Coo--4347-4
Conf. 780481--3

Characterization of Fly Ash from Coal Combustion

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ABSTRACT

Fly ash derived from coal combustion contains predominantly spherical particles which consist of an insoluble aluminosilicate glass containing several mineral impurities. An outer layer, 50 to 300 Å thick, is rich in many potentially toxic trace elements in the form of simple and complex sulfates. This layer, which is soluble in water, contains essentially all of the particulate sulfur present in fly ash in the form of sulfate. The actual mechanism(s) of formation of particulate sulfate salts are ill-defined but probably involve adsorption of condensation of gaseous sulfur species onto fly ash surfaces within the power plant stack system.

INTRODUCTION

At the present time approximately 80% of the electric power generated in the United States is derived from the combustion of fossil fuels. Of this total, coal combustion accounts for approximately 70% with the balance made up by natural gas and oil. Furthermore, it is now clear that increased coal utilization will be the primary means of meeting the nation's electrical energy needs for the next several decades at least.

It is well established (1) that sulfur present in coal is mobilized, almost quantitatively, into the stack gas stream as a result of combustion in coal-fired power plants. In conventional combustion operations, most of this sulfur is present as sulfur dioxide,

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together with small amounts in the form of sulfur trioxide, sulfuric acid, and particulate sulfate salts. The latter are associated primarily with fly ash particles whose physical and chemical characteristics may play a controlling role in determining the environmental impact of both emitted sulfate salts and of other sulfur species (e.g., sulfur dioxide) which may interact with fly ash following emission.

It is the purpose of this paper to summarize the available information about the physical and chemical characteristics of coal fly ash and to assess the status of present knowledge about sulfur species associated with fly ash. In both cases emphasis is placed on what is known about the fundamental processes which control the formation, transformation, and subsequent environmental behavior of coal fly ash and its sulfur-containing constituents.

NATURE OF COAL FLY ASH

A number of workers have undertaken detailed physical and chemical studies of coal fly ash (2-5), and its general characteristics are now quite well known. It is, however, important to note that fly ash derived from different power plants may exhibit considerable variability due, primarily, to differences between coal types and the nature of the combustion conditions. In this regard, combustion temperature is a very important factor insofar as it determines whether or not the fly ash matrix is molten at any stage and whether potentially volatile species actually experience a vapor phase history. It is also extremely important to recognize that most studies of fly ash are conducted on samples which are retained by particle control devices so do not truly represent material emitted to the atmosphere.

Morphology and Matrix Composition

Derived from mineral impurities present in the coal, coal fly ash particles are primarily inorganic in nature. Consequently, the amount of mineral matter present in a given coal strongly influences the particle emission factor for that coal. The major elemental constituents of coal fly ash are Si, Al and Fe, together with minor amounts of Ca, Mg, K, Na, Ti, and S. Some typical concentration ranges of these elements in U.S. coal fly ashes are presented in Table 1 (6). In general, fly ashes derived from western U.S. coals have a higher ash content and exhibit higher alkali and alkaline earth metal contents than do those from eastern coals, which are typically higher in sulfur.

Table 1. Typical Matrix Element Composition Ranges of Some U.S. Coal Fly Ashes Expressed as Weight Percentages of the Oxides

	Matrix element composition, wt-% of oxide
Major constituent	
Al_2O_3	14-30
SiO_2	22-60
Fe_2O_3	3-21
K_2O	0.2-3.5
CaO	0.5-31.0
Minor constituents	
Li_2O	0.01-0.07
Na_2O	0.2-2.3
MgO	0.7-12.7
TiO_2	0.6-2.6
P_2O_5	0.1-1.1
SO_4*	0.1-2.2

*Soluble sulfate

During combustion in a modern coal-fired power plant, the mineral impurities in coal melt and form small, mostly spherical, particles. The extent to which these molten particles coalesce or disintegrate into even smaller droplets is determined in part by the geometry, flow characteristics, and combustion conditions within the plant. Consequently, the size distribution of the particles produced may vary significantly between different plants. In a few plants of obsolete design (e.g., chain grate stoked), as well as in modern fluidized bed plants, combustion temperatures are not sufficiently high to melt the fly ash matrix, so that irregularly shaped particles are formed. Since these cannot readily disintegrate, their size distribution is generally centered around larger, median values than those encountered with spherical fly ash particles.

The aerodynamic equivalent mass median diameters of coal fly ashes in the absence of particle control devices typically lie in the range 8 μm to 30 μm (7), and the mass is reasonably approximated by a log-normal distribution. The mass median diameters of fly ashes emitted from control devices are considerably smaller than indicated above and depend largely on the collection efficiency of the control devices. In the case of electrostatic precipitators, mass removal efficiencies in excess of 98% are often achieved, and aerodynamic mass median diameters of emitted fly ash are typically in the range 0.5 μm to 2 μm.

While a number of distinct morphological forms of fly ash can be distinguished (10), only three are highly abundant. The first involves solid, or slightly voided, spheres and accounts for most fly ash particles having physical diameters less than about 5 μm. The second morphological form consists of hollow spheres whose interior voids are filled with carbon dioxide at a pressure of about 0.2 atm (4). These particles predominate in the physical diameter range 10 μm to 60 μm. Finally, and most intriguing, are hollow particles filled with large numbers (10 to 200) of small solid particles. This encapsulation phenomenon is encountered primarily for particles in the physical diameter range 20 μm to 60 μm (8). The phenomenon of particle encapsulation in fly ash is not fully understood; however, there is good evidence to show that encapsulated particles are actually formed inside their hosts so are not available to interact with external vapors and gases such as SO_2 (9).

As a result of the widespread occurrence of hollow and encapsulating fly ash particles, the measured density of coal fly ash is essentially unrelated to the density of the matrix material. X-ray and electron diffraction studies of fly ash indicate that the matrix consists, for the most part, of an aluminosilicate glass together with small amounts of the minerals α quartz (SiO_2), mullite ($3Al_2O_3.2SiO_2$), hematite (Fe_2O_3), and magnetite (Fe_3O_4). Fly ashes derived from western U.S. coals also have some crystalline gypsum ($CaSO_4.2H_2O$) and lime (CaO). It is apparent, therefore, that coal fly ash is highly heterogeneous in nature and is likely to exhibit low aqueous solubility.

Trace Element Distribution

The specific concentrations (μg/g) of individual trace elements in coal fly ashes depend primarily on the trace element content of the original coal. In general, a fly ash which contains high concentrations of one trace element will also have high concentrations of most others as well. However, the relative elemental concentrations encountered in fly ash may differ markedly from those in the original coal due to the different partitioning characteristics of individual trace elements between bottom ash and fly ash. Table 2 lists some typical specific concentration ranges for a number of trace elements encountered in coal fly ash and compares them with values for oil fly ash.

Table 2. Specific Concentrations of Elements in Coal and Oil Fly Ashes

Element	Coal Fly Ash Specific concentration, μg/g	Oil Fly Ash Specific concentration, μg/g
Al	70,000-140,000	100-5000
As	2-500	30
Au	0.004-0.1	--
B	10-600	--
Ba	500-7000	500-10,000
Be	1-10	--
Br	0.3-20	--
Ca	6000-180,000	10-1000
Cd	0.1-50	--
Ce	100-300	--
Cl	10-500	--
Co	5-100	90
Cr	50-300	66
Cs	1-20	--
Cu	50-650	50-2000
Fe	25,000-300,000	10,000-100,000
Ga	10-250	--
Hf	5-10	--
Hg	0.02-0.4	--
I	0.5-7	--
In	0.1-0.3	--
K	1500-35,000	1000
La	35-100	--
Lu	0.5-2	--
Mg	11,000-60,000	500-5000
Mn	50-500	1-100
Mo	5-40	--
Na	1200-18,000	2000-50,000
Ni	5-100	--
Pb	5-1000	200-2000
Rb	40-300	--
Sb	1-15	5
Sc	10-40	--
Se	1-20	5
Sm	10-20	--
Sn	30-30	--
Sr	50-4000	--
Ta	0.5-1.5	--
Th	15-70	--
Ti	3500-8500	--
Tl	2-30	--
U	5-20	--
V	100-500	100-200,000
W	3-10	--
Yb	3-7	--
Zn	50-5000	200-3500

It is now well established (2)(3)(8) that a number of elements, including As, Cd, Cu, Ga, Mo, Pb, S, Sb, Se, Tl, and Zn, tend to increase in specific concentration with decreasing particle size. This is attributed to a mechanism whereby certain elements, or their compounds, are volatilized during combustion and then condense back onto the surfaces of co-entrained fly ash particles as the temperature falls to the dewpoint of each vapor species. A great deal of evidence has been presented in support of this mechanism (2)(3)(10); however, it is becoming increasingly apparent that several additional factors may also operate. For example, recent work (8) suggests that the physical and chemical behavior of individual elements during combustion can be correlated with their geochemical classification. Thus, the chalcophile, lithophile, and siderophile elements exhibit different partitioning behavior which determines their distribution in coal fly ash. In addition, a distinct influence of individual particle matrix composition and specific surface area is observed.

Undoubtedly the most important consequence of the volatilization-condensation phenomenon exhibited by some trace elements is their pronounced enrichment in the region of individual particle surfaces. An example of such enrichment is presented in Figure 1 in which the concentration dependence of lead on depth below the particle surface is illustrated. The importance of this surface enrichment lies in several factors, viz.

(1) It is the particle surface which comes in direct contact with the external environment so that the highest concentrations of potentially toxic and reactive trace elements are mostly readily accessible. A rough comparison of estimated surface and bulk concentrations of several elements in a coal fly ash is presented for illustration in Table 3.

(2) Material present in the region of surface enrichment is readily soluble in aqueous media (Figure 1), thereby rendering the most environmentally undesirable trace elements mobile and available for interaction with the external environment. In this regard it should be recognized that only about 2%-3% of the total mass of coal fly ash is soluble in water.

(3) Conventional analyses of bulk fly ash grossly underestimate the effective concentrations of most trace elements which are actually available for interaction with the external environment (Table 3).

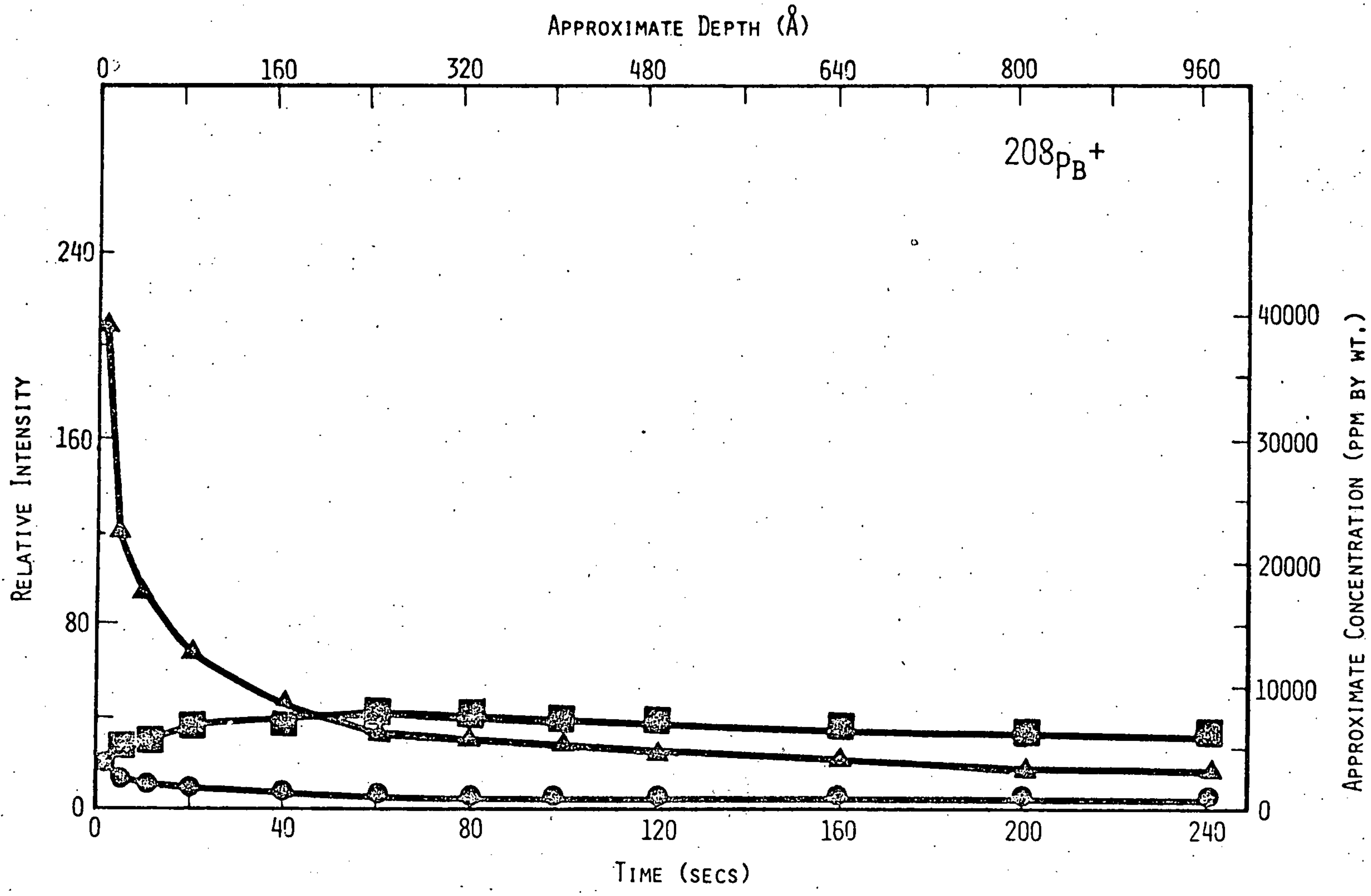

Figure 1. Dependence of the elemental concentration of lead on depth below the surface of a coal fly ash particle before (▲) and after leaching with water (●) and dimethyl sulfoxide (■) as determined by secondary ion mass spectrometry.

Table 3. Estimated Surface Concentrations of Elements in Coal Fly Ash

Element	Bulk concentration, µg/g	Estimated surface concentrated in 300 Å layer, µg/g
As	600	1,500
Cd	24	700
Co	65	440
Cr	400	1,400
Pb	620	2,700
S	7,100	252,000
V	380	760

When one takes account of the fact that condensation of trace metals onto fly ash particle surfaces almost certainly takes place at much higher temperatures than does condensation of SO_3, or adsorption of SO_2, it will be recognized that much of the interaction of sulfur species with fly ash is likely to be with trace metal species rather than with the particle matrix material. This may be extremely important in determining both the nature of the interactions and their resulting products.

SULFUR IN COAL FLY ASH

Current information about the chemical and physical status of sulfur present in fly ash is fragmentary. Nevertheless, a useful picture of its probable behavior can be assembled. For this purpose, it is helpful to consider the inter- and intra-particle distribution of sulfur, its chemical forms, and the probable mechanisms of formation of particulate sulfate salts.

Distribution of Sulfur

As pointed out earlier, sulfur is one of those elements which increase in specific concentration with decreasing particle size (2). However, unlike most of the trace metals, which exhibit such size dependence, a linear correlation between specific concentrations of sulfur and particle surface area is difficult to establish (2)(3). Indeed, separation of the dependences of concentration on physical size, density, and feromagnetism, as illustrated in Table 4, indicates a rather complicated dependence on both particle size and density. The reasons for these dependences are not clear.

Table 4. Distribution of Sulfur Concentration (% by wt) as a Function of Physical Size, Density, and Ferromagnetic Character in Coal Fly Ash

Particle Size (μm)		Density (g/cm³)			
		<2.1	2.1-2.5	2.5-2.9	>2.9
Nonmagnetic	<20	0.24	0.40	0.22	--
	20-44	0.11	0.48	0.82	0.43
	44-74	0.21	0.37	1.26	1.02
	>74	0.31	0.12	0.48	0.71
Magnetic	<20	--	--	0.16	0.19
	20-44	--	--	0.45	0.09
	44-74	0.10	0.21	0.34	0.28
	>74	--	0.43	0.20	0.14

Analyses of individual particles and groups of particles by means of ion microprobe mass spectrometry and Auger electron spectrometry (10) establishes beyond reasonable doubt that the sulfur associated with coal fly ash is present in a layer of the order of 50 Å thick at the particle surfaces (Figure 2). Furthermore, this layer is sufficiently soluble to enable almost quantitative removal of all sulfur species by continued washing with water or mineral acids. An example of such removal is presented in Figure 3 which illustrates the dependence of sulfate concentration on time in individual washings during Soxhlet extraction of coal fly ash with water at 25°C. (This technique is later referred to as Time Resolved Solvent Leaching, TRSL.)

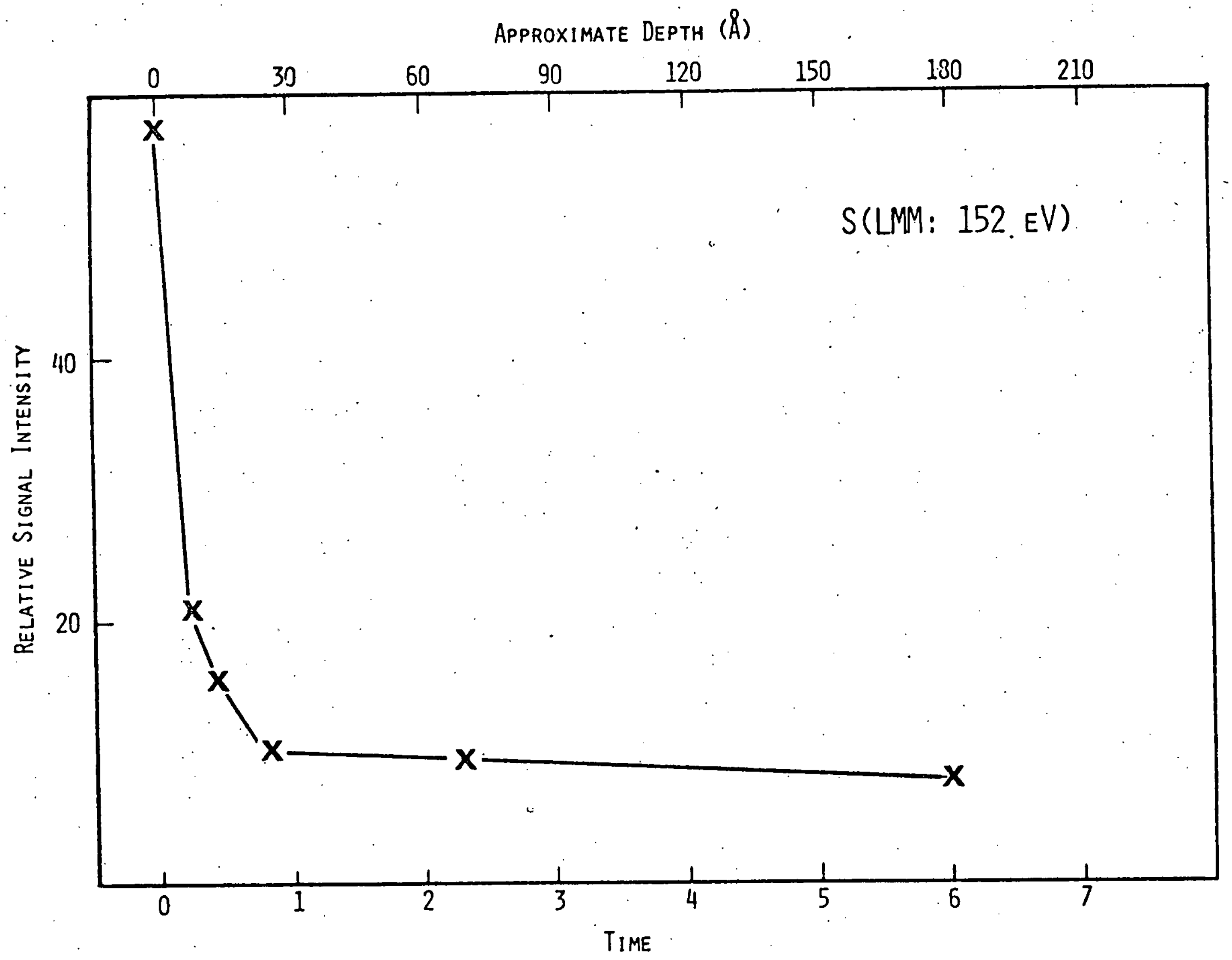

Figure 2. Dependence of the elemental concentration of sulfur on depth below the surface of a coal fly ash particle as determined by Auger electron spectrometry.

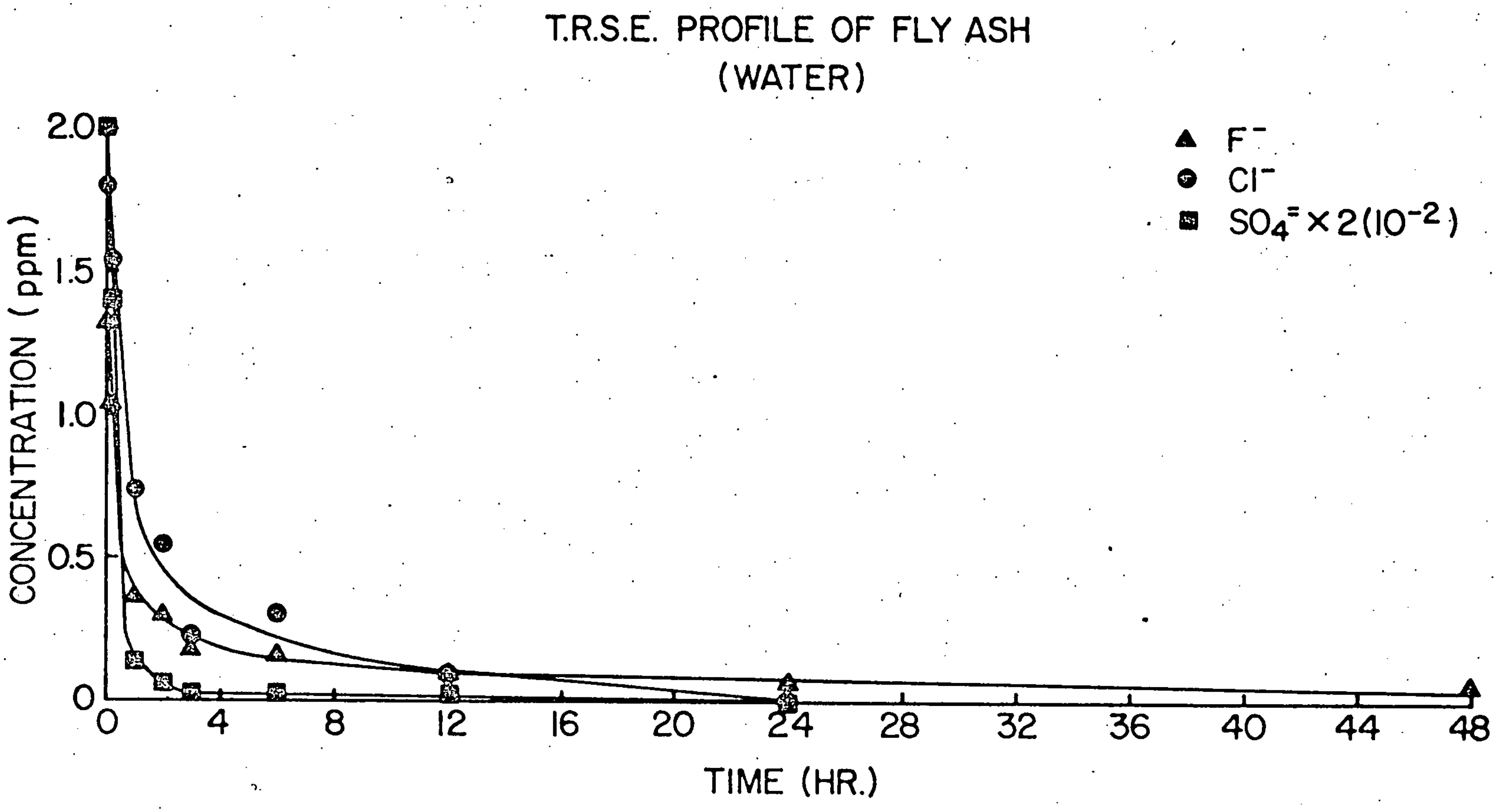

Figure 3. Time resolved leaching profile for sulfate, chloride and fluoride anion extraction from coal fly ash,

Analyses of fly ash which has been exhaustively leached with water indicate that very little, if any, sulfur remains, even though only 2%-5% of the fly ash mass actually dissolves. It is apparent, therefore, that sulfur is, at most, only a trace constituent in the fly ash matrix even though it is a major component of the particle surface layers.

Chemical Forms of Sulfur

Studies of fly ashes derived from the oxidative combustion of coal and oil using Electron Spectrometry for Chemical Analysis (ESCA) show that sulfur is present in the +6 oxidation state (10). Particulates derived from coal conversion processes, which involve reducing conditions, contain sulfur in the -2 oxidation state, however (11). Neither result is unexpected. Time resolved solvent leaching studies of coal fly ash, in which analyses of soluble anions are performed by means of ion chromatography, indicate that sulfate is the only sulfur-containing anion leached by water.

It is probable, therefore, that the sulfur species present in the surface layer of coal fly ash is, at least predominantly, and probably exclusively, in the form of sulfate.

Some evidence is available regarding the cations which are associated with sulfate species in coal fly ash. Thus, X-ray powder diffraction patterns of some fly ashes indicate the presence of either anhydrite ($CaSO_4$) or gypsum ($CaSO_4 2H_2O$). These species are present most commonly in fly ashes derived from western U.S. coals which contain especially high levels of calcium. The two forms result, apparently, from exposure of the highly hygroscopic anhydrite to moisture. In a sense, therefore, the occurrence of gypsum is probably artefactual.

Quite strong indications have also been obtained for the existence of several trace metal sulfates in coal fly ash. Thus, both Fourier Transform Infra Red Spectroscopy and Time Resolved Solvent Leaching (TRSL) provide evidence for the presence of Cd, Co, Cr, Mo, and Ni sulfates in coal fly ash. The alkali metals Ba, Cu, and Ca are also present, at least partly, in the form of sulfates. Even stronger evidence is available (12) for the existence of Al and Fe as sulfates in the surface layer of fly ash.

While definitive evidence is lacking, present indications are that essentially all of the elements present in the so-called surface layer of coal fly ash exist in the form of sulfates. Two points must, however, be recognized. First, the actual sulfate compounds are probably not simple but may consist of mineral forms which may include double salts. For example, the existance of alkali iron tri-sulfates has been suggested (10). Secondly, it is clear (at least in the case of the minor elements such as Ba, Ca, Mg, K, and Na) that a given metal may be present in more than one chemical form. No evidence has been found for the presence of free H_2SO_4 in fly ash particles.

Association of Sulfur with Fly Ash

The fact that sulfur present in coal fly ash is present almost entirely in the so-called particle surface layer provides very strong support for the proposition that sulfur-containing gases or vapors interact with the surfaces of co-entrained fly ash particles in a power plant stack. What is not clear is whether the interaction is via condensation, adsorption, or chemical reaction, or whether sulfur dioxide, sulfur trioxide, or sulfuric acid is the primary reactant.

Simple vapor pressure calculations indicate that condensation of SO_3 and H_2SO_4 is unlikely to occur at the temperatures encountered in a coal-fired power plant. Yet fly ash with well-formed sulfate surface layers is routinely collected at such temperatures (e.g., from electrostatic precipitators). One is inclined, therefore, to rule out condensation processes as being responsible for surface deposition of sulfates unless direct condensation of a metal-sulfate from the vapor phase occurs. As far as we are aware, there is no evidence whatsoever to support such an idea.

By default, therefore, one is left with the process of adsorption of SO_2, SO_3, or H_2SO_4 as being responsible for formation of particulate sulfate salts. In this regard it should be noted that adsorption of SO_2 would require fairly rapid (possibly catalytic) oxidation to the sulfate species.

It is apparent from the foregoing remarks that further research into the mechanism(s) of formation of particulate sulfate salts is required. In this regard, it is stressed that the toxicological implications of particulate sulfate salts make such research far from academic insofar as knowledge of formation mechanisms may well provide information necessary for development of effective control strategies.

CONCLUSIONS

Overall, it appears that the physical and chemical characteristics of coal fly ash are quite well defined. Thus, the material is in the form of spherical particles which consist primarily of an alumino-silicate glass containing several effectively insoluble, mineral forms. On the surface of this insoluble substrate, however, there exists a thin layer (50-300 Å) of readily soluble material which is rich in trace metals and which contains essentially all of the particulate sulfur in the form of metal sulfates.

It seems highly probable that the soluble sulfate layer present on the surface of coal fly ash particles is formed by gas-to-particle conversion of sulfur species involving adsorption and/or condensation processes. Certainly, the necessary increase in specific concentration of sulfur with decreasing particle size is observed, although agreement with theoretically predicted size dependences is poor. Essentially nothing is known about the actual species which are involved in gas-to-particle conversion.

Due to their potential toxicity it is important to identify and quantitate the mechanism(s) of formation of particulate sulfate salts.

ACKNOWLEDGMENTS

Aspects of the work referred to herein were supported in part by grants ERT-74-24276, MPS-74-05745 and DMR-73-03026 from the United States National Science Foundation; by grant R-803950-03 from the United States Environmental Protection Agency, Environmental Research Laboratory-Duluth; and by grant EE-77-S-02-4347 from the United States Department of Energy.

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