geochemistry of the mineral matter. While an examination of Table 1 shows that several elements are enriched which might not be expected on the basis of oxide boiling points, a detailed thermochemical assessment of fifteen trace elements has indicated that the preferred forms of the vaporized elements are not always oxides. Indeed, chlorides (of Cd, Cu, Pb, Hg, Ni, Se and Zn) as well as several other compounds [$\text{Be}(\text{OH})_2$ and oxychlorides of Mo and Cr] are predicted^(52b).

FIGURE 2. Average concentration versus particle size profiles for six elements apparently volatilized during combustion.

In order to discuss the flyash concentration versus particle size data and the implications for surface layer formation, it is worthwhile to consider a simple model developed in this laboratory which can rationalize these results⁽³⁾. To apply a volatilization-condensation model to a larger range of particle sizes, it is advantageous to generalize the approach by assuming a surface layer of thickness L to be deposited over spherical particles, and to ignore changes in surface layer thickness resulting from the increasing particle size due to condensation. The fact that the surface layer may be altered or distorted by other processes (including diffusion) after condensation does not affect the calculated concentration profiles. For the case where L is independent of diameter (the free molecule regime), the relationship between the bulk concentration (C) of particles of diameter D , the concentration of the matrix (C_m), and the concentration in the surface layer (C_s) of thickness L , is given by eq. 3:

$$C = \frac{C_m \rho_m 1/6\pi(D - 2L)^3 + C_s \rho_s 1/6\pi D^3 - C_s \rho_s 1/6\pi(D - 2L)^3}{\rho_m 1/6\pi(D - 2L)^3 + \rho_s 1/6\pi D^3 - \rho_s 1/6\pi(D - 2L)^3} \quad (3)$$

for $2L \leq D$, and $C = C_s$ for $2L \geq D$, where: D = particle diameter, $D - 2L$ = diameter of matrix material before condensation, ρ_m = density of matrix material, ρ_s = density of surface layer. Or simply:

$$C = \frac{C_m \rho_m (D - 2L)^3 + C_s \rho_s D^3 - C_s \rho_s (D - 2L)^3}{\rho_m (D - 2L)^3 + \rho_s D^3 - \rho_s (D - 2L)^3} \quad (4)$$

This equation may be simplified by assuming $\rho_m = \rho_s$, to give eq. 5:

$$C = \frac{C_s D^3 + (C_m - C_s) (D - 2L)^3}{D^3} \quad (5)$$

Similarly, a form of the volatilization-condensation model appropriate for the continuum regime ($L \propto D^{-1}$) is an equation of the form:

$$C = \frac{C_s D^3 + (C_m - C_s) (D - f/D)^3}{D^3} \quad (6)$$

where $C = C_s$ when $D \leq \sqrt{f}$ (μm), f = a constant, and $L = f/2D$.

Again, this approach is only an approximation for particle sizes where the surface layer comprises the bulk of the particle, since changes in particle size are not considered. A more rigorous analysis shows that these relationships are adequate over most of the particle size range, and that $\sqrt{f}$ defines the upper particle size for particles composed only of surface material(3). Since this approach does not consider the effect of increasing particle size during condensation, it tends to underestimate the enrichment at $D \rightarrow \sqrt{f}$.

A result of this approach is that at some small particle size ($\sqrt{f}$ μm), the surface layer thickness will equal the particle radius. Physically, this corresponds to particle formation by homogeneous condensation; however, heterogeneous condensation on existing nuclei, or coalescence of particles formed by homogeneous condensation, would yield essentially the same profile, since the mass of the original nuclei would become insignificant.

A striking feature of these relationships is the good fits obtained to the experimental data. The data used for comparison are similar to those presented in Figure 2. These data are useful for comparison with theory, since the size fractions are well resolved (e.g., standard deviations of less than 1.2 for all except the two smallest particle sizes), and the calculations use the actual physical particle size as determined by electron microscopy.

The assumption of spherical particles is excellent, since nearly all particles less than 20 μm in diameter are spherical, and are probably still liquid at the time of condensation. Most of the nonspherical particles are in the larger size fractions, and the equations derived above can be used to show that condensation on particles greater than 20 μm in diameter is negligible. For particles having a 100 μm diameter, it can be shown that increases in the surface area of 10^4 to 10^5 would be necessary to significantly alter the concentration versus particle size profiles. It has been observed that flyash particles have surfaces often covered with submicron-size crystals; again, these crystals must be formed well after condensation, and, indeed, the evolution of crystals on surfaces can be observed to occur in the weeks following collection. The presence of hollow particles, which might be expected to increase the concentration of volatilized elements, has a negligible impact on the concentration profiles for similar reasons. The hollow particles are present in significant number only for the larger size fractions ($>10 \mu\text{m}$), where the effect of condensation of volatilized elements becomes minor.

A recent publication by Biermann and Ondov(52c) reported similar results for finely sized flyash collected on cascade impactors. In this case, the total volatilization of inorganic material was apparently less but results were in agreement with the simple model discussed above. They found the best agreement was with the $1/D^2$ dependence upon particle size and estimated the surface layer thickness for 0.1 μm particles to be about 20% of the particle diameter.

In Figure 2, eqs. 5 and 6 were used to obtain visual fits to the data for six elements which are apparently volatilized during the combustion process. It should be noted that the best fits are obtained when C_m is somewhat greater than zero. This implies only partial volatilization of the element under consideration. These relationships have been used to estimate the volatility of individual elements during coal combustion given the particle size versus concentration profiles⁽³⁾. One should note that the enrichment between the smallest and largest particles is proportional to C_s/C_m for these particular profiles. The extent of volatilization calculated for most volatile elements which show enrichments was in the 20 to 70% range.

A further extension of this volatilization-condensation model can be used to qualitatively account for relative amounts of the volatile and nonvolatile components in the original coal, as well as a diffusion-limited volatilization process. The existence of both volatile and nonvolatile components in the original coal is reasonable due to the wide range of chemical species present; clearly, both high and low boiling forms of some elements will be present. Additionally, many elements show evidence for only partial volatilization, suggesting the existence of high boiling compounds of these elements, or diffusion-limited volatilization from the particle during coal combustion⁽³⁾.

Not all of the potentially volatile trace elements in coal will volatilize during pulverized combustion where residence time in the high-temperature region is brief. Transport processes will determine the availability of individual species at the surface. The assumption of chemical equilibrium at the surface has often been invoked, but gas-phase diffusion processes must also be considered. A sizable portion of potentially volatile elements may be

trapped in a matrix often composed primarily of Al_2O_3 and SiO_2 .

Volatilization of these species will, therefore, depend on diffusion processes in the condensed phase. Equation 6 may be modified to include a simplified diffusion process by addition of an additional term (R), which is simply the distance (independent of particle size) to the surface through which the component can diffuse. Modifying eq. 6, and considering the different densities of the two components, we find:

$$C = \frac{\rho_s C_s D^3 + [V/(N + V)] \rho_m C_m (D - f/D - 2R)^3 + \{\rho_m C_m [N/(N + V)] - \rho_s C_s\} (D - f/D)^3}{(\rho_m - \rho_s) (D - f/D)^3 + \rho_s D^3} \quad (7)$$

where V and N are the volatile diffusion-controlled portion, and the nonvolatile portion of the coal mineral fraction, respectively. This equation reduces to eq. 6 when V or R = 0, and $\rho_m = \rho_s$. Interestingly, introduction of a diffusion-limited volatilization process will, in many cases, result in a minimum in the concentration versus particle size profiles.

Figure 3 shows the concentration versus particle size profiles calculated for the two situations described above, one including introduction of the diffusion parameter. The curve for the V = 1 case shows a minimum which results from a depletion of the element from the matrix material for particles approximately 2R in diameter. These simple calculations illustrate that diffusion processes can, indeed, result in variations in the particle size versus concentration profiles. However, while some minor experimental evidence may be interpreted to support such a process⁽³⁾, it is currently believed that existing data are more readily interpreted in terms of a simple volatilization-condensation model. An evaluation of these processes and

Figure 3. Concentration vs. particle size profiles calculated using Equation 7., to compare the effects of a volatile ($V=1$) and a nonvolatile ($V=0$) constituent, for a diffusion limited volatilization process. The calculations assume the values $C_s = 100$, $C_m = 10$, $f = 0.01$, $R = 1 \mu\text{m}$, and $\rho_s = \rho_m$.

further implications of this model have been published⁽³⁾; a more detailed analysis of the particle formation processes must necessarily await further experimental data concerning surface characterization and the rates of various diffusion processes within individual particles. The limited relevant experimental data are reviewed in the next section.

3.0 ENRICHMENT ON FLYASH SURFACES AND RELATED SURFACE STUDIES

As indicated in the last section, there is a considerable body of data supporting the occurrence of a volatilization-condensation process during coal combustion. The simple model described in the last section predicts condensation of volatilized elements onto a primarily aluminosilicate matrix. One would therefore expect to find a considerable enrichment of these elements on the surfaces. Since the degree of volatilization can be estimated on the basis of the concentration versus particle size data, one might also reasonably expect the surface enrichment (or the expected surface-depth concentration profile) could also be predicted. This assumes that insufficient time is available for diffusion processes to distribute the condensed material throughout the particle, or for formation of crystal phases, or for a significant contribution of competing surface segregation processes. The precise variation of concentration for a specific element with depth must, of course, depend on the amount of other material condensing, the concentration of the nonvolatile portion of the element in the flyash bulk, and the occurrence of any subsequent diffusion processes.

Quantitative surface analyses for materials as complex as flyash are very difficult to obtain, and are susceptible to a suite of potential experimental artifacts. First, most surface analysis techniques for samples as small as flyash particles must look at a field of particle surfaces. Sputtering of these particles, particularly the smallest particles of most interest, usually exposes not only the interior of particles, but also the surface and sides of particles due to the limited resolution of the sputtering beam. For this

reason most studies of flyash surfaces reported to date have been relatively large particles ($>25\text{ }\mu\text{m}$ diameter) rather than for particles usually considered to be in the respirable size range (0.1 to $10\text{ }\mu\text{m}$). More severe problems may result if the particles examined are not restricted to a narrow size distribution. In obtaining concentration versus depth profiles, additional problems are encountered. The sputtering or etching techniques may cause an element to flow to the surface, or be removed preferentially, distorting its apparent concentration profile. The particular difficulties and potential experimental details associated with each technique will be discussed in more detail in Section 5.0.

The first experimental verification of the surface predominance of certain trace elements on flyash surfaces was due to the work of Natusch and co-workers(11,12). Using ion microprobe mass spectrometry, these workers were able to obtain approximate depth profiles by slowly sputtering large (75 to $100\text{ }\mu\text{m}$) particles in a $100\text{ }\mu\text{m}^2$ surface area, using an oxygen ion beam. The ratio of concentrations (which Linton et al. describe as minimum values) for the elements on the surface divided by the concentration at an estimated depth of $500\text{ }\text{\AA}$ (factor of two uncertainty) are given in Table 1. Auger and electron microprobe techniques were also employed. The large enrichment for Na on the surface (15.2) is probably due to an experimental artifact related to Na flow during sputtering. However, it has been suggested that an outward migration of Na during fusion can occur, leading to both increased surface concentrations and volatility. The surface enrichments determined by Natusch and co-workers in Table 1 are compared to data for enrichment in the smaller flyash particles obtained from analysis of sized fractions.

Comparison of the data summarized in Table 1 indicates a fair to good correlation between elements which have been volatilized during combustion and those which show surface enrichment. However, the agreement noted in these studies is certainly not quantitative. A few elements (e.g., Na, Mn, Be) show greater surface enrichments than expected on the basis of the particle size results and it appears that experimental artifacts or some diffusion process subsequent to condensation are contributing. Other elements which are quite volatile (Li, K, V) show surface enrichments but also significant concentrations at sputtering depths sufficient to be indicative of bulk composition. This might be ascribed to either the diffusion limited volatilized process included in the model discussed in the last section or a post-condensation transport mechanism.

In later experiments, Linton et al. were able to demonstrate that the same elements concentrated on flyash surfaces have substantial leachabilities to various solvents, supporting the data showing surface enrichment and demonstrating an increased environmental availability⁽⁵²⁾. These experiments have also suggested the utility of leaching techniques for the indirect characterization of flyash surfaces.

Lindfors and Hovland⁽⁵³⁾ have also used Auger electron spectroscopy (AES) and XPS (ESCA) to study flyash particles collected from the inlet and outlet of the electrostatic precipitators. The AES results for the inlet particles are consistent with other results showing a relative uniformity of particle surfaces (as opposed to their bulk composition⁽³⁾) and surfaces enriched in Na and K. Interestingly, analysis of the precipitator outlet samples indicated two particle types, one similar to the inlet particles and

another type which appeared darker in color and which were apparently enriched in Ca and C. In contrast, ESCA results for both the inlet and outlet samples indicated similar surfaces enriched in Na, K, and C. These results cannot be readily interpreted but do suggest that, in addition to the expected selectivity of the precipitators, other important processes involving organic reactions may be modifying particle surfaces as the combustion effluents cool on their passage through the precipitators. Further studies are necessary to investigate these possibilities.

Some interesting results have been reported by Hulett and co-workers^(15,54,55). Following their earlier studies of flyash surfaces,⁽⁵⁴⁾ they have examined the microstructure of particles etched using a 1% HF solution for removing the glass phases from the aluminosilicate matrix. Left behind are the crystalline mullite and quartz phases. They find that alkali, rare earth and many transition elements are more concentrated in the glass phase than in the quartz-mullite phase. Exceptions to these observations are the elements Cr and Ga. Thus, it can be speculated that the glass phases probably contain most of the potentially toxic trace elements. Hulett et al.⁽⁵⁵⁾ state that the qualitative nature of the flyash is independent of the coal source and firing conditions. They suggest that the distribution of trace elements in flyash is in a near equilibrium state rather than as a transient state frozen during rapid cooling after combustion. They conclude that, in the few seconds following combustion, the trace elements are concentrated into the glass phase and even suggest that these results can explain the previous results reporting surface segregation of flyash. While these results do provide some evidence for diffusion processes, the rate of

these processes and their temperature dependence is unknown. There is no evidence yet available to determine if the crystal phase formation is an extremely rapid process which occurs as the flyash cools from high temperatures, or is a much slower process which occurs at ambient temperatures in the weeks following collection. Additionally, since the ash analyzed by Hulett et al.(15,55) was collected from either the mechanical cyclone, upstream from the precipitator, or from the precipitator, the ash would have spent a considerable period at elevated temperatures, possibly on the order of days. Since it has been established that crystal growth can occur slowly at ambient temperatures on flyash surfaces in the weeks following collection(5), the interpretation of these results is uncertain. Experimental studies are required to determine the rates and mechanisms of diffusion and surface segregation processes in both the post-combustion region and for extended periods at ambient temperatures.

The ability of XPS to determine the oxidation states of a number of major and minor elements on flyash surfaces has been demonstrated in this laboratory by Campbell et al.(13) and later by Rothenberg et al.(56). These studies also demonstrated the utility of sputtering procedures to obtain surface depth profiles similar to those obtained by Natusch and co-workers using ion microprobe techniques(11). Significant differences between the ash from a conventional pulverized coal combustor and an experimental fluidized bed combustor were reported(56).

There has been only one attempt to date to examine flyash surface-depth profiles as a function of particle size(14). The most reasonable model for the condensation of volatilized elements upon flyash surfaces (see

Section 2.0) suggests that the surface layer thickness (L) will increase with decreasing particle size $L \propto D^{-1}$. To examine any effects of particle size upon the surface species, two sized flyash samples with median physical diameters of 1 μm and 26 μm were examined using a sputtering technique in conjunction with XPS. The 1 and 26 μm sizes represent the two extreme ranges for the bulk concentration versus particle size profiles, as illustrated in Figure 2.

The results of Campbell et al.⁽¹⁴⁾ show the expected decrease for some of the major elements near the surface due to the presence of increased amounts of condensed species (which may include sulfates, sulfuric acid, organics, and volatile trace species). However, the results show no dramatic increase in surface layer thickness for the smaller particles, but rather suggest a more gradual increase in concentration.

Due to the uncertainties and possible artifacts in the analyses (discussed in Section 5.0), and the possible diffusion of condensed species into the liquid or solid particle (which will be temperature dependent and therefore particle size dependent), these results cannot be readily interpreted at the present time. Surface analyses do provide valuable qualitative information which clearly supports the volatilization-condensation mechanism. They also have the potential of characterizing the state of species condensed on flyash surfaces; this is potentially valuable information in determining the environmental and biological impact of coal flyash.

The diffusion of uncharacterized species to form well-defined crystal structures on flyash surfaces over a period of several weeks has been documented, and may tend to obscure the meaning of surface versus depth

concentration profiles. Hulett and Weinberger⁽⁵⁵⁾ have also demonstrated the formation of crystal phases, accounting for up to 40% of the mass of some flyash particles. The formation of these crystals clearly demonstrates a mechanism for migration of species in flyash. While it was assumed that the crystal phases were formed during cooling and solidification, much slower processes, as noted above, cannot yet be eliminated.

Remarkably little work has been reported addressing the mechanism and rates of trace element transport to and away from flyash surfaces during formation. One aspect of this, of course, involves the inherent mineral matter in coal and its behavior during the rapid heating following injection in the combustion region. In a recent review⁽³⁾, we have discussed the trace elements and mineral matter in coal with respect to its behavior during combustion. The reader is referred to this review. While an extensive literature exists dealing with a wide range of materials, the only study reported to date of surface segregation of trace species in mineral matter relevant to flyash formation and heating to high temperatures has been that reported by Stinespring and Stewart^(10,57). These workers have used AES and sputtering techniques to examine the effects of heating upon illite, an aluminosilicate mineral which is chemically similar to a portion of the mineral matter found in coal. Samples of illite were heated at temperatures from 150 to 1100°C in inert atmospheres for 12 hours. The surface concentrations of Fe, K, Ca and S were determined as a function of temperature and the surface segregation of these elements observed was found to be comparable with that previously observed by Natusch and co-workers in flyash. Crude calculations indicated that segregation equilibration times might be on

the order of 1 sec at combustion zone temperatures. If transport rates were, indeed, in this range, the diffusion limited volatilization process discussed previously may very well be reasonable. Also, it would be likely that the condensation processes, while leading to enrichment in the smaller flyash particles, might not solely determine the surface composition, as the presently available experiment evidence suggests.

The theoretical basis for an understanding of transport processes in complex mineral or glass materials does not exist. The complex chemical and physical nature of the mineral matter in coal obviously precludes a rigorous microscopic treatment. Some understanding of these processes, however, might be obtained by comparison with simpler (and more easily studied) metal and metal alloy systems. The behavior in binary systems can often be accounted for with simple models. In such cases, equilibrium and nonequilibrium segregation processes constitute the two major categories. The nonequilibrium processes are considered to result from trace element diffusion through lattice vacancy gradients resulting from heating, while in the equilibrium process only minimization of the total free energy of the system is considered. The studies reported by Stinespring and Stewart cannot distinguish between these two processes; however, these workers tend to favor equilibrium segregation. A realistic evaluation of the diffusion process will necessarily involve surface characterization as a function of time as well as temperature. Well-characterized samples and model ash systems, where processes such as grain boundary diffusion can be controlled, will be necessary to better evaluate the diffusion mechanisms relevant to flyash formation.

4.0 ORGANIC TRANSFORMATIONS ON FLYASH SURFACES

The interactions of organic compounds with flyash surfaces are directly relevant to a number of environmental concerns related to coal combustion. Other potentially relevant effects include the surface resistivity of the ash which will partially determine collection efficiency in electrostatic precipitators. The organic compounds of concern are those which are formed during the combustion process, although, depending upon combustion conditions, some organic compounds may be directly related to the initial coal devolatilization products. Thus, one is primarily concerned with organic compounds which will condense or adsorb at lower temperatures than relevant for most of the inorganic elements (with exceptions usually including Hg, Se, halogens, etc.; see Table 1). Therefore, the gas-solid reactions which may occur depend not only upon temperature, but also upon the surface composition as it evolves through the post-combustion region. Flyash collected in electrostatic precipitators, for example, will usually contain large concentrations of relatively nonvolatile oxidized organic compounds (acids, etc.)⁽³⁾. Although these compounds appear to be of only minor environmental concern, compounds which condense at temperatures closer to ambient (i.e., the polynuclear aromatic compounds of major environmental concern) may exhibit a surface chemistry influenced by their presence. The possible transformations on such surfaces have not been studied, but one can anticipate that substantial variations in reactivity are likely.

To date, there have been only a few studies of organic transformations on flyash surfaces. A study by Kalkwarf and Garcia⁽⁵⁵⁾ examined the

transformations of several polynuclear aromatic compounds, from an actual combustion source, adsorbed on flyash as the plume evolved. They sampled the plume at distances of up to 40 km from the stack and were able to show degradation of these compounds. Degradation rates (reported as half distances) ranged from 3 km for fluoranthene to 12 km for benzo[a]pyrene. Such studies are extremely difficult and expensive and, due to the minute sample sizes, have large error limits. These studies, however, support laboratory studies which show that transformations of these emitted pollutants occur readily on flyash surfaces.

A number of laboratory studies have been conducted of aromatic transformations on flyash or model surfaces (quartz and glass) using large concentrations of known compounds(58-63). Pyrene has been the model compound of choice in many studies. Korfmacher et al.(59) adsorbed a number of polycyclic aromatic hydrocarbons onto coal flyash and determined the susceptibility of each to photodecomposition. A number of surprising results were reported. Several compounds, including the pro-mutagen benzo[a]pyrene, were found to photolyze efficiently in liquid solution but were also highly resistant to decomposition when adsorbed on flyash. However, several of these compounds were found to photolyze with high efficiency when adsorbed on activated alumina surfaces, clearly indicating the important role of the surface in these reactions. Korfmacher et al.(60) also found a number of these compounds, particularly those with a benzylic carbon, will spontaneously oxidize on flyash surfaces in the absence of light. Pitts et al.(63) have reported the transformation of benzo[a]pyrene on particulate matter to form mutagenic nitro derivatives in simulated atmospheres. The application of

flash photolysis to pyrene adsorbed on a porous glass surface has also been demonstrated⁽⁶¹⁾. A theoretical study of the adsorption of polynuclear aromatic hydrocarbon vapors on flyash has been reported by Natusch and Tomkins⁽⁶²⁾. At the present time, these studies have utilized only indirect analytical techniques (such as GC-MS⁽⁶³⁾) and no studies relevant to flyash systems have been reported using modern surface analysis techniques.

There is an extensive literature, of course, dealing with the application of surface analysis techniques to the study of simple organic molecules on well-defined surfaces. However, the study of more complex systems is precluded by most methods due to either the low concentrations (partial monolayer surface coverages) or limitations inherent in the analytical techniques. One exception is the low bombarding ion current version of secondary ion mass spectrometry, named static-SIMS or molecular-SIMS. This technique, discussed in more detail in the next section, was pioneered by Benninghoven^(64,65) in the mid-1970's. In recent years, there has been a rapid growth in this method as a tool for the analysis of nonvolatile or thermally labile organic compounds on surfaces. A wide range of organic compounds on a variety of surfaces have been analyzed in this manner. While Benninghoven^(64,65) has discussed the application of this technique and presented a few examples for kinetic and mechanistic studies, very little work has been done. Smith et al.⁽⁶⁶⁾ have recently described the incorporation of the SIMS technique into a new analytical instrument designed to characterize nonvolatile and thermally labile liquid chromatographic effluents. New approaches and techniques discussed in the next section

suggest that this method, or a close variation (such as fast atom bombardment,^(67,68) where the high-energy ions are converted to neutral atoms by charge exchange) will provide the necessary analytical tool for model flyash studies.

5.0 SURFACE ANALYTICAL TECHNIQUES FOR FLYASH

SURFACE CHARACTERIZATION

As reviewed in Section 3.0, there have been a number of studies of flyash surfaces utilizing surface analysis techniques. Studies using ion microprobe or secondary ion mass spectrometry (SIMS), as well as XPS (X-ray photoelectron spectroscopy—sometimes referred to as ESCA), and AES have been reported; no data have been reported using other surface techniques.

Each surface analysis technique has inherent limitations in terms of sensitivity, size resolution, surface specificity, and the type of chemical information obtained. There is a wide variation in the depth into the surface effectively analyzed by each technique and the extent of surface damage which occurs. The techniques often complement each other and it is typical to find two or three methods used in analyzing a surface in order to avoid the artifacts which might be attributed to any one approach. A brief description of each technique is presented below, with an evaluation of the technique for the study of flyash or model surfaces.

5.1 AUGER ELECTRON SPECTROSCOPY (AES)

AES has been used in a number of studies of flyash surfaces including those reported by Linton et al.⁽¹²⁾, Lindfors and Hovland⁽⁵³⁾, Powell and Spicer⁽⁶⁹⁾, as well as unpublished work from this laboratory. AES has the advantage of being sensitive to a very thin surface layer (5 to 20 Å) and high spatial resolution may be achieved limited by the width of the exciting electron beam. The limit of resolution is approximately 300–500 Å due to beam

spreading on the sample; modern state-of-the-art AES systems attain resolutions close to this limit. In AES, a beam of essentially monoenergetic electrons, usually in the 2 to 10 keV range, is focused on the sample. Beam diameters of $<0.2\text{ }\mu\text{m}$ may be obtained in principle, allowing the potential of single particle analyses. (Powell et al.⁽⁷⁰⁾ have attempted single particle analyses with mixed success, primarily due to problems with surface charging and electron beam damage to the surface.) In common usage, however, incident electron beam diameters of 0.1 to 1 mm are typical and 3 to 10 μm beams are also common. The bombarding electrons can induce the emission of other electrons (Auger electrons) following the ejection of a core shell electron. The Auger electron energy is characteristic of the atom from which emitted and typical energies are less than 2 keV. The low energy of these electrons only allows escape from the first few atomic layers resulting in the extreme surface selectivity noted above. While the AES technique is highly surface sensitive, it has insufficient sensitivity to detect trace concentrations on surfaces. Virtually all elements heavier than Li may be detected. Typical elemental detection limits are in the 0.1 to 0.5 atom percent range.

The electron beam width can be varied to examine single particles, as mentioned above, or scanned over a large surface to obtain an average composition. The AES technique can be used in conjunction with ion sputtering to obtain depth profiles. The technique has been used successfully to characterize fields of flyash particles; the major limitations for analysis of actual flyash samples are the insufficient sensitivity for trace species and the surface charging that results for insulating materials such as flyash. The latter problem can make analysis impossible in extreme cases. Other

problems sometimes encountered in AES are associated with matrix effects and often involve the sputtering process for obtaining depth profiles. Charging can result in energy and intensity shifts and affect AES peak shapes. Intense electron beams can alter the surface composition and cause mixing or diffusion processes. The sputtering process can be highly matrix dependent and can vary between elements⁽⁷¹⁾. AES may be more useful for model studies including surface segregation processes on mineral and model surfaces. The excellent spatial resolution of this technique can be useful in determining the role of surface imperfections and structures in segregation mechanisms. AES shares the advantage with XPS of nearly constant elemental sensitivities—response as atom percent does not vary by more than an order of magnitude between elements; this is in contrast to SIMS where extreme differences are often encountered.

5.2 X-RAY PHOTOEMISSION SPECTROSCOPY (XPS OR ESCA)

In XPS the incident particles are nearly monochromatic high energy (1 to 10 keV) photons (X-rays) having an incident energy resolution of typically 0.5 to 1.5 eV. The photon flux is usually quite low and the angle of incidence with the surface typically 70 to 85°. Emitted photoelectrons are energy analyzed. As with AES, XPS is a highly surface sensitive technique since the emitted photoelectrons are relatively low energy and have escape depths of from 5 to 20 Å. In contrast to the electron beams in AES, X-ray beams are difficult to focus and beam diameters are usually in the 1 to 3 mm range. This poor spatial resolution precludes the analysis of individual flyash particles. The high energy resolution of the incident beam, and the known

energy deposition, however, allow small energy shifts in the XPS spectra to be interpreted for chemical information. This is not practical in AES since ionization of the core electron shell does not always involve transfer of a discrete amount of energy. The technique is applicable to all elements heavier than and including Li, has detection limits in the 0.1 to 1 atom percent range, and has the advantage of relatively constant sensitivity from element to element. It may also be used in conjunction with sputtering to obtain depth profiles with the possible artifacts noted for AES.

The unique feature of XPS is the utilization of high resolution energy analysis to extract chemical information from the energy shifts. Another contrast with AES is the more gentle nature of incident beam; surface damage and the resulting experimental artifacts are less important.

X-ray photoelectron spectroscopy has proven quite useful as an analytical tool for surface analysis and identification of oxidation states of elements present in particulates⁽⁷²⁻⁷⁴⁾. Hulett et al.⁽⁷²⁾ used ESCA to show the presence of sulfate and SO_3 absorbed onto smoke particles and flyash. In a similar study, Araktingi et al.⁽⁷³⁾ collected particulate samples from air on fiberglass filters for electron spectrometric analysis. Sulfur in the samples was found to be present primarily as sulfate. Novakov and coworkers⁽⁷⁴⁾ described an application of ESCA for the determination of lead, sulfur, and nitrogen in smog particles.

XPS was used in this laboratory⁽¹³⁾ several years ago to identify and determine the oxidation states of a number of major and minor elements present on the surface of flyash particles. With the use of a sputtering-etching procedure, relative concentrations as a function of depth were obtained for

Si, Al, Fe, Ca, Na, C, O, and S. The concentrations of Na, C, O, and S were found to decrease and Si, Al, and Fe were found to increase upon sputtering to a depth of approximately 50 Å. A later study also examined variations in 1 µm and 26 µm diameter particles⁽¹⁴⁾, as described in Section 3.0. A more recent study by Rothenberg et al.⁽⁵⁶⁾ has reported on XPS analyses of flyash samples from several different types of combustions. The results were in excellent agreement with the studies of Campbell et al.^(13,14).

5.3 SCANNING ELECTRON MICROSCOPY (SEM) AND RELATED TECHNIQUES

SEM, while not a true surface analysis technique in the manner of AES or XPS, is a useful tool for evaluating surface morphology in conjunction with these techniques. In SEM, a beam of focused high-energy electrons (~10–30 keV) is rastered (scanned) over the sample. Electrons scattered or emitted from the surface are used to reconstruct the surface features on a CRT. The finely-focused electron beams used in this technique (~100 Å diameter), coupled with a large depth of field, allow excellent quality pictures of sample surfaces. To avoid problems with insulating particles such as flyash, the sample may be coated with a monolayer of conducting material (usually gold, silver, or carbon). Many pictures illustrating the topographical features typical to flyash particles have been published (see, for example, reference 3).

A common feature of many modern SEM's is the capability to perform energy-dispersive X-ray (EDX) analysis of the emissions from the sample. These X-rays are characteristic of the elements present in the sample and generated as a result of the high-energy electron beam. This feature allows a

semiquantitative evaluation of the concentrations of elements heavier than Na with detection limits in the 0.1 to 1 atom percent range. A major drawback of this technique, as commonly employed, is that the X-ray emissions have analytical escape depths of up to several μm or more. Variation of electron beam energy to obtain variation in analysis depth is possible but difficult and requiring of corrections to account for particle size and shape. Thus, the effective surface layer analyzed is approximately 10^3 thicker than AES, XPS, or SIMS. Not only does EDX probe a deeper surface layer, but spreading of the beam below the surface results in an increased analysis area. In the case of flyash, where the effective surface layers of interest are on the order of 10 to 100 Å, this technique is of little value for surface characterization. However, it can be a highly valuable semiquantitative tool for evaluation of surface features, bulk analyses, and estimation of the extent of particle heterogeneity⁽³⁾.

5.4 SECONDARY ION MASS SPECTROMETRY (SIMS)

SIMS (or ion microprobe analysis) developed in the 1960's as an analytical tool for elemental analysis of materials. In SIMS an ion beam (of positive or negative ions) is directed at a surface and the emitted (or secondary) ions are analyzed using a mass spectrometer. For conventional elemental analyses, bombarding ion currents in the range of 1 to 100 $\mu\text{A}/\text{cm}^2$ are employed. Ion beam diameters on the order of 1 μm can be achieved providing the SIMS technique with high lateral resolution, comparable to AES and approximately three orders of magnitude better than XPS. The ions striking the surface (at energies usually in the 1 to 10 keV range) cause the

emission of secondary ions by apparently a number of complex processes, the details of which are still subject to debate^(64,65,71,83,84). The emitted secondary ions are usually energy analyzed (to prevent degradation of mass spectrometer resolution and reduce noise due to scattered high-energy ions) and analyzed with a mass spectrometer. The strengths of the technique are the good lateral resolution and surface sensitivity. Emitted secondary ions are indicative of the first or first few atomic monolayers^(84b). Additionally, most elements can be analyzed at detection limits ranging down to 1 ppm and below. A disadvantage of SIMS is that sensitivity can vary greatly between elements; variations of up to 10^4 are possible. SIMS spectra can also be complicated by the formation of complex ions due to various reactions at or near the interface during analysis. Additionally, SIMS is an inherently destructive technique as opposed to XPS, AES, or SEM. Since the SIMS ion beam is usually just a slightly lower current version of the ion beams used for sputtering, these techniques are compatible and results are obtained continuously through the sputtering process. One should also note, however, that SIMS is subject to all the potential experimental artifacts inherent in sputtering techniques; these have been discussed at some length by Linton⁽⁷¹⁾.

Despite these difficulties, SIMS has proven to be a powerful analytical technique. It is the only truly surface-sensitive method capable of detecting trace elements. Techniques are being developed to better understand the SIMS process and reduce the experimental problems inherent in this technique which limits its value for quantitative trace element analyses.

A relatively recent variation on the SIMS approach has been named static-SIMS or molecular-SIMS. In this technique, the method of secondary ion mass spectrometry is used in conjunction with extremely small bombarding ion currents ($\sim 10^{-9}$ amp/cm²), ion currents about 10^4 less than typically employed in conventional SIMS. The result is a technique which is extremely surface-sensitive and results in a negligible amount of surface damage. For example, the time required for removal of one monolayer under these conditions is on the order of minutes to hours. Another advantage of the technique is that it is extremely gentle. Often molecular species are ionized with only extremely small amounts of fragmentation. Energy selection of the secondary ions allows the sensitivity for molecular species to be maximized. Since ionization occurs directly at the surface, the mass spectra are indicative of the bonding patterns of molecular species at the surface. Thus, static-SIMS offers a powerful technique for the study of diffusion processes to and away from surfaces. It allows the study of organic reaction intermediates on surfaces and related processes. This technique can provide additional information concerning the nature of surface bonding patterns with various adsorbed species and aid in the interpretation of results obtained using other methods. The major uncertainty related to this technique rests in the interpretation of the spectra which can be complex due to recombination, cationization, and other processes. Although the technique is relatively new, recent work has demonstrated its power and capabilities for the analysis of complex materials on surfaces. We have recently incorporated this technique into a new approach for liquid chromatography-mass spectrometry which involves deposition of the liquid on a moving ribbon, evaporation of the solvent, and analysis of the ribbon surface using molecular-SIMS⁽⁶⁶⁾.

Other new developments in mass spectrometry promise to extend these capabilities even further. At PNL, we have developed a new molecular-SIMS instrument which includes a triple quadrupole mass spectrometer. This approach allows ions mass-selected in the first quadrupole to undergo collision-induced dissociation (CID) in the second quadrupole (using a gas such as argon) and then have the collision products analyzed in the third quadrupole. This approach allows for structural analysis of the mass-selected ions and should be particularly useful for analysis of complex organic products since structural data can be obtained. The greatly increased selectivity of this approach can be considered comparable with that which might be obtained with high resolution mass analysis, but with the added capability allowing the extraction of structural features. Another new development which promises to expand this research area is the technique of fast atom bombardment, which is simple replacement of the ion beam with an atomic beam by a simple charge exchange process^(67,68). This approach apparently eliminates problems due to surface charging and apparently reduces surface damage to some extent.

5.5 OTHER TECHNIQUES

A number of other techniques are applicable to studies of simple model systems, or more complex systems in some cases. A number of such techniques, including several that are not solely used for surface characterization, are described in this section.

Temperature Programmed Desorption (TPD) and Electron Stimulated Desorption (ESD) can be applied to various coverages of deposited species to

assist in determining chemisorption states, the extent of dissociative chemisorption, and desorption mechanisms. Modulated molecular beam studies of atomic and molecular species directed at surfaces at various temperatures can be used to evaluate reactive and nonreactive scattering and reaction efficiency. Velocity distributions can provide supplementary information on energy accommodation and related adsorption energies. Samples can be treated in adjacent reaction chambers and transferred to a high vacuum chamber for analysis. Samples can also be cooled to subambient temperatures to allow study of adsorbed layers formed at higher pressures. The temperature of the impinging molecular beams can be varied independently of the surface temperature; such information can be deconvoluted to determine the effect of internal excitation upon chemisorption and reaction efficiency. Such studies can aid in identifying initial reaction steps, intermediates, surface states, preference for specific reaction sites, alternative reaction channels, etc. Electron spin resonance (ESR) can be used to monitor radical species on surfaces. ESR spectra can be obtained as a function of time to monitor variations in radical concentrations. Previous studies have shown ESR to be a powerful technique for the characterization of surface-related reactions. The technique of Laser Raman spectroscopy can be applied to the analysis of surface species by using a rotating reaction cell similar to that described by Cheng et al.⁽⁷⁵⁾. This technique has the potential of producing data over a wide range of temperatures and pressures but considerable uncertainties exist in the application of this technique to the present problem (i.e., sensitivity, useful spectroscopic data, etc.) and the interpretation of the data. The surface enhancement effect⁽⁷⁶⁻⁷⁸⁾, often observed in Raman

scattering from adsorbed surface species, is probably not large for model flyash systems; application of this technique is questionable.

Fourier transform infrared (FTIR) attenuated total reflectance (ATR) and absorption spectroscopy can be applied to in-situ studies of mineral and to model systems for flyash evolution. The FTIR approach allows rapid, highly sensitive analyses to be obtained while eliminating thermal contributions. IR studies can provide significant fundamental data⁽⁷⁹⁻⁸²⁾. The ATR technique in conjunction with FTIR allows the study of surface reactions well into the submonolayer regime. Observation of bonding patterns in the far IR, between adsorbed species and the substrate, can complement other approaches. An advantage of this technique is that the depth of penetration may be varied by changing the angle of incidence to the crystal surface. This allows "spectroscopic microtoming" to subtract contributions from various depths. This technique can be used to selectively observe processes at the surface and to eliminate contributions from the chemically rich gas phase region near the surface. The application of these techniques to complex flyash systems is probably premature at this point; however, several will undoubtedly find application for attacking specific problems not amenable to conventional approaches.

Finally, there are several techniques which may also find limited application, which we will not consider in detail due to the fact that the escape depths are larger than for XPS, AES, and SIMS, and that this is expected to limit their application for studies requiring analysis of the first few monolayers. These techniques include proton-induced X-ray excitation (PIXE) and Rutherford Backscattering. Both are in less common

usage than other methods discussed here but have advantages in specific applications^(82b,c). Other techniques such as low-energy electron diffraction (LEED) are of practical value only in the study of very simple model systems and are not expected to have applications to the systems under consideration in the near future.

6.0 SURFACE STUDIES RELEVANT TO FLYASH FORMATION--RECOMMENDATIONS

Much of the current knowledge concerning flyash formation during coal combustion is summarized in the Introduction (Section 1.0). The characterization of flyash surfaces, and their role during combustion, in the postcombustion region, and in pollutant formation and transformation, is clearly limited by our knowledge of the details of the combustion process. Specific questions which need to be addressed are discussed below in order of the physical process of flyash formation and its passage through the combustion facility. These questions are limited to those considered within the scope of this report; the nature of flyash surfaces, their formation, and effect upon the subsequent chemistry.

1. Mineral Matter Transformations and Flyash Formation

The inorganic material in coal may be divided into two categories: the distinct mineral matter inclusions and the organically-bound material (i.e., associated with the organic matter in a manner essentially unknown⁽³⁾ at present). The behavior of these various materials needs to be studied under simulated combustion conditions as well as simpler model studies. The surface segregation of various elements in both free mineral matter and mineral matter inclusions contained within primarily coal particles may be quite different due to the presumably more highly reducing conditions encountered in the latter. Thus, the process needs to be studied under both oxidizing and reducing conditions at high temperatures. The rates and mechanisms of transport of minor and trace elements to surfaces under these conditions need to be determined.

As discussed in the Introduction, the flyash matrix material is composed primarily of constituents which can be ascribed to the mineral matter inclusions in coal. Indeed, in the simplest case there is evidence suggesting that individual flyash particles can be traced to individual or small groups of mineral matter inclusions, such as illustrated in Figure 1. Thus, the chemistry of the included mineral matter in coal during rapid heating, and the relevant diffusion and surface segregation processes, are directly relevant to understanding flyash formation. The inorganic elements in coal (all elements other than C, H, O, S, and N) may account for anywhere from 2 to 40% of the coal by weight, with a content of 5 to 15% being most common (as determined by low temperature ashing). The major mineral constituents are aluminosilicates, metal carbonates, sulfides and sulfates, and silica. Other trace elements are also included in these matrix minerals, in amounts related to their isomorphous replacement of a major element, or the number of random inclusions in holes in the primarily crystal lattice. The distribution of inorganic elements between coal particles composed primarily of "inherent" (organically associated) mineral matter (particles containing both organic and mineral matter) and free mineral matter tend to vary somewhat with particle size. The larger particles often contain a larger fraction of organic particles, which typically account for 40 to 70% of pulverized coal particles⁽³⁾. The smaller particles (<10 μm) can contain more than twice as much discrete mineral matter as the larger particles.

The transport of minor and trace elements in minerals representative of the included matter in coal needs to be studied to determine the rates of surface segregation and subsequent transfer to the gas phase. It will be

necessary to determine rates for these reactions over a wide range of temperatures and to establish the equilibrium concentrations by profiling concentrations of specific elements as a function of depth.

The scope of such studies is quite large. For the starting mineral matter (an aluminosilicate, for example) the dominant transport mechanism can be expected to change during the heating process as the physical structure alters. At the highest temperatures, the remaining liquid ash particle should exhibit very rapid elemental transport rates. It is possible that diffusion rates during this stage will be sufficiently fast that surface segregation rates at lower temperatures, during heating of the mineral matter, will be insignificant in determining either the ultimate extent of trace element volatilization or surface segregation prior to cooling. Since most of the chemistry of concern occurs after the combustion products leave the furnace, it is possible that the chemistry of mineral matter during the initial heating stage is of little relevance. Studies of the transport rates over a wide range of temperatures, including the molten ash, are necessary to investigate these possibilities. Surface studies of mineral matter which has undergone rapid heating, followed by more rapid cooling, might be useful in determining transport rates and possible mechanisms. Such experiments could utilize drop-tube furnace techniques such as used by Padia^(85,86). It should be noted that for lower temperature coal combustion, such as in fluidized beds, the expected processes will be quite different with reduced volatilization; thus the rates of the mineral matter surface segregation processes are likely to be more important.

2. Condensation and Surface Segregation Upon Flyash Cooling

After the fluid ash particle leaves the furnace region and begins to cool, various diffusion processes will continue; the extent of surface segregation at equilibrium is expected to be somewhat temperature-dependent. Thus, we have the complex situation where the surface depth concentration profiles may continue to evolve coupled with the condensation of various trace components during cooling. The condensing materials can therefore be expected to also undergo diffusion away from the surface leading to a more uniform distribution through the flyash matrix material.

It is suggested that such processes at the onset of particle cooling are likely to play a significant role in determining the ultimate surface composition. Experimental studies are required to determine the diffusion rates of deposited layers into the flyash matrix. The equilibrium concentration profiles can be determined from model studies where samples composed of fused flyash (or a synthetic flyash glass) are heated to various temperatures for known periods. These experiments can then be followed by others in which a layer of material is condensed upon the model surface at a given temperature. The surface coverage could then be observed as a function of time using AES, XPS or static-SIMS. Upon completion of the experiment or at given intervals, surface-depth profiles could also be obtained to investigate diffusion rates or the approach to equilibrium. SEM techniques should also be used to determine the extent of crystal formation at this stage; such experiments can be coupled using the etching procedure developed by Hulett and Weinberger⁽¹⁵⁾. These experiments should be particularly valuable in determining the dominant processes affecting flyash surface evolution in the postcombustion region.

3. Organic Transformations on Flyash Surfaces

The organic reactions which occur on flyash surfaces are of major interest from the viewpoint of formation of the possible environmental impact of coal combustion. The area of study can be divided into two categories: (a) the study of higher temperature gas-solid reactions which are probably quite fast and less sensitive to the precise nature of the surface and (b) the lower (near ambient) temperature surface transformations of condensed or adsorbed compounds. These reactions may be slower and strongly dependent upon the nature of the surface, as indicated in Section 4.0.

The direct study of surfaces with condensed or adsorbed organic overlayers will require a highly sensitive technique capable of monitoring molecular species. The new technique of static-SIMS appears to be the best technique available for such studies. The high sensitivity of this technique, 1 part in 10^6 for a monolayer, combined with the ability to detect and identify (using CID) organic species, is unique among the surface analysis tools now available. The static-SIMS technique has also been shown to be particularly useful for identifying relatively nonvolatile highly polar and thermally labile compounds which cannot be analyzed by conventional chromatographic techniques^(64,65). Such compounds are likely to be among the most important products of the transformations on flyash surfaces. Studies in this laboratory of pyrene reacting with SO_2 on flyash surfaces produce products which have not been characterized but suggest the formation of such compounds. It is suggested that these techniques be directed to the study of rates, mechanisms and products of the transformations of several

compounds on well-defined model flyash surfaces. These studies should examine the interactions with various gas phase species important in the past combustion and atmospheric chemistry (e.g., SO_x , NO_x).

4. Surface Techniques for Flyash Analysis

It is clear that each surface analysis technique discussed in detail in Section 5.0 has desirable features as well as certain failings. The use of two or more techniques, a common practice in surface analysis, is clearly necessary to avoid experimental artifacts for complex insulating materials like flyash. Since most modern surface analysis instrumentation includes two or more analytical techniques, this multiple-method approach should be feasible and should be strongly encouraged.

The technique of static-SIMS, particularly with the CID feature discussed previously, seems to be a major new tool in the array of surface analysis techniques. However, since it is a relatively recent development, it remains to be placed on a firm theoretical basis^(84b). The unique capabilities (extreme surface sensitivity and the ability to extract chemical information for even complex organic compounds) make its use for the analysis of flyash particularly attractive. The use of this tool, carefully backed by more established surface techniques where possible, should be utilized in the study of flyash surface phenomena.

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