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METALLIC SPECIES DERIVED FROM FLUIDIZED BED COAL COMBUSTION

Final Report

By
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Colorado State University
Fort Collins, Colorado

U. S. DEPARTMENT OF ENERGY

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METALLIC SPECIES DERIVED FROM
FLUIDIZED BED COAL COMBUSTION

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ABSTRACT

Samples of fly ash generated by the combustion of Montana Rosebud coal in an experimental 18 inch fluidized bed combustor were collected. The use of a heated cascade impactor permitted collection of size fractionated material that avoided condensation of volatile gases on the particles. Elemental concentration trends were determined as a function of size and temperature and the results compared to published reports for conventional power plants. The behavior of trace metals appears to be substantially different in the two systems due to lower operating temperatures and the addition of limestone to the fluidized bed. Corrosion of the impactor plates was observed at the highest temperature and lowest limestone feed rate sampled during the study. Data from the elemental concentration and leaching studies suggest that corrosion is most likely due to reactions involving sodium sulfate. However, it is concluded that corrosion is less of a potential problem in fluidized-bed systems than in conventional coal-fired systems.

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Introduction

It is now apparent that deficits in the energy budget of the United States will, for the rest of this century at least, be made up primarily by increased usage of coal. Indeed, the relative abundance and ease of accessibility of coal in the United States suggests that it will constitute a major source of the nation's energy during the next century as well (Landsberg et al., 1979).

At the present time, the processes whereby useful energy can be derived from coal fall under four rather general headings. These are:

1. Coal Combustion - this includes the great majority of current processes.
2. Coal Gasification - this includes a wide variety of processes which produce low, medium or high btu content gas which can be utilized either for production of electricity or for direct substitution for natural gas.
3. Coal Liquefaction - this includes several processes which produce a liquid product which can be utilized either for energy production or as a fuel stock for chemical industry.
4. Other Processes - these involve several processes which are more or less novel in concept such as magnetohydrodynamics (MHD).

Of the above processes, only coal combustion is currently being utilized on an operational scale in this country, although it is generally agreed that both coal gasification and liquefaction processes will reach full scale dimensions during the next few decades. Presently, development is slowed by economics and by technological/chemical problems (Landsberg et al., 1979). Most other processes are not likely to be commercially viable for many years, if at all.

Direct combustion of coal has been utilized for decades as the primary energy source used in electric power generation. Unfortunately, coal combustion generates large amounts of many substances that have a demonstrated or suspected adverse environmental impact. Chief among these substances are sulfur dioxide gas and solid ash (either bottom ash or fly ash). The former is the primary suspect in the so-called "acid rain" problem observed in the Eastern and Northeastern United States (Liken, Bormann and Johnson, 1972; Homolya and Fortune, 1978; Cronan and Schofield, 1979; Babich et al., 1980; Henmi, 1980; Dittenhoeter and De Pena, 1980). The latter presents problems of solid waste disposal that are staggering (US DOE and US EPA, 1978) in terms of the amount of material that is generated. In addition, the possible problems from soluble trace metals and respirable particles is considerable (Natusch and Taylor, 1980).

One of the more promising solutions to the problem of sulfur oxide emissions is the use of the fluidized bed combustor (FBC), (Fennelly et al., 1977). In this system coal is burned in conjunction with limestone or dolomite which in turn react with the acidic sulfur gases emitted by the combusted material. Operating temperatures are much lower than in a conventional power plant and well within the ranges shown to be most efficient in promoting the SO_2 reactions (Reid, 1970; Coutant et al., 1970, Combustion Power Company, Inc., 1977).

Because the development of fluidized bed combustors dedicated to power production is comparatively recent, the in plant behavior of toxic and non-toxic trace metals is far from well defined, although some work has been reported in both areas (Combustion Power Company, 1977; Carpenter et al., 1978). Similarly, the effect of metals and/or metal salts on plant components such as occurs in conventional power plant-boiler systems (Reid, 1971) is not clearly established.

Although little information is available on trace metal behavior in fluidized bed fly ash, their behavior has been extensively studied in fly ash derived from conventional coal combustion systems. Thus, a large number of investigators have reported that many trace elements found in coal fly ash exhibit an inverse dependence of concentration on particle size (Loh, 1975; Davison, et al., 1974; Block and Dams, 1976; Klein et al., 1975; Cambell, et al., 1978; Coles, et al., 1979; and Smith et al., 1979).

This behavior is undesirable from several points of view.

1. It results in many potentially toxic metals becoming associated with particles that present a greater hazard to human health in terms of pulmonary deposition when inhaled (Natusch, et al., 1974).
2. Small particles are more difficult to remove or control with conventional particle collection devices (White, 1963).
3. Small particles have longer atmospheric residence times (Butcher and Charlson, 1972).
4. Small particles with their enriched surfaces provide a better site for heterogeneous reactions, both in terms of their larger specific surface area and their trace metal content.
5. It potentially results in several corrosive species (e.g., alkali metal compounds) being readily available to power plant components such as gas turbines.

In general, elemental concentration trends are reported in terms of three classifications. These are Group I (no trends), Group II (increasing concentration with decreasing size), and Group III (intermediate behavior or concentration decreases with decreasing size). The generally accepted classification of the different elements in coal fly ash is given in Table 1.

Table 1

Summary of Elemental Concentration Dependence on Particle Size*

A. Elements showing clear inverse concentration-particle size dependence (Group II)

As	Cl	Mo	Sb
Br	Ga	Nb ³	Se
Cd	I ²	Pb	Tl ⁴
Cu	In ²	S	Zn

B. Elements showing less well established inverse concentration-particle size dependence (Group III).

Ag ²	Cr	U ⁶
Au ²	Mn	V
Be ⁵	Na	W
Cs	Ni	Zr ³

C. Elements showing no concentration-particle size dependence (Group I)

Al	Ce	Fe	Mg	Si	Ta	Yb
Ba	Co	Hf	Nd	Sm	Tb	
Bi ¹	Dy	K	Rb	Sn ⁴	Th	
Ca	Eu	La	Sc	Sr	Ti	

* Based on the data of Loh (1975); Davison, et al. (1974); Coles, et al. (1979); Klein, et al. (1975); Cambell, et al. (1978); and Block and Dams (1976). Elements listed reflect the classifications of a majority of the authors cited.

1 Data of Klein, et al. (1975) and Block and Dams (1976) only.

2 Data of Block and Dams (1976) only.

3 Data of Cambell, et al. (1978) only.

4 Data of Davison, et al. (1974) only.

5 Data of Davison, et al. (1974) and Coles, et al. (1979) only.

6 Data of Coles, et al. (1979) and Klein, et al. (1975) only.

Examination of Table 1 reveals several facts. First, while most of the matrix elements consistently fall within Group I and many of the more volatile elements into Group II, many elements either exhibit intermediate behavior or else fall into different categories, depending on the particular study. The discrepancies between results are probably a function of the many different coals, combustion conditions and collection and analysis systems utilized by the different workers.

Three major theories have been suggested to explain the preferential association of different metals with small particles. They are generally based on volatilization and subsequent condensation or adsorption of the particular element, geochemical fractionation, or the "bursting" of larger particles.

In support of the volatilization and adsorption/condensation hypothesis, it is noteworthy that all the elements (except Nb) listed in Table 1A have boiling points comparable to or below the temperature of the coal combustion zone (1300-1600°C) (see Table 2). This is also true of Ba, Sr and Rb, as determined by Sparks (1973). This implies that metal compounds are reduced to the element before volatilization. However, while reduction in the combustion zone is certainly feasible, such reduction is not necessary to the basic hypothesis. It is suggested that these elements have access to the vapor phase as sulfides, halides, oxyhalides, or even as carbonyls, whose highly transient formation during coal combustion has been postulated (Schroeder, 1971). Mercury, of course, undoubtedly volatilizes as the element and is predicted to exhibit a dependence of concentration on particle size if the proposed mechanism is valid. A more detailed treatment of the volatilization/condensation theory can be found in the article by Davison, et al. (1974).

Table 2

Boiling Points of Possible Inorganic Species
Evolved During Coal Combustion

<u>Species Boiling or subliming < 1550°C</u>	<u>Species boiling or subliming > 1550°C</u>
As, As ₂ O ₅ , As ₂ O ₃ , As ₂ S ₃	Al, Al ₂ O ₃
Ba	Be, BeO
Bi	Bi ₂ O ₃
Ca	C
Cd, CdO, CdS	CaO
Cr(CO) ₆ , CrCl ₃ , CrS(1550)	Co, CoO, CoS
K	Cr, Cr ₂ O ₃
Mg	Cu, CuO
Na, Na ₂ O	Fe, Fe ₂ O ₃ , Fe ₃ O ₄ , FeO
Ni(CO) ₄	MgO, MgS
Pb	Mn, MnO, MnO ₂
Rb	Ni, NiO
S	Si, SiO ₂
Se, SeO ₂ , SeO ₃	Sn, SiO ₂
Sb, Sb ₂ S ₃ , Sb ₂ O ₃ (1550)	SrO
SnS	Ti, TiO ₂ , TiO
Sr	U, UO ₂
Tl, Tl ₂ O, Tl ₂ O ₃	
Zn, ZnS	

Several authors (Block and Dams, 1976; Coles, et al., 1979); Klein, et al., 1975) have suggested that the preferential concentration of certain elements in small particles is a result of their lithophilic or chalcophilic properties. Lithophilic elements are those generally found associated with alumino-silicate materials, while chalcophiles are associated with sulfide-containing minerals. This classification of elements generally relies on the scheme proposed by Mason (1966), although slight differences exist with other reports (Krauskopf, 1972; Nicholls, 1968).

Most reports indicate that Al, Ba, Be, Ca, Cs, Hf, K, Mg, Mn, Na, Rb, Ta, Th, Ti, U, V, and the rare earths (Ce, Dy, Eu, La, Nd, Sm, Tb, and Yb) are classified as lithophiles. Similarly, As, Cd, Ga, Mo, Pb, Sb, Se, and Zn are chalcophiles. Elements that may be either lithophilic or chalcophilic in their behavior include Cr, Co, Cu, Fe, Ni, and W. In terms of small particle behavior, the lithophiles belong mainly to Group I, showing little preferential concentration on small particles. The Group II elements, which are much more easily volatilized during combustion, are generally chalcophiles. Group III elements include, but are not limited to, those elements that may belong to both classes.

In general, this geochemical classification scheme is consistent with the volatilization-condensation theory suggested. The ultimate behavior of the different elements is still determined by the coal and combustion facility, but prior analysis of the coal based on its geochemistry may permit better predictions concerning which elements, if any, will be preferentially concentrated in small particles.

Recently, a third hypothesis concerning trace metal-small particle relationships was proposed (Smith, et al., 1979). In this study, it was found that concentrations of trace elements that increased with decreasing particle size in the range of 1 to 10 μm became independent of size below

1 μm . As a result, the authors suggested that gas expansion caused a "bursting" of larger particles, with the resulting production of a large number of small particles. These small particles then coagulate into the 0.1-1.0 μm size particles. Condensation would occur concurrently with the bursting and coagulation process. Data to support this hypothesis are largely circumstantial.

In addition to being preferentially associated with small particles, several metals have been reported as predominant on fly ash surfaces (Linton, et al., 1977). Among those reported as surface associated are Be, Ca, Cr, K, Li, Mn, Na, Pb, S, Tl, U, and Zn. Of these elements, only Pb, S, Tl, and Zn are reported as showing a definite inverse concentration size dependence.

The possible small particle dependence of trace elements for fluidized bed combustor fly ash has not been extensively addressed. Carpenter, et al. (1978) found that Bi, Ga, Hf, Ni, Sn, U, and Y were preferentially associated with smaller particles. None of these elements, except Ga, has been shown (Table 1) to consistently exhibit similar behavior in coal fly ash from a conventional power plant. The lower operating temperatures of a fluid bed make a mechanism such as volatilization-condensation less of a viable possibility, but there are still many species that can be volatilized at such temperatures.

External corrosion, especially corrosion as the result of alkali metal sulfate interactions with iron and steel furnace components, is another problem that has been extensively studied under a number of differing conditions. It is a problem that has plagued power plants and boiler operations for some time (Reid, et al., 1945; Krause, et al., 1973). Thus, the deterioration of pipes and ducting, side walls, heat exchangers, and similar areas is a problem that has been extensively studied. In spite

of considerable effort, the mechanism(s) of corrosion in coal-fired furnaces is still not completely understood; in part due to the complexity of the fuel and its waste products, the differences in operating conditions, and the high probability that several different competing reactions are occurring simultaneously. (Cain and Nelson, 1961; Reid, 1962; Boll and Patel, 1961; Krause, et al., 1969; Cutter, et al., 1971; Reid, 1971). However, most studies indicate that temperature, alkali metal concentrations and sulfur-sulfur oxide concentrations are the most significant variables affecting the corrosion process (Sedor, et al., 1960; Nelson and Cain, 1960; Weintraub, et al., 1961; Burrows and Hills, 1966; Krause, et al., 1968; Krause et al., 1969; Cutler, et al., 1971).

The first detailed studies of alkali metal-sulfur gas corrosion mechanisms were those of Reid, et al., (1945) and Corey, et al. (1945). These studies indicated that high-temperature boiler corrosion problems were not a result of direct sulfuric acid attack since, under normal operating conditions, temperatures were too high to permit condensation. Surveys of a large number of power plants indicated that corrosion was most prevalent at temperatures near 600°F or else above 1000°F. It was also found that SO_3 , Na_2O , K_2O and small amounts of SiO_2 , Al_2O_3 and CO were the most common compounds in and around corrosion deposits. Deposits contained approximately five percent iron (computed as Fe_2O_3) and solubility tests showed the samples were highly soluble--and highly acidic. Alkali metal compounds appeared to account for most, but far from all, of the SO_3 .

The authors (Reid, et al., 1945; Corey, et al., 1945) generally concluded that:

1. Tube metals experiencing corrosion were at temperatures usually less than 800°F and rarely exceeding 900°F.
2. Temperatures in corroded areas appeared to be lower than in adjacent, uncorroded locations.

3. Active corrosion occurred in areas of high CO concentration.
4. The amount of SO_2 in the corroded areas was not particularly high.
5. The rate of heat transfer in the corroded areas was not significantly greater than in other parts of the furnace.

Following these initial reports, a large number of investigators attempted to ascertain the contributory factors and mechanism(s) most responsible for alkali metal corrosion. As a result of this work, it has been firmly established that (1) neither air nor SO_2 oxidation contributes significantly to the corrosion process; that (2) sulfur trioxide is crucial to the process; that (3) chloride has relatively little effect on corrosion; that (4) the presence of CO near corrosion sites is of little significance; that (5) corrosion of iron or steel by alkali metal sulfates is a very complex process involving more than one mechanism, and that (6) the different mechanisms are highly temperature dependent.

The minor role of SO_2 and O_2 and the important role of SO_3 were established fairly quickly. Thus, studies with radioactive sulfur gases indicated that SO_3 was 30,000 times more reactive than $\text{SO}_2 + \text{O}_2$ in forming complex sulfates with mixtures of sodium sulfate and iron oxide over the temperature range of 900 to 1300°F (Krause, et al., 1968; Krause, et al., 1969). Earlier work by Corey, et al., (1945) and Corey, et al., (1949) clearly established the importance of SO_3 to corrosion by alkali metal sulfates. These same workers explored the role of CO in corrosion and found it was not a contributory factor. Other workers who investigated the role of chloride found it, too, had little effect, except under specialized conditions (Raask, 1963; Cutler, et al., 1971). Iron or steel containing chromium or nickel is that most affected by the presence of chloride (Alexander, 1963; Cutler, et al., 1971).

Several mechanisms to describe alkali metal corrosion have been suggested. No single mechanism appears adequate to describe corrosion at all temperatures or under all conditions. Many of the reactions are closely related. One of the best known is that of Corey, et al., (1945). They identified three separate corrosion layers. Nearest the metal surface was wustite (FeO). The wustite was followed by a layer of magnetite (Fe_3O_4) and then by an outer layer of hematite (Fe_2O_3). The actual suggested sequence of events is as follows:

1. An oxide film forms on the metal surface.
2. Alkali sulfates, originating from the alkalies in the fuel ash and the sulfur oxides in the furnace atmosphere, are deposited on this oxide layer. As an example, this deposit could be K_2SO_4 .
3. The outer surface of the K_2SO_4 layer becomes sticky because of the increasing temperature gradient, so that particles of fly ash are captured. The temperature of this fly ash increases to the point where SO_3 is released by thermal dissociation of sulfur compounds in the ash, and this SO_3 migrates toward the cooler metal surface. A layer of slag forms on the outer surface. The SO_3 is formed from SO_2 on catalytically active surfaces.
4. As more ash is collected, reaching an equilibrium thickness, the temperature falls in the K_2SO_4 layer, and reaction with the oxide scale and SO_3 occurs to form $\text{K}_3\text{Fe}(\text{SO}_4)_3$. With this removal of the oxide scale, the metal oxidizes further.
5. Deslagging occurs because of normal temperature excursions in the furnace, exposing the $\text{K}_3\text{Fe}(\text{SO}_4)_3$ layer to temperatures high enough to dissociate it in part, releasing some SO_3 . Part of this SO_3 moves toward the cooler part of the deposit, where it reacts with K_2SO_4 still present and the oxide scale on the tube

to form additional amounts of $K_3Fe(SO_4)_3$. Further oxidation of the metal occurs to provide the normal equilibrium thickness of scale.

Unless promoted by chemical or mechanical removal of the scale or by cracking, oxidation proceeds quite slowly. However, provided such removal does occur, the reactions are endlessly repeatable. This mechanism collaborated those of other workers (Hatfield, 1927) but it was difficult to explain given the generally low levels of SO_3 , (although not present in significant amounts under normal conditions, it is catalytically formed by oxidation of SO_2 on iron oxide (Jenkinson, 1963; Reid, 1963; Levy and Merryman, 1965)). This particular series of reactions is most probable over 1000°F, partially because other mechanisms seem more probable below this temperature and partially as a result of thermodynamic considerations, (Boll and Patel, 1961).

Formation of SO_3 is especially important at lower (<1000°F) temperatures where corrosion by other mechanisms, such as alkali metal pyrosulfates ($K_2S_2O_7$ and $Na_2S_2O_7$) is most significant. At temperatures over 1000°F, pyrosulfates are thermodynamically unstable. The large SO_3 requirements of pyrosulfate formation (10,000 ppm SO_3 to form $K_2S_2O_7$ at 1000°F, for example) makes large-scale pyrosulfate corrosion questionable, but they undoubtedly are a contributory source. Corey, et al., (1945) and Reid (1971) suggested a pyrosulfate corrosion mechanism for the temperature range of 750 to 900°F. Not too surprisingly, it is very similar to that for the alkali iron trisulfates.

1. Deposition of alkali metals, probably as oxides, on exposed metal surfaces.
2. Conversion of alkalies to Na_2SO_4 and K_2SO_4 .
3. Oxidation of SO_2 in the bulk flue gas to SO_3 on catalytically active surfaces.

4. Formation of pyrosulfates, $\text{Na}_2\text{S}_2\text{O}_7$ and $\text{K}_2\text{S}_2\text{O}_7$, by reaction of sulfates with SO_3 .
5. Reaction of pyrosulfates with oxide films on metal surfaces.

Typically:

or alternatively,

followed by

The metal then reoxidizes

Other mechanisms that have been postulated involve similar reactions, although pyrosulfates are not directly involved. Cain and Nelson (1960) suggest that the crucial reaction is:

or else

On the other hand, Adams and Raask (1963) were unable to find support for Cain and Nelson's (1960) mechanism or for that of Corey (1945). Their results suggested that the sulfate reduction proceeded only to the formation of SO_2 rather than sulfate. As a result, they suggested the two-stage reaction given below:

The aluminum in the reaction was not derived from the metal surface being corroded and most likely would come from the ash. The second reaction would occur at the metal/oxide interface. In the case of a protective chromic oxide film, the similar reactions

or

would apply.

Electrochemical reactions involving molten salts have also been investigated (Burrows and Mills, 1966). Again, the most significant factor is the SO_3 concentration; but the existence of a true molten salt coating on the metal surface is difficult to establish.

Finally, Anderson and Diehl (1955) suggested corrosion by alkali iron trisulfates formed by reaction of fly ash deposits on metal surfaces with the sulfur oxides in the flue gas. Their proposed mechanism was as follows:

1. Loose unbounded fly ash accumulates on a tube surface.
2. Alkalies in this deposit begin to form sulfates by reaction with the SO_3 originally in the gas stream and that formed by oxidation of SO_2 .
3. The deposit nearest the tube metal continues to react with SO_3 to convert a major part of the alkalies in this inner layer to sulfates.
4. Iron oxide in the ash and SO_3 react with these sulfates to form alkali iron trisulfates immediately next to the tube.
5. Alkali iron and alkali aluminum sulfates form low-melting phases that bond firmly to the tube metal.
6. Both the inner and the outer layers of deposit increase in thickness, so that the temperature of the outer layer is higher and

sintering occurs.

7. The surface temperature eventually becomes high enough that fly ash sticks to the deposit and the rate of build-up of deposit accelerates.

Although not comprehensive, the different mechanisms and scenarios described above give an overview of the potential corrosion problems that are possible in the case of alkali metal sulfates. As will be discussed later, CaO, MgO, limestone (CaCO_3), and dolomite ($\text{CaCO}_3 + \text{MgCO}_3$) would be expected to appreciably affect these reactions.

Experimental

Sampling

Samples of ash were collected on May 26, 1979 at the Morgantown Energy Research Center in Morgantown, West Virginia. Collection was made during run RB-5 periods 2 and 3. Rosebud coal, a Montana sub-bituminous type, sand and limestone were used for both runs. Attempts to fluidize the bed utilizing only coal and sand and no limestone (run RB-5 period 1) were unsuccessful. The run conditions are outlined in Table 3.

Sampling was conducted at three locations (temperatures). Two of these were sampling points installed by the Lovelace Institute while the third was added by personnel from CSU. The Lovelace sampling port characteristics were recently described (Newton et al., 1980). All sampling points are identified in the accompanying diagram (Figure 1). The first location corresponded to Lovelace position 4 (Carpenter et al., 1978), a point between the first heat exchanger and the first cyclone. The temperature at this point was approximately 910°F. The second location was also installed by Lovelace (but not utilized in their sampling). This site was situated between Lovelace positions 2 and 3 (Carpenter et al., 1978) just beyond cyclone number 2 and prior to the second heat exchanger. The temperature at this position was approximately 640°F. The third position was added at a previously used but available sampling port located at a bend in the flue between the second and third heat exchangers just prior to the two bag houses. The temperature at this location was about 530°F.

A diagram of the sampling train used in the studies is shown in Figure 2. The same sampling train was used, without modification, for both sets of samples that were collected. The Andersen Mark III Particle Sizing Stack Sampler (Andersen Samplers, Inc., Atlanta, Georgia) was used with the cyclone pre-separator which is shown in the diagram. The sampler

Table 3

Test Matrix for Fluidized-Bed Combustion of Montana
Sub-Bituminous "Rosebud" Coal Run No. 5

Period No.	Coal Feed Rate lb/hr	Air Feed Rate SCFH	Limestone Feed Rate lb/hr	Ca/S mole ratio	Bed Temperature °F/°C	Sup Gas Velocity Ft/Sec	Excess Air %	Bed Depth Ins
1	50.78	5496	----	0.90	1650/900	3.50	10	37
2	50.78	5496	3.66	3.00	1650/900	3.50	10	37
3	50.78	5496	6.28	4.50	1650/900	3.50	10	37

Figure 1. Sampling Positions Used In Sampling METC Fluidized Bed Combustor (FBC)

Figure 2. Schematic of Sampling Train

was enclosed in a 2-foot long stainless steel tube furnace. The heating coils for the furnace were purchased from the Lindberg Company (Watertown, Wisconsin). The furnace itself was constructed at the Department of Chemistry at CSU. The entire system was designed to permit collection of samples at the temperature of the exhaust stream.

The actual sampling at all three positions utilized a number of fittings to provide maximum flexibility and speed. It was found that Swagelok[®] tubing connectors provided the easiest way to disconnect the sampler quickly and efficiently once the one minute samples had been collected. This connector can be seen in Figure 3. At the two Lovelace positions it was necessary to suspend the furnace by its handle using hooks attached to an overhead cross bar. The furnace's height was controlled by turnbuckles. One eight-inch cable was found to be sufficient to support the furnace although one quarter-inch was also used. Although this arrangement, depicted in Figure 3 proved adequate, it left considerable room for improvement.

The newly installed 530° position did not permit a suspension system to be used. Instead the sampling train had to be supported by a step-ladder-lab jack combination, an unstable arrangement that required constant attention to prevent its collapse. This position, if it is to be used again, will require an entirely new support arrangement. The positioning of the pump, furnace potentiostat, condenser and flow meter remained fairly uniform throughout all the positions and was located on the adjacent floor. For the two highest positions 3/8" copper tubing was used to connect the half-inch pipe "handle" leading from the stack sampler to the condenser. For the coldest position heavy wall rubber tubing was used instead.

The typical sequence used in sample collection is as follows:

1. Furnace position adjusted.
2. Sampler inserted into furnace and connected to the sampling point.

A. Overall Connection of Sampling Tree Showing Furnace Placement

B. End on View of Furnace Showing Pipe Leading to Pump

Figure 3. Location of Furnace and Sampling Connections

C. Close-up of Sampling Train Connection to Probe

Figure 3. Location of Furnace and Sampling Connections (Continued)

3. Furnace raised to desired temperature and equilibrated.
4. Pump turned on.
5. Ball valve opened for one minute, flow adjusted to $\sim 0.6-0.7$ cfm.
6. Ball valve closed.
7. Pump shut down.
8. Sampler removed from sampling point and the tubing connector covered with aluminum foil.
9. Sampler carefully slid out of furnace and placed in upright position.
10. Lower end of sampling train is disconnected and the end sealed with aluminum foil.
11. Hot sampler removed to clean room where it was disassembled while being maintained upright in a vise.
12. Once cool the stainless steel plates were swept clean with a small hand brush with the samples going into small glass sample vials.
13. Stainless steel plates and sampler were then washed with water and mild soap, blotted dry using paper towels, inspected and reloaded.

The entire sampling procedure required 1 1/2-2 hours a sample. This time could have been cut back and more samples obtained if a means of overcoming three time consuming steps could have been found. These problems included

1. Equilibrating the furnace at different temperatures.
2. Waiting for the sampler to cool.
3. Cleaning the plates, removing the sample and washing the sampler components.

It is recommended that more than one sample be collected at each position in the future. This would reduce the time for 1. and make operations generally more efficient. This would, however, require more than five

hours sampling time, the present time span for a stable combustion run at METC.

In addition to the fractionated samples of which varying amounts were obtained, samples from the bed, the two cyclones and the one operating bag house were obtained during the middle of each run. A large amount of these three samples was collected just before shutdown of period 3. Samples of the Rosebud coal, limestone and glass sand used in run-RB-5 were also obtained.

Materials

As a result of this sampling trip and an earlier trip to METC, a large number of samples were on hand for analysis. These samples are listed in Table 4.

Apparatus

Morphological studies were carried out on a Hitachi HHR-2S scanning electron microscope. Energy dispersive X-ray analyses were obtained by using the same instrument and a Kevex Model 5000A X-ray Spectrometer equipped with a Model 6000 Data Analyzer. This combination permitted qualitative information on elemental composition.

Elemental compositions were obtained by instrumental neutron activation analysis (INAA) at the University of Illinois Advanced Reactor Facility. The reactor has a flux of approximately 10^{12} neutrons/sec/cm². The resulting X-ray spectra were collected with a Ge(Li) detector and the count data converted to concentration using the PIDAQ program (Maney et al., 1977). INAA provided non-destructive multielemental analysis, essential given the sample size.

Digested ash samples and sample leachates from cyclones 1 and 2 and the bag house were analyzed for major and trace metal constituents by plasma-atomic emission spectrometry. The Spectraspan III Spectrometer (Spectrametrics, Inc., Andover, Mass.) was used and a summary of the

Table 4

Fluidized-Bed Combustor Samples

Period 15

XRL 196	Bag Filter 1 & 2	Several grams of all samples
197	Cyclone #2	
198	Bed material	

Period 16

XRL 199	Bag filter	Several grams of all samples
200	Cyclone #2	
201	Bed material	

Period 18

XRL 205	Bag Filter 1 & 2	Several grams of all samples
206	Cyclone #2	
207	Bed material	

Period 19

XRL 208	Bag Filter 1 & 2	Several grams of all samples
209	Cyclone #2	
212	Bed material	

Limestone to be used in Rosebud run.

Dolomite in Pittsburgh seam coal run.

Run PW-1 Period 9 11-29-77

1100 hours Bag Filter at 490°F 1.7 lbs.

Dolomite bed add 15# Dolomite/hour 1550-1600°F

Run PW-1 Period 9 11-29-77

Cyclone #2 640°F 2 lbs.

Run PW-1 Period 9 11-29-77

Bed 930°F 3 lbs.

Table 4
(continued)

Run RB-5	Period 2	5-26-79
Cyclone #1		
Cyclone #2		
Bag House		
Fractionated Samples	910°F	
	640°F	
	530°F	
Run RB-5	Period 3	5-26-78
Cyclone #1		
Cyclone #2		
Bag House		
Fractionated Samples	910°F	
	640°F	
	530°F	

instrumental parameters may be found in Table 5. The leachate solutions were analyzed for F^- , Cl^- , NO_3^- and SO_4^{2-} by ion chromatography using the System 10 Analytical Ion Chromatograph (Dionex Corp., Sunnyvale, CA). The instrumental conditions used for these analyses are also listed in Table 5.

Surface analyses were performed using either a model 540A Auger Thin Film Analyzer (Physical Electronics Industries, Eden Prairie, MN) or 548 Auger/ESCA Spectrometer (Physical Electronics Division, Perkin-Elmer Corp., Eden Prairie, MN). A 2 KV Ar ion beam was employed for sputtering. Binding energies were referenced to the C 1s line at 285.0 eV.

Procedure

Scanning electron microscope samples were mounted on double sided cellophane tape and coated with carbon or both carbon and gold. Carbon coating was used for those samples examined using the X-ray capability of the instrument.

Bulk analyses of both Pittsburgh seam coal and Rosebud coal were made by first digesting a half gram of sample with a mixture of aqua regia, 30% hydrofluoric acid and distilled water in a bomb for two hours at 110°C. The HF in the resulting 10 ml solution was neutralized with boric acid. The sample was then filtered and diluted to 50 ml with deionized triply distilled water. Samples were analyzed by plasma emission spectrometry (PES).

For all samples analyzed by PES, both digested bulk samples and leachate solutions, a similar procedure was employed.

In this procedure, a series of sample dilutions (8/10, 5/10, 1/10 and 0.1/10) were analyzed to enable the determination of the full range of metals and metalloids detectable by the instrument. A solution of 10,000 μg Cs/ml and 200 μg In/ml in 1 M HNO_3 was added to each sample to produce an internal standard concentration of 20 μg In/ml and an ionization suppressor concentration of 1000 μg Cs/ml. Calibration involved the

Table 5. A Summary of the d.c. Plasma-Spectrometer
and Ion Chromatograph Operating Conditions

Spectraspan III d.c. Plasma Echelle-Spectrometer

Integration time - 10s

Repetitions - 6/sample

Nebulizer - sample flow rate - ca. 2 ml/min
 argon flow rate - ca. 5 ml/min at 20 psi

Electrode assembly - argon flow rate - ca. 1 l/min at 20 psi

Slit assembly - 100 μ m horizontal x 200 μ m vertical

Dionex System 10 Ion Chromatograph

Sample loop - 100 μ l

Separator column - Chromex anion exchange resin, 3 x 250 mm

Suppressor column - Chromex cation exchange resin, 6 x 250 mm

Flow rate - 90 ml/hr

Recorder speed - 1 cm/min

Eluent - 0.0030 M NaHCO_3 /0.0024 M Na_2CO_3

Conductivity meter - variable, 3-100 μ mho full scale

automatic instrumental construction of a two-point calibration curve. The calibration process involved the aspiration of first a solution blank and then a solution standard. The concentration values for the multielement standard are contained in Table 6. Also in Table 6 is a listing of the analytical working ranges for the elements at the 95% confidence limit. Elemental concentration values outside these intervals are considered statistically unreliable. Calcium concentrations in excess of 500 $\mu\text{g/ml}$ give rise to stray light interferences at several analytical wavelengths. This spectral interference is due in part to the broad molecular band emission of certain calcium species, most notably CaO . This intense emission contributes substantially to the spectral background; however, its contribution may be compensated for by the application of simple linear equations. A summary of these equations and the analytical wavelengths for those elements requiring stray light correction are summarized in Table 7. Compensation utilized a simple linear equation of the form:

$$C_T = C_M - a C_{\text{Ca}}$$

where C_T and C_M refer to the true and measured concentrations of the analyte and C_{Ca} refers to the concentration of calcium present. With these corrections, the analytical precision at the 95% confidence limit is within 10-20% relative.

For the anionic analyses, sample solutions were drawn into a 5 ml plastic syringe and filtered through a 0.45 μm Millipore filter prior to injection into the sample loop. Appropriate dilutions of a stock solution containing: 92 $\mu\text{g F}^-/\text{ml}$, 124 $\mu\text{g Cl}^-/\text{ml}$, 145 $\mu\text{g NO}_3^-/\text{ml}$ and 150 $\mu\text{g SO}_4^{2-}/\text{ml}$ were used for calibration. Duplicate or triplicate analyses are performed for each sample. Anionic identification within a sample is based on comparison of peak retention times with standards. Peak heights were used

Table 6. Auto-Range Values for the Multielement d.c. Plasma Emission Spectrometer^a

Channel Number	Elements	Auto-Range Concentrations (µg/ml)	Working Range (µg/liter)
1	B	1.000	100-1100
2	Cd	0.500	50- 600
3	Be	0.500	50- 600
4	Mg	12.5	1.25-12.75
5 ^b	Bc	--	--
6	P	1.000	100-1200
7	Si	1.250	125-1500
8 ^d	Mo	0.500	50- 600
9 ^c	In	20.	--
10 ^d	Mn	1.000	100-1200
11 ^d	Ni	0.500	50- 600
12	Na	12.5	1.25-12.75
13	Cu	0.500	50- 600
14 ^d	Al	1.000	100-1200
15	Ca	15.0	0.5-18.0
16 ^d	Ba	0.375	37.5-450
17	K	10.0	1.0-12.0
18 ^d	Cr	0.500	50- 600
19 ^d	Sr	7.500	500-9000
20 ^d	Pb	0.800	80- 960

^aSpectrospan III - Echelle Grating - Prism Atomic Emission Spectrometer^bBackground Correction^cInternal Standard^dStray light correction necessary for these elements. Refer to Table 7

Table 7. Calcium Stray Light Correction Equations

Element	Wavelength (nm)	Detection Limit ($\mu\text{g/liter}$)	Correction Equation ^a
Al	396.1	10	$\text{Al}_T = \text{Al}_M - 0.905 (\text{Ca})$
Ba	455.4	20	$\text{Ba}_T = \text{Ba}_M - 0.025 (\text{Ca})$
Cr	425.4	5	$\text{Cr}_T = \text{Cr}_M - 0.054 (\text{Ca})$
Mn	257.6	10	$\text{Mn}_T = \text{Mn}_M - 0.031 (\text{Ca})$
Mo	379.8	10	$\text{Mo}_T = \text{Mo}_M - 0.254 (\text{Ca})$
Ni	341.4	10	$\text{Ni}_T = \text{Ni}_M - 0.043 (\text{Ca})$
Pb	405.8	10	$\text{Pb}_T = \text{Pb}_M - 0.546 (\text{Ca})$
Sr	460.7	100	$\text{Sr}_T = \text{Sr}_M - 0.556 (\text{Ca})$

^aCalcium concentration expressed as mg/l. Elemental concentration expressed as $\mu\text{g/l}$.

for quantification purposes resulting in a precision near $\pm 5\%$, relative. When sample dilutions were necessary, the eluent is used to bring the sample to volume. This resulted in less baseline drift and improved analytical reproducibility.

Leaching was conducted by two different methods. First, bulk leaching was accomplished by sonicating a half gram of sample in 20 ml of water then diluting the filtered solution to 50 ml. Secondly, samples of fly ash from cyclones 1 and 2 and the bag house were analyzed using the technique of time resolved solvent leaching (TRSL). Briefly, one gram fly ash samples were placed in 10 x 50 mm cellulose extraction thimbles which were placed in turn into a stainless steel column connected to a standard liquid chromatography pump. The experimental configuration is depicted in Figure 4. The solvent (distilled-deionized water) was then pumped through the column at an approximate flow rate of 2 ml/min. Leachate samples of approximately 10 mls were collected in 35 ml polyethylene containers and were then analyzed for the anions chloride, fluoride, nitrate and sulfate using ion chromatography and for eighteen metals and metalloids using plasma emission spectroscopy as previously described.

Figure 4. Time Resolved Solvent Leaching (TRSL) Apparatus

RESULTS

Elemental Analyses

The results of the bulk analyses of Pittsburgh seam coal ash and Rosebud coal ash obtained by digestion of cyclone 1, cyclone 2 and bag-house material are given in Table 8. These results represent plasma emission data.

A complete list of samples analyzed by INAA appears in Table 9. These samples include the three bulk Rosebud samples as well as a large number of the samples collected at the various sampling temperatures. The samples were selected to provide a cross section of temperatures and sizes from both runs and included most, but not all, samples. The INAA results themselves, presented as a function of bulk collection point or particle size, are given in Tables 10, 11, and 12. Each temperature is broken down into three separate tables of major, minor and trace element concentrations which were arbitrarily defined as $>10,000 \mu\text{g/g}$ (0.1%), 50 to 10,000 $\mu\text{g/g}$ and $<50 \mu\text{g/g}$ respectively. The elements are listed roughly in order of decreasing concentration by impactor stage cut off.* To reflect the uncertainty in some of the numbers (significant figures) but still report the information reported by Illinois, some of the numbers have one or two numbers dropped 1/2 space. Thus $123_4 \pm 1_5$ is the same as 1234 ± 15 but indicates the last two numbers probably do not have too much meaning because of the uncertainty in the tens column. When there is no problem of this nature, the numbers are reported on one line, thus 4321 ± 5 . In some cases, small sample size hindered the analyses and only

*It should be noted that the size cut offs are only approximately aerodynamic values. They were calculated from the manufacturer's information (see Table 13) but were not corrected for particle density. Electron microscopic examination indicates that physical diameters reflected roughly $\pm 50\%$ of the aerodynamic size that is given.

Table 8
Fluidized Bed Coal Fly Ash Bulk Analyses (PES)
($\mu\text{g/g}$)

Pittsburgh Seam Coal

	Cyclone-1	Cyclone-2	Bag Filters
B			
Cd			
Be	< 43.4	< 44.6	< 41.3
Mg	5.31%	2.92%	2.64%
P	< 86.7	< 89.1	< 82.5
Si			
Mo*	< 43.4	< 44.6	< 41.3
Mn	< 86.7	< 89.1	< 82.5
Ni	< 43.4	< 44.6	< 41.3
Na	<1080	<1110	<1030
Cu	< 43.4	< 44.6	< 41.3
Al	> 2.77%	> 2.69%	> 2.91%
Ca	9.32%	5.72%	4.95%
Ba			
K	< 2.31%	3.48%	4.70%
Cr	< 43.4	< 44.6	< 41.3
Sr*	129	222	243
Pb*	73.6	< 71.3	< 66.0

Rosebud Coal

B			
Cd			
Be	< 48.5	< 46.0	< 42.6
Mg	<1210	<1150	<1060

Table 8 (cont.)

	Cyclone-1	Cyclone-2	Bag Filters
P			
Si			
Mo*	< 48.5	< 46.0	< 42.6
Mn	< 97.0	< 91.9	< 85.1
Ni	< 48.5	< 46.0	< 42.6
Na	<1210	<1150	<1060
Cu	< 48.5	< 46.0	< 42.6
Al	> 2.47%	> 2.62%	> 2.82%
Ca	24.9 %	19.8 %	21.9 %
Ba			
K	2.01%	3.08%	3.88%
Cr	< 48.5	< 46.0	< 42.6
Sr*	462	669	782
Pb*	92.1	72.9	114

*Ca stray light corrections applied

Table 9

Samples Analyzed by INAA

Run	Temp (°F)	Stage (50%) Cut off (μm)	Run	Temp (°F)	Stage (50%) Cut off (μm)
I	530	4.2	II	530	9.0
		2.7			6.1
		1.4			4.2
		0.83			2.7
	640				1.4
		9.3			0.83
		6.3			0.57
		4.3			
		2.8		640	9.3
		1.4			6.3
		0.86			4.3
		0.59			2.8
					1.4
	910	10.1			0.86
		6.8	910		
		4.7			10.1
		3.0			6.8
		1.5			4.7
		0.94			3.0
		0.64			1.5
					0.94
490		Bag House			
640		Cyclone #2			
910		Cyclone #1			

Table 10
Elemental Composition of Fluidized Bed Coal Fly Ash (INAA)

Run I - Bulk Samples

Major Elements

Element	Concentration (%)		
	Cyclone 1	Cyclone 2	Baghouse
Ca	11.8 ± 0.03	11.9 ₄ $\pm 0.2_7$	16.1 ₁ $\pm 0.3_5$
Al	5.70 ± 0.02	2.06 ± 0.01	5.43 ± 0.2
Fe	3.26 ± 0.03	3.06 ± 0.04	3.42 ± 0.03
Mg	0.80 ± 0.07	2.26 ± 0.09	3.15 ± 0.08
K	0.55 ₇ $\pm 0.01_4$	0.60 ₇ $\pm 0.2_4$	0.64 ₄ $\pm 0.01_8$
Na	0.1877 ± 0.0007	0.2438 ± 0.0009	0.2433 ± 0.0009

Table 10 (continued)

Run I - Bulk Samples

Minor Elements

Element	Concentration ($\mu\text{g/g}$)		
	Cyclone 1	Cyclone 2	Baghouse
Ba	4640 $\pm$ 60	2710 $\pm$ 40	954 $\pm$ 25
Sr	881 $\pm$ 47	1170 $\pm$ 60	1350 $\pm$ 60
Mn	517 $\pm$ 1	572 $\pm$ 1	749 $\pm$ 1
Zr	< 270	< 440	< 330
Ni	< 98	< 140	< 102
V	58 $\pm$ 4	26.5 $\pm$ 1.9	71 $\pm$ 3

Table 10 (continued)

Run I - Bulk Samples

Trace Elements

Element	Cyclone 1		Cyclone 2		Baghouse	
Cr	50	± 2	60	± 3	90	± 3
Zn	<39		<60		<46	
Ce	36.3	± 0.7	44	± 1	74.2	± 0.8
Rb	31	± 5	40	± 8	44	± 6
La	19.50	± 0.15	29.0	± 0.2	44.0	± 0.2
Ga	15.4	± 1.3	20.4	± 2.2	30	± 2
Nd	<15		<25		39	± 10
As	9.4 ₆	± 0.19	11.9	± 0.3	26.6	± 0.4
Th	7.7 ₅	± 0.13	11.7	± 0.3	16.9 ₄	± 0.16
Se	< 6.2		25	± 4	14	± 2
U	6.6 ₉	± 0.13	8.7	± 0.2	12.7 ₄	± 0.18
Br	5.5 ₉	± 0.18	5.3 ₀	± 0.22	10.5 ₀	± 0.25
Hf	5.7 ₆	± 0.15	6.5	± 0.2	5.6 ₉	± 0.15
Co	5.5	± 0.2	7.4	± 0.4	12.4	± 0.2
Hg	< 5.4		< 7.8		< 5.7	
Ta	5.2	± 0.9	5.1	± 0.8	4.1	± 0.4
Sc	4.67	± 0.02	6.43	± 0.03	10.52	± 0.03
Sm	2.98	± 0.01	4.24	± 0.2	6.31	± 0.2
Dy	2.4 ₉	± 0.12	3.3	± 0.2	4.4	± 0.2
Sb	2.33	± 0.03	2.91	± 0.05	6.21	± 0.5
Cs	2.0	± 0.3	2.8	± 0.4	2.3	± 0.3
W	< 1.6		< 2.6		7.9	± 0.9
Yb	1.36	± 0.05	1.88	± 0.08	2.50	± 0.07
Au	0.84		< 1.1		< 0.74	
Tb	< 0.80		< 1.2		1.4	± 0.4
Eu	0.692	± 0.22	0.803	± 0.033	1.219	± 0.028
Lu	0.45	± 0.02	0.64	± 0.02	0.75	± 0.02
In	0.51	± 0.02	0.81	± 0.03	1.73	± 0.04

Table 11A
 Elemental Composition of Fluidized Bed Coal Fly Ash (INAA)
 Run I - 530°F

Element	Major Elements			
	Stage Cut Off (μ)			
	4.2	2.7	1.4	0.83
	Concentration (%)			
Ca	<15.5	10.7 ± 0.7	11.9 ± 1.2	11.1 ± 1.4
Fe	12.8 ± 1.4	6.4 ₂ $\pm 0.1_4$	7.9 ₇ $\pm 0.3_6$	7.5 ₀ $\pm 0.4_6$
Al	7.3 ₀ $\pm 0.4_3$	3.5 ₅ $\pm 0.1_9$	7.6 ₉ $\pm 0.2_5$	7.9 ₀ $\pm 0.2_7$
Mg	< 3.2	< 1.0	< 1.7	2.4 ± 1.2
K	3.0 ₆ $\pm 0.2_2$	0.76 ₄ $\pm 0.05_4$	0.88 ₄ $\pm 0.05_7$	1.06 ± 0.07
Na	1.8 ₀	0.528 ₈ $\pm 0.008_6$	0.551 ± 0.003	0.636 ± 0.004

Table 11A (continued)

Run I - 530°F

Minor Elements

Stage Cut Off (μ)

Element	Concentration ($\mu\text{g/g}$)			
	4.2	2.7	1.4	0.83
Zr	<36000	< 210	<7020	<8700
Ni	<51000	< 915	<1000	<1240
Zn	< 3900	< 300	< 790	< 980
Ba	$19_{40}^{+2}_{-80}$	$20_{80}^{+1}_{-90}$	$15_{70}^{+1}_{-50}$	$15_{00}^{+1}_{-90}$
Cr	$20_{30}^{+1}_{-30}$	$15_1^{+1}_{-2}$	$41_0^{+2}_{-5}$	$43_0^{+30}_{-}$
Rb	< 2330	< 100	< 400	< 550
Sr	< 1200	$23_{00}^{+4}_{-60}$	$18_{10}^{+1}_{-70}$	$18_{80}^{+200}_{-}$
Mn	$684_{\pm 6}$	$1032_{\pm 9}$	$1026_{\pm 4}$	$1026_{\pm 5}$
Se	< 560	< 34	< 110	< 130
Br	$70_{4\pm 1_1}$	$5.7_{\pm 1.3}$	$84_{\pm 2}$	$108_{\pm 2}$
Ta	$39_{2\pm 3_5}$	< 5.1	$44_{\pm 8}$	$28_{\pm 8}$
Co	$31_{8\pm 2_8}$	$14.9_{\pm 1.6}$	$69_{\pm 6}$	$56_{\pm 7}$
Ce	< 244	$105_{\pm 6}$	$7_1^{+1}_{-5}$	< 64
Hg	< 210	< 0.07	< 44	< 54
V	$9_{5\pm 4_9}$	$9_7^{+22}_{-}$	$5_2^{+2}_{-8}$	$5_3^{+3}_{-7}$
Cs	< 89	< 6.2	< 18	< 18
In	$87_{\pm 1}$	$1.3_{7\pm 0.2_5}$	$34.0_{\pm 0.6}$	$42.9_{\pm 0.7}$
As	$8_{6\pm 1_3}$	$18.1_{\pm 2.4}$	$45_{\pm 3}$	$44_{\pm 4}$
Ga	< 77	$35.2_{\pm 6.5}$	$47_{\pm 6}$	$61_{\pm 7}$

Table 11A (continued)

Run I - 530°F

Trace Elements

Stage Cut Off (μ)

Element	Concentration ($\mu\text{g/g}$)			
	4.2	2.7	1.4	0.83
W	<82	<240	<17	<22
Hf	<58	8.1 ± 1.0	<11	<14
Th	<44	23.1 ± 1.1	20.4 ± 2.6	24.7 ± 3.1
Yb	<48	5.0 ± 0.8	< 9.8	3.9 ± 1.0
U	<32	14.4 ± 2.2	13.5 ± 1.9	13.7 ± 2.6
Sc	33 ± 1	16.7 $\pm 0.1_9$	13.4 ± 0.3	14.6 ± 0.4
Sb	29 ± 2	7.8 ± 0.5	55 ± 7	24.3 ± 0.6
La	31 ± 5.4	6.4 ± 1.4	6.3 ± 1.2	74 ± 1
Tb	<14	1.1 $\pm 0.2_3$	< 2.7	<34
Sm	5.8 ± 0.5	8.3 $\pm 0.1_4$	8.79 ± 0.09	8.7 ± 0.1
Eu	< 2.3	1.30 ± 0.09	1.24 ± 0.08	1.6 $\pm 0.1_1$
Lu	< 2.5	13.0 ± 2.4	0.9 $\pm 0.1_4$	0.8 $\pm 0.1_7$
Dy	2.6 ± 0.8	6.3 ± 1.3	5.7 ± 0.4	6.4 ± 0.5

Table 11B
Elemental Composition of Fluidized Bed Coal Fly Ash (INAA)

Run I - 640° F

Major Elements

Stage Cut Off (μ)

	9.3	6.3	4.3	2.8	1.4	0.86	0.59
Element	Concentration (%)						
Ca	8.2 ± 0.7	5.7 ₇ ± 0.1 ₉	8.8 ± 0.4	8.6 ₃ ± 0.2 ₆	12.5 ± 0.5	12.4 ± 1.0	< 28
Fe	11.8 ₁ ± 0.1 ₇	10.9 ₄ ± 0.1 ₀	10.06 ± 0.08	9.25 ± 0.09	10.4 ₂ ± 0.1 ₀	9.7 ₄ ± 0.3 ₁	13.0 ± 1.1
Al	2.3 ₅ ± 0.5	8.89 ± 0.04	4.9 ₀ ± 0.6 ₆	8.21 ± 0.03	4.6 ₀ ± 0.5 ₅	4.90 ± 0.08	1.25 ± 0.5 ₃
Mg	3.5 ± 0.1 ₅	3.0 ₈ ± 0.1 ₄	5.3 ± 1.4	3.2 ₆ ± 0.1 ₅	9.0 ± 1.5	8.2 ₀ ± 0.7 ₄	< 2.7
K	2.23 ± 0.04	2.09 ± 0.04	1.98 ₅ ± 0.03 ₈	1.51 ± 0.04	1.48 ± 0.03	1.15 ± 0.05	2.8 ± 0.3
Na	0.4880 ± 0.020	0.339 ± 0.002	0.0380 ± 0.01 ₄	0.364 ± 0.002	0.0382 ± 0.01 ₂	0.379 ± 0.002	< 0.1

Table 11B (continued)

Run I - 640°F

Minor Elements

Stage Cut Off (μ)

	9.3	6.3	4.3	2.8	1.4	0.86	0.59
Elements	Concentration ($\mu\text{g/g}$)						
Ti	<1000	*	<3200	*	<2000	*	$7_{400}^{+3}_{-600}$
Ba	530 ± 70	68_{2-6}^{+3}	1130 ± 50	1160 ± 50	1250 ± 70	13_{50-30}^{+1}	<15000
Ni	< 870	< 320	< 360	< 340	< 480	< 680	< 8400
Sr	460 ± 80	680 ± 70	950 ± 70	20_{70-40}^{+2}	1700 ± 100	19_{90-60}^{+1}	< 6000
Cu	< 410	*	< 700	*	<1000	*	< 2300
Mn	274 ± 2	315 ± 1	515 ± 1	641 ± 2	842 ± 2	1136 ± 4	99_{5-30}^{+}
Zn	< 310	< 140	< 120	< 150	< 180	<8600	< 2600
W	< 200	20 ± 2	54_{6-3}^{+2}	22 ± 2	530 ± 30	< 11	< 3200
Zr	< 210	<1030	< 90	<1100	< 120	<4840	< 2000
Cr	19_{3-1}^{+1}	216 ± 6	165 ± 4	192 ± 6	180 ± 6	$282 \pm 1_6$	12_{10-140}^{+}
V	16_{0-7}^{+1}	197 ± 7	18_{5-2}^{+3}	182 ± 8	24_{0-42}^{+}	19_{8-20}^{+}	< 110
Rb	< 110	20_{1-9}^{+1}	13_{3-4}^{+1}	9_{7-18}^{+}	10_{1-19}^{+}	< 290	< 1100
Ce	31 ± 6	64 ± 2	104 ± 2	113 ± 2	136 ± 3	12_{9-11}^{+}	< 240

*Data not available

Table 11B (continued)

Run I - 650°F

Trace Elements

Stage Cut Off (μ)

	9.3	6.3	4.3	2.8	1.4	0.86	0.59
Elements	Concentration ($\mu\text{g/g}$)						
Ga	45.8 ± 4.0	40 ± 3	63.1 ± 4.0	49 ± 4	73.9 ± 3.9	47 ± 5	<150
La	41.1 ± 1.5	38.9 ± 0.3	54.5 ± 0.8	53.8 ± 0.4	76.5 ± 1.1	89.1 ± 0.9	<200
Se	<30	48 ± 8	26 ± 6	59 ± 9	27 ± 7	<66	<390
As	30.8 ± 1.5	27 ± 1	31.3 ± 0.9	26 ± 2	38.9 ± 1.0	52 ± 3	55 $\pm$
Co	30.6 ± 1.7	33.9 ± 0.9	34.1 ± 0.6	33.1 ± 1.0	33.7 ± 0.8	46 ± 4	87 $\pm$
Br	39.3 ± 2.8	30.0 ± 0.7	20.8 ± 1.3	20.7 ± 0.6	18.2 ± 1.8	21.0 ± 0.7	<100
Sc	24.2 ± 0.2	21.76 ± 0.09	27.0 ± 0.1	23.1 ± 0.1	31.9 ± 0.1	19.6 ± 0.2	45.0 $\pm$
Th	15.7 ± 0.9	16.6 ± 0.3	19.3 ± 0.4	22.5 ± 0.3	21.1 ± 0.6	32.6 ± 1.8	< 32
U	< 9.5	14.2 ± 0.4	21.2 ± 1.8	16.9 ± 0.4	31.2 ± 2.7	25.9 ± 1.3	<140
Dy	9.9 ± 0.3	9.7 ± 0.2	10.3 ± 0.2	10.0 ± 0.3	11.1 ± 0.2	10.2 ± 0.4	< 30
Sm	8.3 ± 0.1	8.21 ± 0.03	9.1 ± 0.1	9.52 ± 0.03	12.1 ± 0.1	15.0 ± 0.1	< 10
Cs	8.6 ± 2.2	8.4 ± 0.9	7.6 ± 0.8	5.9 ± 0.9	6.6 ± 1.1	<12	< 57
Lu	< 6.2	0.81 ± 0.04	6.0 ± 0.7	1.03 ± 0.04	9.6 ± 1.0	1.06 ± 0.09	< 75
Yb	4.3 ± 0.7	4.8 ± 0.1	7.9 ± 0.3	4.5 ± 0.1	9.3 ± 0.5	5.7 ± 0.7	< 70
Sb	< 4.1	3.20 ± 0.09	3.6 ± 0.2	6.1 ± 0.1	7.5 ± 0.4	15.4 ± 0.03	< 60
Ta	< 4.0	13 ± 2	< 1.4	19 ± 3	1.5 ± 0.4	<11	< 60
Hf	3.7 ± 0.7	5.1 ± 0.4	4.8 ± 0.3	< 1.7	6.4 ± 0.5	9.3 ± 1.7	< 33
Tb	< 3.5 0.5 ₀	< 2.4	1.9 ± 0.1	< 2.5	< 1.7	< 1.7	< 28
Eu	2.0 ± 0.1	2.03 ± 0.05	1.68 ± 0.04	1.92 ± 0.06	2.31 ± 0.04	2.19 ± 0.07	< 7.0
In	1.5 $\pm$	2.46 ± 0.06	0.67 ± 0.09	2.06 ± 0.05	0.36 ± 0.06	4.4 ± 0.2	< 20
Hg	< 0.05	<16	< 0.08	<18	< 0.12	<28	< 0.7

Table 11C
Elemental Concentration of Fluidized Bed Coal Fly Ash (INAA)

Run I - 910°F								
Major Elements								
Stage Cut Off (μ)								
	10.1	6.8	4.7	3.0	1.5	0.94	0.64	
Element	Concentration (%)							
Fe	12.47 ± 0.08	14.78 $\pm 0.1_6$	6.8 $\pm 0.3_8$	11.0 $\pm 0.1_2$	3.4 $\pm 0.4_5$	15.2 $\pm 0.2_0$	14.7 ± 1.2	
Ca	9.7 ± 0.3	16.4 ± 0.7	9.3 ± 1.1	12.3 ± 0.5	<4.6	< 5.2	<14	
Al	3.5 ± 0.2	1.73 ± 0.09	4.5 $\pm 0.1_7$	2.7 $\pm 0.1_3$	2.09 ± 0.08	2.6 $\pm 0.1_4$	4.0 $\pm 0.1_1$	
K	1.27 $\pm 0.02_0$	0.77 $\pm 0.02_6$	1.29 ± 0.05	0.82 $\pm 0.02_6$	1.74 ± 0.08	0.97 $\pm 0.03_8$	3.8 $\pm 0.1_8$	
Mg	< 0.6	2.4 $\pm 1.1_0$	<1.3	< 0.5	5.7 ± 0.08	< 0.6	8.0 ± 2.1	
Na	0.357 ± 0.0009	0.263 ± 0.0014	0.71 ± 0.0003	0.258 ± 0.0014	0.678 ± 0.004	0.354 ± 0.0021	1.42 $\pm 0.08_7$	

Table 11C (continued)

Run I - 910°F

Minor Elements

Stage Cut Off (μ)

Element	10.1	6.8	4.7	3.0	1.5	0.94	0.64
	Concentration ($\mu\text{g/g}$)						
Ti	$3_{800}^{+1} 300$	$2_{500}^{+1} 200$	*	$16_{00}^{+6} 30$	*	$2_{100}^{+1} 000$	*
Sr	$760_{+} 50$	$4_{80}^{+} 1_{00}$	$6_{20}^{+1} 10$	$6_{20}^{+1} 50$	<360	$10_{60}^{+} 2_{00}$	< 990
Ba	$660_{+} 40$	$690_{+} 70$	$60_3^{+} 9_5$	$780_{+} 90$	$62_5^{+7} 3$	$9_{40}^{+} 2_{10}$	$18_{10}^{+2} 10$
Ni	$460_{+} 80$	< 702	< 0.113	< 520	< 0.140	< 750	< 0.405
Cu	< 600	< 390	*	< 470	*	< 590	*
Mn	$455_{+} 1$	$380_{+} 2$	$361_{+} 2$	$430_{+} 3$	$241_{+} 2$	$436_{+} 3$	$533_{+} 5$
Zn	$70_3^{+} 2_0$	$490_{+} 40$	< 0.106	$36_4^{+} 3_0$	$0.27_0^{+} 0.037$	< 310	< 0.352
Cr	$282_{+} 4$	$35_9^{+} 1_3$	$670_{+} 30$	$267_{+} 9$	560_{+40}	$33_8^{+} 1_4$	$2120_{+1} 20$
W	$25_0^{+} 1_6$	< 160	< 13	< 120	< 26	< 200	< 74
Zr	< 64	< 100	< 0.780	< 120	< 1.03	< 130	< 2.74
V	$110_{+} 20$	< 8.7	$6_8^{+} 2_4$	$125_{+} 17$	$3_7^{+1} 9$	$6_3^{+} 1_3$	< 140
Se	$19_{+} 4$	< 21	<120	< 16	<170	< 27	< 470
Rb	$65_{+} 9$	$80_{+} 2_3$	<570	$60_{+} 1_7$	<720	< 94	<2010

*Data not available

Table 11C (continued)

Run I - 910°F

Trace Elements

Stage Cut Off (μ)

	10.1	6.8	4.7	3.0	1.5	0.94	0.64
Element	Concentration ($\mu\text{g/g}$)						
Ce	52.7 ± 1.2	66 ± 4	54	49 ± 3	<73	<17	<213
La	35.1 ± 0.6	29.8 ± 1.0	24.2 ± 0.7	29.4 ± 0.8	4.4 ± 0.9	34.2 ± 1.4	18 ± 4
Co	23.9 ± 0.4	27.8 ± 1.1	35 ± 6	20.7 ± 0.8	57 ± 9	30.9 ± 1.5	140 ± 21
Ga	31.2 ± 2.1	18.9 ± 2.6	<20	21.2 ± 2.5	<25	23.2 ± 3.9	< 53
As	26.4 ± 0.6	13.9 ± 1.5	42 ± 3	21.6 ± 1.0	69 ± 4	22.9 ± 2.0	141 ± 12
Sc	15.36 ± 0.06	17.28 ± 0.15	9.5 ± 0.3	12.85 ± 0.11	7.8 ± 0.3	19.40 ± 0.20	23.8 ± 0.9
Br	8.6 ± 0.9	<10	40.4 ± 0.9	10.0 ± 1.9	73 ± 1	17.4 ± 2.8	175 ± 4
Th	11.9 ± 0.3	13.1 ± 0.7	11.1 ± 2.7	9.7 ± 0.5	<13	12.4 ± 1.0	< 37
Cd	< 5.6	<11	*	< 8.5	*	<13	*
U	8.0 ± 1.1	< 8.0	6.0	< 5.9	< 9.1	12.4 ± 1.0	26 $\pm$
Lu	4.7 ± 0.5	9.0 ± 1.7	< 0.46	6.7 ± 1.2	< 0.74	< 6.0	< 2.1
Cs	5.0 ± 0.6	11.2 ± 1.7	<20	3.3 ± 1.3	<26	< 5.4	< 70
Sm	6.50 ± 0.08	7.57 ± 0.17	4.28 ± 0.07	5.62 ± 0.13	0.84 ± 0.10	5.10 ± 0.34	2.9 ± 0.03
Dy	6.19 ± 0.19	4.1 ± 0.3	3.1 ± 0.3	5.61 ± 0.41	<35	6.7 ± 0.6	< 9.5
Yb	4.93 ± 0.23	4.6 ± 0.6	<10	3.4 ± 0.4	<15	< 4.6	< 41
Hf	3.88 ± 0.24	3.5 ± 0.6	<12	2.6 ± 0.5	<15	< 2.7	< 46
Ta	< 1.1	< 3.3	<19	< 2.5	36 ± 9	< 3.8	< 74
Sb	2.80 ± 0.21	3.0 ± 0.4	9.4 ± 0.4	2.3 ± 0.3	15.2 ± 0.5	< 4.5	30.5 ± 1.4
Tb	< 1.4	0.87 ± 0.16	< 3.0	< 2.2	< 4.1	< 3.0	< 12

*Data not available

Table 11C (continued)

Run I - 910°F

Trace Elements

Stage Cut Off (μ)

(Continued)

	10.1	6.8	4.7	3.0	1.5	0.94	0.64
Element	Concentration ($\mu\text{g/g}$)						
In	<0.31	1.21 ± 0.07	11.5 ± 2	1.36 ± 0.21	< 0.37	<1.1	<1.1
Eu	1.207 ± 0.026	0.80 ± 0.03	0.51 ± 0.07	0.88 ± 0.03	< 0.63	1.08 ± 0.05	0.989 ± 0.071
Hg	<0.016	<0.04	<46	<0.03	<64	<0.05	<0.06

Table 12A
Elemental Composition of Fluidized Bed Coal Fly Ash (INAA)

Run II - 530°F

Major Elements

Stage Cut Off (μ)

	9.0		6.1		4.2		2.7		1.4		0.83		0.57	
Element	Concentration (%)													
Ca	13.0	± 2.7	14.1	± 0.5	18.0	± 0.5	19.0	± 0.6	22.9	± 0.7	19.1	± 0.7	<38	
Fe	6.2	± 0.3	3.41	± 0.07	3.55	± 0.05	3.65	± 0.06	3.52	± 0.06	3.9 ₂	$\pm 0.1_0$	8.0	± 1.8
Al	2.7 ₈	$\pm 0.2_4$	3.4 ₀	± 0.29	2.6 ₇	$\pm 0.1_4$	2.1 ₀	$\pm 0.1_1$	2.2 ₂	$\pm 0.1_2$	2.5 ₀	$\pm 0.1_2$	< 0.66	
Mg	< 1.1		< 0.9		5.0	± 1.3	< 0.62		2.1	± 1.0	7.9	± 2.5	< 0.83	
K	0.6 ₇	$\pm 0.1_1$	0.83 ₇	± 0.037	0.60 ₁	$\pm 0.1_9$	0.40 ₇₀ ⁺²⁶⁰		0.4 ₂	$\pm 0.01_4$	0.95	± 0.09	< 1.4	
Na	0.0397 ₀ ^{+0.006₆}		0.367 ₁ ^{+2₀}		0.267 ₀ ^{+0.001₂}		0.188 ₅ ^{+1₄}		0.1637 ^{+0.0007}		0.0198 ₉ ^{+2₁}		< 0.1250	

Table 12A (continued)

Run II - 530°F

Minor Elements

Stage Cut Off (μ)

Element	9.0	6.1	4.2	2.7	1.4	0.83	0.57
	Concentration ($\mu\text{g/g}$)						
Sr	< 3300	16_{30-2}^{+60}	$10_{90} \pm 1_{40}$	14_{30-1}^{+80}	$1420_{\pm 90}$	<1370	< 7700
Ti	< 2100	<1600	$3_{600} \pm 1_{500}$	<1300	$3200_{\pm 1100}$	$6400_{\pm 1700}$	< 1300
Ba	$1900_{\pm 400}$	11_{90-1}^{+100}	1060 ± 60	$780_{\pm 80}$	$680_{\pm 50}$	7_{80-1}^{+170}	<20000
Mn	$870_{\pm 9}$	$789_{\pm 5}$	801 ± 4	$816_{\pm 5}$	$824_{\pm 2}$	$910_{\pm 9}$	710
Cu	< 900	< 630	< 490	< 520	6_{70-3}^{+60}	< 490	< 800
Ni	100_{80-9}^{+40}	< 510	< 390	< 420	< 360	< 640	<11000
Cr	$4520_{\pm 70}$	$433_{\pm 9}$	336 ± 5	$235_{\pm 6}$	$149_{\pm 5}$	25_{3-1}^{+10}	23_{70-2}^{+20}
Zn	< 570	< 170	< 120	< 150	< 140	< 230	< 3100
W	< 770	< 130	< 80	< 100	13_{6-2}^{+7}	< 180	< 4600
Zr	< 480	< 120	< 77	< 96	< 90	< 150	< 2600
Rb	< 250	< 57	< 37	< 48	< 40	< 75	< 1500
V	10_{0-2}^{+7}	$78_{\pm 16}$	$2.3_{\pm 1.8}$	< 10	9_{4-1}^{+5}	12_{0-1}^{+8}	< 125

Table 12A (continued)

Run II - 530°F

Trace Elements

Stage Cut Off (μ)

Element	Concentration ($\mu\text{g/g}$)						
	9.0	6.1	4.2	2.7	1.4	0.83	0.57
Ce	<65	57 ± 4	62.3 ± 2.1	67.9 ± 2.8	70.3 ± 2.7	86 ± 5	<380
La	34 ± 4	45.7 ± 0.7	47.9 ± 0.5	45.1 ± 0.6	50.8 ± 0.8	63.2 ± 1.0	<210
Ga	<37	31.8 ± 3.7	29.6 ± 2.3	31.8 ± 3.2	41.6 ± 2.4	41.8 ± 5.3	<200
As	<20	27.4 ± 1.8	31.1 ± 1.1	23.5 ± 1.7	34.2 ± 0.8	45.3 ± 2.1	<100
Se	<90	<18	<12	<14	<12	<24	<570
U	<33	10.6 ± 1.1	13.3 $\pm 0.7_1$	17.7 ± 1.1	8.9 ± 1.6	15.1 ± 1.8	<160
Lu	<21	13.1 ± 1.5	18.6 ± 1.1	14.3 ± 1.2	6.0 ± 0.9	13.0 ± 1.9	<130
Co	34 ± 4	13.6 ± 0.9	12.2 ± 0.6	32.1 ± 1.0	11.5 ± 0.6	15.4 ± 1.2	110 ± 30
Th	11.1 ± 2.6	15.8 ± 0.6	17.2 $\pm 0.3_4$	15.2 ± 0.5	16.5 ± 0.5	19.5 ± 0.7	< 43
Br	<50	17.1 ± 1.5	10.7 ± 0.8	7.3 ± 1.0	8.5 ± 1.3	20.2 ± 3.8	<100
Sc	11.0 ± 0.3	11.2 $\pm 0.1_1$	11.97 ± 0.08	11.63 ± 0.09	11.57 ± 0.09	13.9 $\pm 0.1_4$	25.4 ± 1.7
Sb	9.9 ± 1.8	4.9 $\pm 0.2_1$	6.1 $\pm 0.1_5$	7.0 $\pm 0.2_0$	7.5 ± 0.3	9.4 ± 0.3	< 87
Sm	< 2.4	6.34 ± 0.07	6.96 ± 0.05	6.98 ± 0.07	6.7 $\pm 0.1_2$	8.3 $\pm 0.1_2$	< 11
Cd	<49	< 4.4	< 2.8	< 3.9	< 7.0	< 6.7	<220
Dy	4.4 ± 1.3	5.0 ± 0.8	4.6 ± 0.5	5.8 ± 0.8	5.3 $\pm 0.2_5$	5.8 ± 1.6	< 30
Hf	< 8.0	4.2 ± 0.5	3.9 $\pm 0.3_3$	2.6 ± 0.4	3.8 ± 0.4	5.2 ± 0.7	< 47
Cs	<14	< 3.4	3.9 ± 0.7	< 2.4	< 1.3	< 4.6	< 80
Yb	<17	2.2 ± 0.4	3.3 $\pm 0.2_5$	2.2 $\pm 0.3_3$	--	4.2 ± 0.6	<100
Ta	<15	< 3.3	1.8	< 2.2	< 1.8	< 3.7	< 86
Tb	< 7.0	< 1.9	1.00 ± 0.09	0.8 $\pm 0.1_2$	< 1.6	< 2.4	< 40
Au	< 6.2	< 2.1	< 1.2	< 1.2	< 0.6	< 1.9	< 30
In	4.3 ± 0.5	1.1 $\pm 0.1_0$	< 0.22	< 0.82	0.49 ± 0.04	< 2.2	< 20
Eu	< 2.0	1.02 ± 0.05	1.10 $\pm 0.02_5$	1.20 $\pm 0.05_4$	1.28 $\pm 0.02_5$	1.1 $\pm 0.1_1$	< 10
Hg	< 0.17	< 0.04	< 0.02	< 0.03	< 0.03	< 0.05	< 1.0

Table 12B
Elemental Concentration of Fluidized Bed Coal Fly Ash (INAA)

Run II 640 °F												
Major Elements												
Stage Cut Off (μ)												
9.3		6.3		4.3		2.8		1.4		0.86		
Element	Concentration (%)											
Ca	6.5	±0.5	10.0 ₁	±0.1 ₁	14.1	±0.4	8.1 ₀	±0.4 ₁	18.6	±0.6	12.2	±0.5 ₇
Fe	10.5 ₉	±0.1 ₂	7.8 ₈	±0.2 ₆	8.24	±0.08	14.5	±1.6	5.39	±0.08	< 6.2	
Mg	3.8	±0.6	7.75	±0.03	3.2	±1.3	5.1 ₃	±0.1 ₁	< 0.56		4.2 ₃	±0.0 ₈
Al	3.1 ₀	±0.1 ₅	2.7 ₂	±0.1 ₉	3.0 ₀	±0.1 ₅	14.4	±2.0	2.3 ₀	±0.1 ₂	9.2	±1.3
K	1.97 ₁	±0.03 ₈	1.8 ₈	±0.0 ₅	1.38 ₂	±0.03 ₅	1.3 ₈	±0.0 ₉	0.70 ₄	±0.02 ₆	--	
Na	0.0284 ₉	±0.001 ₄	0.327	±0.002	0.0285 ₂	±0.001 ₅	0.702	±0.005	0.128 ₉	±0.001 ₃	0.679±0.005	

Table 12B (continued)

Run II 640 °F						
Minor Elements						
Stage Cut Off						
	9.3	6.3	4.3	2.8	1.4	0.86
Element	Concentration (μg/g)					
Ti	$13_{00}^{+6}_{-40}$	*	<1200	*	$21_{00}^{+7}_{-80}$	*
Sr	650 ± 70	690 ± 90	$12_{50}^{+1}_{-90}$	$9_{60}^{+200}_{-}$	$15_{80}^{+2}_{-40}$	$17_{30}^{+2}_{-50}$
Ba	390 ± 60	$66_{1}^{+4}_{-5}$	970 ± 30	$7_{60}^{+200}_{-}$	880 ± 90	$7_{40}^{+200}_{-}$
Mn	276 ± 1	364 ± 2	583 ± 4	689 ± 4	791 ± 5	914 ± 5
Cu	< 590	*	< 530	*	< 450	*
Ni	$12_{60}^{+1}_{-60}$	< 400	< 440	<1210	< 56	< 1580
Cr	$16_{8}^{+1}_{-0}$	237 ± 7	154 ± 5	$77_{6}^{+35}_{-}$	193 ± 7	3140 ± 80
Zn	< 240	< 190	< 170	<1070	< 150	< 1260
V	150 ± 20	178 ± 8	$20_{0}^{+2}_{-4}$	$15_{7}^{+38}_{-}$	130 ± 20	$10_{9}^{+37}_{-}$
Zr	< 140	<1240	< 110	<8230	< 120	<10750
Rb	< 72	116 ± 1	$13_{4}^{+1}_{-4}$	< 570	< 52	--

*Data not available

Table 12B (continued)

Run II - 640°F

Trace Elements

Stage Cut Off

	9.3	6.3	4.3	2.8	1.4	0.86
Element	Concentration (μg/g)					
Ce	46 ± 5	99 ± 3	80.3 ± 2.4	61 ± 1.7	80 ± 3	< 84
La	35.4 ± 1.1	38.3 ± 0.4	52.6 ± 0.6	44.4 ± 1.3	57.6 ± 0.7	61 ± 2
Ga	39.7 ± 3.1	42 ± 4	37.8 ± 3.1	< 27	40.0 ± 3.2	37 ± 9
As	29.9 ± 1.1	35.4 ± 0.8	32.1 ± 1.2	47 ± 5	39.6 ± 1.4	66 ± 6
Co	26.7 ± 1.0	30.7 ± 1.2	28.2 ± 0.8	69.9 ± 7.7	19.5 ± 0.9	100 ± 12
Sc	19.8 ₈ $\pm 0.1_4$	19.9 ₂ $\pm 0.1_0$	23.7 ₂ $\pm 0.1_1$	17.9 ± 0.4	17.7 ₇ $\pm 0.1_1$	22.4 ± 0.4
Th	12.0 ± 0.6	17.5 ± 0.6	18.2 ± 0.5	16.6 ± 2.4	19.0 ± 0.6	< 14
Se	< 18	49 ± 9	18 ± 4	< 127	< 16	< 168
Lu	< 3.8	0.79 $\pm$ 0.04	17.2 ± 1.2	< 0.51	18.2 ± 1.4	< 0.78
U	< 7.7	11.7 ± 0.5	15.9 ± 0.9	14.0 ± 3.2	15.0 ± 1.0	< 13
Br	40.0 ± 2.3	31.6 ± 0.8	8.0 ± 0.9	85 ± 2	12.9 ± 1.2	191 ± 3
Dy	7.7 ₂ $\pm 0.2_9$	8.6 ± 0.3	9.6 ± 0.6	5.6 ± 0.5	8.7 ± 0.8	6.0 ± 0.6
Sm	7.6 ₈ $\pm 0.1_7$	7.34 $\pm$ 0.03	9.34 $\pm$ 0.07	10.8 ± 0.2	8.54 $\pm$ 0.08	4.15 $\pm$ 0.2 ₀
Cd	< 11	*	< 4.3	*	< 4.8	*
Cs	10.9 ± 1.5	6.5 ± 1.1	4.5 ± 1.0	< 22	3.4 ± 1.0	< 28
Yb	4.6 ± 0.5	3.9 ₃ $\pm 0.1_8$	6.4 ± 0.3	< 12	5.5 ± 0.4	< 15
Hf	< 2.1	< 2.0	6.2 ± 0.5	< 12	5.4 ± 0.5	< 17
Sb	1.9 ± 0.4	3.4 ₃ $\pm 1_1$	3.9 ₇ $\pm 0.2_1$	22.7 ± 0.6	8.6 ₈ $\pm 0.2_3$	18.4 ± 0.9
Ta	< 2.7	< 10	2.1 ± 0.5	< 20	< 2.4	< 29
Eu	1.53 ₉ $\pm 0.03_9$	1.73 $\pm$ 0.06	1.46 $\pm$ 0.04	1.14 $\pm$ 0.12	1.43 $\pm$ 0.04	1.3 ₆ $\pm 0.1_3$
Au	< 0.84	< 3.0	< 1.3	--	< 1.4	--
Tb	0.6 ₂ $\pm 0.1_3$	< 2.8	1.3 ₀ $\pm 0.1_1$	< 3.1	1.3 ₅ $\pm 0.1_5$	< 4.1
In	< 1.6	5.74 $\pm$ 0.08	< 0.55	154 ± 2	< .47	123 ± 2
Hg	< 0.04	*	< 0.03	*	< 0.03	*
W	< 130	24 ± 3	280 ± 30	< 20	21 ₄ $\pm 3_4$	< 28

Table 12C
Elemental Concentration of Fluidized Bed Coal Fly Ash (INAA)

Run II - 910°F										
Major Elements										
Stage Cut Off (μ)										
Concentration (%)										
Element	10.1		6.8		4.7		3.0		1.5	
Ca	15.7	± 0.5	17.6	± 0.5	19.6	± 0.6	20.7	± 0.7	25.4	± 0.8
Fe	5.63	± 0.06	4.31	± 0.04	4.00	± 0.03	3.92	± 0.06	3.81	± 0.07
Mg	< 0.8		1.8	$\pm 0.7_7$	7.8	± 2.6	9	± 3	3.3	± 0.8
Al	3.6 ₀	$\pm 0.2_7$	1.7 ₀	$\pm 0.1_3$	2.9 ₀	$\pm 0.2_1$	2.7 ₀	$\pm 0.3_0$	2.0	± 0.1
K	0.909	$\pm 0.01_9$	0.92 ₈	$\pm 0.02_0$	0.71	$\pm 0.01_8$	0.61 ₃	$\pm 0.01_6$	0.38 ₇	$\pm 0.1_{90}$
Na	0.3225	± 0.0009	0.369 ₅	$\pm 0.001_1$	0.369 ₆	$\pm 0.001_1$	0.2275	± 0.0008	0.162 ₁	$\pm 0.001_6$
									0.356 ₇	$\pm 0.004_0$

Table 12C (continued)

Run II - 910°F						
Minor Elements						
Stage Cut Off (μ)						
	10.1	6.8	4.7	3.0	1.5	0.94
Element	Concentration ($\mu\text{g/g}$)					
Ti	<1900	<1400	$4_{700}^{+1}800$	<2220	$23_{00}^{+8}30$	2400 ± 1000
Sr	930 ± 70	1260 ± 70	1500 ± 80	1410 ± 80	$12_{70}^{+1}10$	<2900
Ba	1040 ± 50	990 ± 50	810 ± 50	640 ± 40	660 ± 70	<2800
Mn	603 ± 2	639 ± 2	687 ± 2	722 ± 2	735 ± 3	900 ± 10
Cu	< 600	< 420	< 670	< 780	< 380	< 600
Ni	< 240	< 240	< 310	< 390	< 440	<1300
Zn	< 90	$60_{4}^{+1}9$	$62_{7}^{+}24$	< 140	$39_{8}^{+}29$	< 560
W	$14_{5}^{+1}7$	$5_{8}^{+1}2$	< 85	$13_{6}^{+2}6$	< 100	< 650
Cr	138 ± 3	116 ± 3	109 ± 4	109 ± 5	123 ± 6	$21_{1}^{+}26$

Table 12C (continued)

Run II - 910°F

Trace Elements

Stage Cut Off (μ)

	10.1	6.8	4.7	3.0	1.5	0.94
Elements	Concentration ($\mu\text{g/g}$)					
Zr	< 61	< 53	< 76	< 100	< 100	< 440
Rb	4 ₉ $\pm$ 1 ₀	34 $\pm$ 9	< 37	< 46	< 52	< 230
Ce	54 $\pm$ 2	49 $\pm$ 2	66.1 $\pm$ 1.9	74.4 $\pm$ 2.8	59 $\pm$ 4	118 $\pm$ 20
La	36.4 $\pm$ 0.6	45.3 $\pm$ 0.7	42.9 $\pm$ 0.8	45.8 $\pm$ 0.8	49.6 $\pm$ 1.1	59 $\pm$ 3
Ga	31.3 $\pm$ 2.2	27.3 $\pm$ 2.3	33.0 $\pm$ 2.5	36 $\pm$ 2	33.2 $\pm$ 2.6	36.9 $\pm$ 8.4
V	7 ₃ $\pm$ 2 ₀	24 $\pm$ 8	< 14	29 $\pm$ 1 ₇	10 ₀ $\pm$ 1 ₄	3 ₆ $\pm$ 2 ₃
As	14.4 $\pm$ 0.8	19.4 $\pm$ 0.7	23.3 $\pm$ 0.8	27.6 $\pm$ 1.1	34.3 $\pm$ 1.0	44.9 $\pm$ 6.2
Th	13.0 $\pm$ 0.3	15.3 $\pm$ 0.3	< 1.3	14.0 $\pm$ 0.5	14.2 $\pm$ 0.5	23.1 $\pm$ 2.5
Co	14.6 $\pm$ 0.4	12.4 $\pm$ 0.4	11.9 $\pm$ 0.5	12.4 $\pm$ 0.6	11.6 $\pm$ 0.7	17 $\pm$ 5
Se	< 7.9	12 $\pm$ 3	< 10	< 14	< 15	< 83
Sc	11.32 $\pm$ 0.06	11.88 $\pm$ 0.06	11.76 $\pm$ 0.07	11.27 $\pm$ 0.09	11.81 $\pm$ 0.1 ₀	15.4 $\pm$ 0.4
Br	8.7 $\pm$ 1.8	5.9 $\pm$ 1.1	9.8 $\pm$ 1.5	< 7.5	11.1 $\pm$ 1.8	< 34
Cd	< 6.1	< 5.4	< 6.8	< 7.4	< 11	< 33
U	< 4.0	10.3 $\pm$ 1.1	17.1 $\pm$ 1.4	6.4 $\pm$ 1.6	14.7 $\pm$ 2.2	< 23
Cu	5.0 $\pm$ 0.6	5.3 $\pm$ 0.6	7.1 $\pm$ 0.8	6.4 $\pm$ 1.0	5.3 $\pm$ 1.0	< 17
Sm	6.02 $\pm$ 0.09	6.65 $\pm$ 0.08	6.3 ₀ $\pm$ 0.1 ₀	5.7 ₂ $\pm$ 0.1 ₅	7.0 ₅ $\pm$ 0.1 ₇	7.0 $\pm$ 0.6
Dy	5.1 $\pm$ 0.2	4.5 $\pm$ 0.2	4.9 $\pm$ 0.2	5.0 $\pm$ 0.2	5.2 $\pm$ 0.3	8.0 $\pm$ 1.4
Sb	2.4 ₆ $\pm$ 0.2 ₁	3.9 ₈ $\pm$ 0.2 ₁	4.8 ₄ $\pm$ 0.2 ₆	6.9 $\pm$ 0.3	8.3 $\pm$ 0.4	10.9 $\pm$ 1.3
Hf	4.5 $\pm$ 0.3	4.5 ₁ $\pm$ 0.2 ₃	3.9 $\pm$ 0.3	3.9 $\pm$ 0.4	4.1 $\pm$ 0.5	< 7.1
Cs	< 1.9	3.6 $\pm$ 0.5	2.2 $\pm$ 0.6	< 2.7	< 3.1	< 13
Yb	2.6 ₀ $\pm$ 0.2 ₂	4.0 ₉ $\pm$ 0.2 ₃	3.4 $\pm$ 0.3	2.3 $\pm$ 0.4	--	6.3 $\pm$ 1.9
Ta	< 1.1	< 1.2	< 1.1	< 2.0	< 2.3	< 13
Tb	0.86 $\pm$ 0.07	0.93 $\pm$ 0.07	< 1.3	< 1.8	< 1.7	< 6.8
Eu	0.98 ₃ $\pm$ 0.02 ₃	0.94 ₁ $\pm$ 0.02 ₄	1.05 ₂ $\pm$ 0.02 ₄	1.32 ₆ $\pm$ 0.02 ₈	1.18 $\pm$ 0.04	1.2 ₅ $\pm$ 0.1 ₄
Al	< 0.43	< 0.42	< 0.54	< 0.7	< 0.66	< 4.3
In	< 0.25	< 0.48	0.32 $\pm$ 0.06	0.43 $\pm$ 0.03	1.07 $\pm$ 0.09	< 1.8
Hg	< 0.016	< 0.016	< 0.02	< 0.03	< 0.03	< 0.15

a "less than" value could be reported. The samples were sent in on two separate occasions and the data was compiled separately. As a result, the data for a particular run and a particular temperature will appear in several tables depending on the size cut off analyzed.

Scanning Electron Microscopy (SEM)

1. Sizing Studies

Electron microscopy was used in three major capacities in the analysis of METC samples. The first of these measured the uniformity and size of the fractionated samples. Specifically, samples from the middle temperature (640°) collection period during the second Rosebud run (6.28 lb/hr limestone feed rate) were examined. The particle sizes were quite uniform, at least for the larger stages. Stage cuts of 7-11 μm , 5-7 μm , 4-5 μm , 2-4 μm , $\sim 2 \mu\text{m}$ and $\sim 1 \mu\text{m}$ were observed for stages 1 to 6 respectively. Stages 7 and 8 could not be sized due to the small amount of material collected. These values agree well with those indicated by the manufacturer. For comparative purposes, the manufacturer's values for different flow rates and air temperatures is given in Table 13. It should be noted that the density of the fly ash is higher ($2-3 \text{ g/cm}^3$) than that of the representative particle given in the table. Mechanically sized material from cyclones 1 and 2 (sieved with a Model Corp. Sonic Sifter, ATM Corp., Milwaukee, Wisc.) resulted in the size distributions given in Table 14. Not unexpectedly, this ash is considerably larger than that collected using the stack sampler.

2. Morphological and X-ray Analysis

Material from various stages was examined with the SEM to obtain qualitative information on particle morphology and chemical composition. The particles were similar in appearance to those shown in the Lovelace report (Carpenter, et al. 1978). Representative particles are shown in

Table 13

Anderson Marle III Stack Sampler
 50% Effective Cut Diameter
 Particle Density = 1.0 gm/cc

Flow acfm	Stage No. 0	Preimpactor	Cyclonic Preseparator	Stage No. 1	Stage No. 2	Stage No. 3	Stage No. 4	Stage No. 5	Stage No. 6	Stage No. 7
Air Temp = 300°F										
0.1	34.0	31.6	25.4	21.3	14.5	9.9	6.4	3.3	2.1	1.4
0.2	24.0	22.4	18.0	15.0	10.2	7.0	4.5	2.3	1.4	0.99
0.3	19.5	18.2	14.6	12.2	8.3	5.6	3.6	1.8	1.1	0.79
0.4	16.9	15.8	12.7	10.6	7.2	4.9	3.2	1.6	1.0	0.68
0.5	15.1	14.2	11.4	9.5	6.4	4.4	2.8	1.4	0.88	0.60
0.6	13.7	12.9	10.3	8.6	5.8	4.0	2.5	1.3	0.79	0.54
0.7	12.8	11.9	9.6	8.0	5.4	3.7	2.4	1.2	0.73	0.49
0.75	12.4	11.6	9.3	7.7	5.2	3.6	2.3	1.1	0.70	0.48
Air Temp = 500°F										
0.1	36.6	34.3	27.4	22.9	15.6	10.7	6.9	3.5	2.2	1.5
0.2	25.9	24.3	19.4	16.2	11.0	7.5	4.9	2.5	1.5	1.1
0.3	21.1	19.8	15.8	13.2	9.0	6.1	4.0	2.0	1.2	0.86
0.4	18.3	17.1	13.7	11.4	7.8	5.3	3.4	1.7	1.1	0.74
0.5	16.3	15.4	12.3	10.2	6.9	4.7	3.0	1.5	1.0	0.65
0.6	14.9	14.0	11.2	9.3	6.3	4.3	2.8	1.4	0.86	0.59
0.7	13.8	13.0	10.4	8.6	5.8	4.0	2.6	1.3	0.79	0.54
0.75	13.3	12.6	10.0	8.3	5.6	3.8	2.5	1.2	0.76	0.52
Air Temp = 1000°F										
0.1	42.0	38.6	31.4	26.3	17.9	12.2	7.9	4.0	2.5	1.8
0.2	29.7	27.4	22.2	18.6	12.6	8.6	5.6	2.8	1.8	1.2
0.3	24.2	22.3	18.1	15.1	10.3	7.0	4.5	2.3	1.4	1.0
0.4	21.0	19.3	15.7	13.1	8.9	6.1	3.9	2.0	1.2	0.85
0.5	18.7	17.3	14.1	11.7	8.0	5.4	3.5	1.8	1.1	0.76
0.6	17.1	15.8	12.8	10.7	7.3	5.0	3.2	1.6	1.0	0.68
0.7	15.8	14.6	11.9	9.9	6.7	4.6	2.9	1.5	0.92	0.63
0.75	15.3	14.2	11.5	9.5	6.5	4.4	2.8	1.4	0.88	0.60

Table 14
Physical Size Distribution of RB-5 Material

	Cyclone 1	Cyclone 2
> 75 m	67.0%	29.4%
60-75	7.9	27.4
45-60	7.3	2.1
20-45	15.4	19.9
< 20	2.5	21.0
Recovery	98.0%	90.0%

Figure 5. SEM-EDS X-ray analyses indicated that the concentrations of most trace elements were below the detection limits of the instrument (1-2% atomic). The main elements observed with this technique were silicon, aluminum, calcium, iron and sulfur. It should be emphasized that the presence of alkali or transition elements is not ruled out, but it is clear that their surface concentrations, at least, are relatively small.

3. Corrosion of Impactor Plates

One set of stainless steel cascade impactor plates were corroded during the initial (low limestone - 910° temperature) sampling period. The corroded sections of the plates were examined using the SEM and the results compared to those obtained from uncorroded areas of the same plates. Both areas are shown in the electron photomicrograph in Figure 6. X-ray analysis of the smooth and corroded part of the plates using the SEM was unable to distinguish between the two areas. Normalized signal intensity ratios showed Fe 1.00; Cr 0.56; and Ni 0.22 for both areas.

Surface Analysis

In general, surface analyses provided limited information to the corrosion studies. Only elements characteristic of the known bulk ash composition were observable. The elements found using Auger Electron Spectrometry are given in Table 15. Analyses reported in Table 15 were done only on the smallest bulk sample, that from the bag house.

Table 15 also lists some of the problems accompanying the analyses. A considerable problem was encountered in the detection of both sodium and potassium, the two metals of greatest interest in the corrosion problems observed in fluidized beds.

Leaching

The results of the bulk leaching (using the sonic disrupter) of both Pittsburgh Seam Coal fly ash and Rosebud Coal fly ash are given in Table 16.

Figure 5. Representative Fluidized Bed Combustor Particles
(1000X) (1 cm = 10 μm)

A. Unexposed (5000X)

B. Exposed to FBC Fly Ash and Gas Stream at 910°F (5000X)

C. Higher Magnification of B (10,000X)

Figure 6. Electron Photomicrograph of Impactor Plate

Table 15

Auger Electron Spectrometry (AES) Analyses of FBC Bag House Samples

<u>Sample</u>	<u>Elements Observed</u>	<u>Comments</u>
Rosebud Coal	P, S, C, Ca, Ti O, Fe, Mg, Al, Si	1. Sample homogeneity: fair 2. Sample charging Ep = 3kv: Minimal Ep = 5kv: No information below 200 eV
Pittsburgh Coal	S, C, Ca, Ti, O	1. Sample homogeneity: poor Ep = 3kv: + 15eV shift; no information below 130-200 eV Ep = 5kv: + 15eV shift; no information below 250 eV

Note: S/N fair, minimum detectable concentration ~0.5%. Low primary beam current used to prevent decomposition.

TABLE 16
FBC Fly Ash Bulk Leaching Analyses
($\mu\text{g/g}$)

Pittsburgh Seam Coal

	Cyclone-1	Cyclone-2	Bag Filters
B	41.3	36.6	
Cd	<5.88	<6.11	<5.93
Be	<5.88	<6.11	<5.93
Mg	<147	<153	<148
P	19.3	<12.2	15.3
Si	790	605	1280
Mo*	10.5	8.07	11.32
Mn	<11.8	<12.2	<11.8
Ni	<5.88	<6.11	<5.93
Na	214	276	454
Cu	<5.88	<6.11	<5.93
Al	68.3	27.4	39.6
Ca	3.20%	2.36%	2.17%
Ba	22.0	17.2	18.7
K	262	466	401
Cr*	<5.88	<6.11	<5.93
Sr*	45.5	75.3	105
Pb*	30.9	13.3	18.0

Rosebud Coal

B	<6.59	<6.36	<6.24
Cd	<6.59	<6.36	<6.24
Be	<6.59	<6.36	<6.24
Mg	<165	<160	<156

TABLE 16 (CONT.)

	Cyclone-1	Cyclone-2	Bag Filters
P	<13.2	<12.7	<12.5
Si	82.9	79.4	47.8
Mo*	15.8	16.0	10.0
Mn	<13.2	<12.7	<12.5
Ni	<6.59	<6.36	<6.24
Na	<165	<158	<156
Cu	<6.59	<6.36	<6.24
Al	58.9	51.3	46.0
Ca	6.70%	5.90%	4.35%
B	29.0	57.2	56.1
K	228	226	246
Cr*	<6.59	<6.39	<6.24
Sr*	195	232	387
Pb*	34.4	30.9	20.8

* stray light corrections applied.

These results are limited to the bulk samples since there was insufficient fractionated material to leach.

In Tables 17 through 19 can be found the anionic data from Time Resolved Solvent Leaching (TRSL) of the bulk Rosebud samples. Some of the results are also presented graphically in Figures 7 to 11. A similar presentation of the corresponding cationic results can be found in Tables 20 to 22. Figures 12, 13, and 14 show the leaching curves for Ba, Ca, and Si respectively.

Table 17
Anionic Results of TRSL of Cyclone 1 FBC Fly Ash
Concentration
($\mu\text{g/g}$ fly ash)

70

Time (min)	F^-	Cl^-	NO_3^-	$\text{SO}_4^{=}$
10	13.5	7.18	<1.06	8350
20	20.0	22.4	<1.06	>3200
40	12.6	3.59	<1.06	2750
80	12.3	<1.06	<1.06	1380
160	5.29	<1.06	<1.06	744
320	<1.06	<1.06	<1.06	316
640	<1.06	<1.06	<1.06	109
1280	<1.06	<1.06	<1.06	4.23
1460	<1.06	<1.06	<1.06	0
1800	<1.06	<1.06	<1.06	0

Table 18
Anionic Results of TRSL of Cyclone 2 FBC Fly Ash
Concentration
($\mu\text{g/g}$ fly ash)

Time (min)	F^-	Cl^-	NO_3^-	$\text{SO}_4^{=}$
10	16.9	<0.20	<0.20	13400
20	15.2	5.44	<0.20	1190
40	11.9	<0.20	<0.20	452
80	6.38	<0.20	<0.20	278
160	2.92	<0.20	<0.20	210
320	1.01	<0.20	<0.20	126
640	0	0	<0.20	51.3
1280	0	0	<0.20	24.6
1460	0	0	<0.20	24.6
1800	1.41	0.80	<0.20	29.8

Table 19
Anionic Results of TRSL
of Bag House FBC Fly Ash
($\mu\text{g/g}$ fly ash)

Time (min)	F^-	Cl^-	NO_3^-	$\text{SO}_4^{=}$
10	12.4	15.1	10.4	800
20	6.21	13.0	7.24	267
40	1.92	1.92	4.79	162
80	1.84	1.84	4.60	76.0
160	2.09	2.09	2.09	54.9
320	2.02	2.02	2.02	34.4
640	2.12	2.12	2.12	25.4
1280	2.05	2.02	<2.02	<2.02
1460	2.05	2.02	<2.02	<2.02
1800	1.70	1.70	<2.02	<2.02

Table 20
Cationic Results of TRSL
of Cyclone 1 FBC Fly Ash
(% of fly ash)

Time (min)	B	Si	Al	Ca	Ba
10	--	--	7.48	--	--
20	0.639	2.97	4.90	2.30	0.742
40	0.553	1.80	3.72	1.81	0.405
80	0.600	2.03	3.32	9.990	0.219
160	0.898	--	4.40	0.0454	--
320	0.542	--	4.65	0.0428	--
640	0.275	--	4.51	0.0340	0.128
1280	0.301	2.54	0.916	0.0147	0.154
1460	--	2.51	0.781	0.0138	0.200
1800	0.389	2.41	0.906	0.0112	0.296

Table 21
Cationic Results of TRSL of Cyclone 2 FBC Fly Ash
Concentration
(% of fly ash)

Time (min)	B	Ba	Si	Al	Ca
10	0.358	0.928	1.21	1.38	1.26
20	0.327	0.817	2.12	2.26	--
40	0.513	0.644	3.36	--	0.270
80	0.472	0.350	--	--	0.0814
160	0.448	0.110	--	3.05	0.0561
320	0.557	--	--	2.81	0.0197
640	0.495	--	5.05	1.68	0.0158
1280	0.371	--	3.12	1.04	0.0130
1460	0.379	0.0995	2.86	0.742	0.0122
1800	0.363	0.134	2.84	0.611	0.0127

Table 22
Cationic Results of TRSL of Bag House FBC Fly Ash
Concentration
(% of fly ash)

Time (min)	Si	Al	Ca	Ba	K
15	--	7.6	0.195	0.622	37.3
25	2.96	5.19	0.0552	0.575	32.9
45	3.06	--	0.0260	0.624	--
80	3.59	5.25	0.0331	0.329	--
160	4.89	3.18	0.0436	0.228	--
320	3.99	2.61	0.0338	0.136	--
640	4.09	2.01	0.0343	0.279	--
1280	--	--	0.0219	--	30.9
1460	--	--	0.0205	--	28.5
1800	--	--	0.0249	0.147	31.5

Figure 7. Fluoride Concentration as a Function of Time (TRSL)

Figure 8. Chloride Concentration as a Function of Time (TRSL)

Figure 9. Nitrate Concentration as a Function of Time (TRSL)

Figure 10. Sulfate Concentration as a Function of Time (Cyclones 1 and 2)(TRSL)

Figure 11. Sulfate Concentration as a Function of Time (Bag House)(TRSL)

Figure 12. Barium Concentration as a Function of Time (TRSL)

Figure 13. Calcium Concentration as a Function of Time (TRSL)

Figure 14. Silicon Concentration as a Function of Time (TRSL)

Discussion

The size and/or temperature dependence of the elemental concentrations presented in Tables 11 and 12 were evaluated statistically. The analyses were facilitated by the assumption that fly ash from Run I and Run II was chemically similar in spite of differing limestone feed rates. Earlier work reported by Carpenter, et al. (1978) supports this assumption. These authors concluded that the limestone was not a significant contributor to FBC fly ash. The specific concentrations of various elements in Rosebud coal and limestone are given in Table 23.

The validity of this assumption was examined further statistically by comparing the differences between the two runs. The actual probability levels are given in Table 24. At the $\alpha = 0.01$ level, five elements, Ca, Fe, K, La, and V, were significantly related to changes in the two runs. Only Sc was significantly related at the $\alpha = 0.05$ level and Cr, Hg, Na and Th were significantly related to the different runs at the $\alpha = 0.1$ level. It would appear that these elements are the most influenced by changes in the limestone feed rate. Although most of these elements are present in higher specific concentrations in limestone than in coal, only Ca and La were present in high specific concentration in Run II; the run with the higher limestone feed rate.

The first relationship evaluated was that between size and temperature combined and elemental concentration. Eleven elements were significantly correlated at the one percent level. Thus, the probability of the relationships being the result of a random event are one in a hundred. Elements at this level of significance include As, Ba, Cr, Eu, Ga, La, Lu, Sr, Ti, U, and W. Three additional elements, Cu, V and Yb, showed a size-temperature dependence at the $\alpha = 0.1$ level.

The dependence of elemental concentration on size and temperature were

Table 23

Specific Elemental Concentration ($\mu\text{g/g}$) In Rosebud Coal And Limestone
Used In Fluidized Bed Combustor Run RB-5*

Element	Specific Concentration ($\mu\text{g/g}$)		Element	Specific Concentration ($\mu\text{g/g}$)	
	Coal	Limestone		Coal	Limestone
Al	0.5%	>1%	Mg	0.12	>1%
As	>0.59	4.1	Mn	69	89
Au	>0.1	>0.1	Na	41	190
Ba	0.13%	0.027%	Ni	2.6	14
Ca	>0.5%	>1%	Rb	21	9.0
Cd	0.10	0.13	S	>0.5%	0.010%
Ce	11	13	Sc	0.49	3.1
Co	1.2	2.1	Se	1.4	0.24
Cr	2.4	39	Sm	0.85	0.43
Cs	3.3	0.86	Sr	160	280
Cu	1.5	9.4	Ta	>0.10	0.14
Dy	2.1	0.54	Tb	0.23	>0.1
Eu	0.19	0.23	Th	4.3	3.4
Fe	0.17%	>0.5%	Ti	1200	440
Ga	1.4	1.6	U	0.75	2.7
Hf	1.3	1.2	V	16	25
Hg	NR**	NR	W	1.3	>0.19
In	—***	—	Yb	>0.35	0.92
K	0.07%	0.34%	Zn	1.2	22
La	6.4	6.4	Zr	24	70
Lu	>0.10	>0.1			

* Data from Carpenter, et al., 1978

** NR = Not Reported

*** Internal Standard

Table 24

Probability Level of Element Concentrations Varying
with Inverse Size, Temperature and Size-Temperature

	Al	As	Ba	Br	Ca	Ce	Co	Cr
Run	.1812	.5657	.3391	.3941	.0006	.3806	.1874	.9393
Inverse Size	.3825	.0001	.0000	.6520	.0023	.0001	.4156	.0074
Temperature	.0996	.6026	.0000	.5620	.1994	.0617	.5173	.0240
Size-Temperature	.1853	.0463	.0000	.8157	.2983	.4228	.7466	.0123
	Cs	Cu	Dy	Eu	Fe	Ga	Hf	Hg
Run	.1444	.8030	.1750	.1093	.0010	.1440	.2226	.0728
Inverse Size	.0030	.0264	.0077	.0000	.2608	.0000	.0039	.6443
Temperature	.3542	.1300	.2091	.0000	.1122	.0000	.2720	.3483
Size-Temperature	.6976	.0575	.1700	.0000	.7076	.0034	.7817	.9302
	In	K	La	Lu	Mg	Mn	Na	Ni
Run	.8333	.0060	.1180	.0107	.4848	.4899	.0767	.3447
Inverse Size		.0024	.0000	.0000	.8326	.0459	.8165	.6406
Temperature	.3949	.0428	.0000	.0000	.1759	.0114	.0956	.1713
Size-Temperature	.8087	.1740	.0004	.0000	.6217	.4990	.1345	.6960
	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb
Run	.1208	.2674	.0217	.1662	.5691	.4766	.2283	.1720
Inverse Size	.0144	.0001	.0048	.0011	.7880	.0000	.6038	.0009
Temperature	.3711	.0082	.0000	.2363	.0045	.0000	.3392	.0202
Size-Temperature	.7585	.2624	.4070	.6768	.6063	.0002	.7532	.3263
	Th	Ti	U	V	W	Yb	Zn	Zr
Run	.0910	.2587	.3299	.0047	.8922	.3562	.1929	.3430
Inverse Size	.0061	.0257	.0000	.4298	.0000	.0000	.3646	.8009
Temperature	.0368	.9629	.0000	.0000	.0000	.0274	.2271	.3123
Size-Temperature	.5240	.0126	.0000	.0056	.0000	.0972	.3064	.7342

also evaluated independently. Those elements showing a statistically significant ($\alpha = 0.01$) increasing concentration with decreasing size trend included As, Ba, Ca, Ce, Cs, Dy, Hf, K, Sb, Sc, Se, Th, and Yb. A smaller number of elements (Cr, Mn and Ti) showed significance at the five percent level.

Temperature dependence did not appear to be as common. In fact, only Al, Ce, and Na showed a statistically significant ($\alpha = 0.1$) change (increase in concentration) with decreasing temperature. Three additional elements (K, Tb, and Th) showed the same trends at the $\alpha = 0.05$ level of significance and one, Mn, at the $\alpha = 0.01$ level.

Before the fluidized bed ash trends can be compared with trends observed for conventional coal-fired power plant trends (Table 1), it is important to consider the differences in the two systems. First, the combustor used in the present study is part of a small pilot-scale facility rather than a large commercial power plant. Second, operating temperatures are much lower in the fluidized bed system (1600 - 1800°F versus 2300 - 2800°F). Third, limestone or dolomite is added as an essential component of the fluidized bed system. Finally, the FBC samples were collected and fractionated at the temperature of the process stream and not allowed to cool until after the system was disconnected from the ducting. This was not the situation in the literature reports on conventional coal fly ash.

With these differences in mind, a comparison between Tables 23 and 1A-C can be made. Table 1A gives those elements which exhibit an inverse size dependence-concentration relationship. Of these, five elements also were found to show either a significant size or size-temperature dependence. These include As, Cu, Ga, Sb, and Se, all relatively volatile elements with the exception of copper and gallium.

Elements in ash from the FBC that were found to show an inverse size dependence in either system were Al, Co, Fe, Mg, and Ta. Surprisingly, a large number of elements that showed a significant size or size-temperature relationship have not been reported as displaying a temperature dependence in conventional power plants. These include Ba, Ca, Ce, Dy, Eu, Hf, K, La, Rb, Sc, Sr, Tb, Th, Ti, and Yb.

The results of the present study differ slightly from those reported by Carpenter, et al. (1978) for the same FBC. They reported that Bi, Ga, Hf, Ni, Sn, U, and Y were enriched in small particles, however, the present study did not measure the elements Bi, Sn and Y, making comparison difficult. In contrast to this earlier report, the present study concludes that Ni does not exhibit a size dependence. For the elements Ga, Hf and U, the two studies are in agreement. Since the same coal, limestone and two sampling ports (although not sampling conditions) were used in both studies, it is surprising that so many more elements appear to show either a size or size-temperature dependence in the present work than in that of Carpenter, et al. (1978).

Correlations between elemental pairs are given in Table 25. This table gives an idea of the interrelationships between the individual elements that were measured in the various runs. These correlations, because of the limited data set, should be interpreted carefully. To provide a better picture of the data, those elements that exhibited a significant correlation (based on the table given by Young (1962)) are given in Table 26. In Table 27 the elements correlated above 0.8 (at least 64 percent of variability in concentration of an element is associated with the other element). Correlations are generally at the $\alpha = 0.001$ level. Table 25 shows that four elements (Mg, Mn, Sn and Ti) show no significant correlations at any level. The other elements vary between a few significant

Table 25

Correlation Coefficients of Elemental Concentrations of Fluidized Bed Combustor Ash

	Al	As	Au	Ba	Br	Ca	Cd	Ce	Co	Cr	Cs	Cu	Dy	Eu	Fe	Ga
Al																
As	0.1212															
Au	-0.6466	0.8876														
Ba	-0.2516	0.4174	0.9879													
Br	0.3215	0.5642	0.7503	0.1243												
Ca	-0.4724	0.2348	0.6773	0.6736	0.0273											
Cd	-0.6138	0.8564	0.9954	0.9865	0.7466	0.6542										
Ce	-0.0870	0.7257	0.9729	0.8134	0.4895	0.5781	0.9526									
Co	0.3264	0.7053	0.9565	0.2799	0.9617	0.0776	0.9399	0.6369								
Cr	0.1297	0.4804	0.5490	0.3430	0.4563	0.1543	0.5670	0.4248	0.5172							
Cs	0.1096	0.8462	0.9913	0.6286	0.7573	0.3204	0.9883	0.8458	0.8788	0.5904						
Cu	-0.1230	0.3564	0.4726	0.6242	0.5941	0.3187	0.4804	0.5486	0.6138	0.3337	0.5902					
Dy	-0.2415	0.4239	0.9439	0.6829	-0.0008	0.2390	0.9345	0.5506	0.1471	0.1139	0.4409	0.7046				
Eu	-0.1809	0.3876	0.9863	0.9638	0.1598	0.6120	0.9827	0.8165	0.3003	0.3452	0.6031	0.6042	0.6630			
Fe	0.3216	0.2329	0.3504	0.1268	0.2898	-0.3322	0.0823	0.2139	0.4011	0.1185	0.3885	0.2558	0.0652	0.1761		
Ga	-0.1327	0.5046	0.9764	0.9328	0.2757	0.6044	0.9642	0.8821	0.4218	0.3330	0.6844	0.6334	0.6478	0.9660	0.1853	
Hf	0.1069	0.8579	0.9846	0.5887	0.7827	0.3487	0.9843	0.8444	0.8897	0.5703	0.9859	0.5999	0.3892	0.5605	0.3216	0.6612
Hg	0.4945	0.3690	0.9981	-0.0518	0.8942	-0.1609	0.9973	0.2810	0.8270	0.2357	0.5542	0.6194	-0.0088	-0.0119	0.1579	0.0956
In	0.7622	0.3134	0.9759	0.0439	0.5400	-0.0986	0.9922	0.1426	0.5411	0.4004	0.3963	0.7129	-0.0880	0.0606	0.2575	0.0873
K	0.2195	0.6577	0.2687	0.2294	0.5673	-0.2100	0.2922	0.4979	0.6609	0.2923	0.6827	0.5746	0.3609	0.2767	0.6156	0.3824
La	-0.1943	0.2852	0.9515	0.8826	0.0170	0.6797	0.9343	0.6901	0.1385	0.2085	0.4262	0.7000	0.5835	0.9053	0.0729	0.8784
Lu	-0.3761	0.3143	0.9777	0.9603	0.0158	0.7318	0.9709	0.7397	0.4195	0.3236	0.5042	0.5063	0.6233	0.9302	0.0070	0.8725
Mg	0.1310	0.2766	-0.2542	-0.1810	0.0315	-0.0910	-0.2052	0.1021	0.0616	-0.0813	0.0201	0.1027	0.0752	-0.0950	0.0146	-0.0107
Mn	0.1763	0.0729	0.0672	0.1841	0.0716	0.3412	0.1076	0.1832	0.0595	0.1406	0.0477	0.4448	-0.0954	0.1599	-0.2935	0.2369
Na	0.3894	0.5444	-0.0106	-0.1295	0.7540	-0.2446	-0.0029	0.2238	0.7550	0.5447	0.6024	-0.1011	-0.1503	-0.1564	0.2673	-0.0694
Ni	0.1270	0.3640	0.8222	0.2458	0.9150	0.1759	0.8410	0.5244	0.8656	0.4390	0.6885	0.5876	0.0102	0.2957	0.2252	0.3694
Rb	0.1727	0.8824	0.9960	0.4778	0.8105	0.2181	0.9948	0.7716	0.9149	0.5878	0.9749	0.6197	0.3548	0.4471	0.3818	0.5578
Sb	0.0653	0.6456	0.9819	0.8389	0.3531	0.5261	0.9792	0.7870	0.5207	0.4313	0.7649	0.5873	0.5720	0.7950	0.1735	0.8332
Sc	0.1329	0.3726	0.5714	0.5002	0.4348	0.1135	0.5376	0.6220	0.5189	0.1973	0.5522	0.7240	0.3886	0.5890	0.6117	0.6574
Se	0.0960	0.8555	0.9977	0.6693	0.7208	0.3621	0.9968	0.8712	0.8501	0.5920	0.9935	0.5959	0.4765	0.6409	0.3373	0.7205
Sm	0.1944	-0.0944	0.4596	0.2873	-0.1478	0.1861	0.4252	0.2651	-0.0843	-0.3506	-0.0628	0.2892	0.0896	0.4026	0.2207	0.4008
Sr	-0.2070	0.3204	0.9678	0.9325	0.0698	0.6943	0.9613	0.7514	0.1986	0.4407	0.5092	0.6502	0.5592	0.9078	-0.0300	0.8731
Ta	0.2150	0.5466	0.9982	0.2284	0.9681	0.1245	0.9976	0.5769	0.9510	0.3948	0.7855	0.5972	0.0666	0.2578	0.2749	0.3642
Tb	-0.0192	0.5398	0.9968	0.7969	0.3466	0.4745	0.9959	0.7179	0.4571	0.4088	0.7041	0.5998	0.5266	0.7762	0.1741	0.8226
Th	0.0874	0.7257	0.8316	0.5844	0.5901	0.3623	0.8022	0.8641	0.7047	0.3014	0.7884	0.4586	0.3645	0.6092	0.2977	0.7115
Ti	-0.0785	0.1676	-0.2115	0.2370	0.1312	0.2633	-0.2201	0.2070	0.1366	-0.0030	0.1887	0.5737	0.2654	0.1751	0.0217	0.2293
U	-0.2217	0.4475	0.9914	0.9815	0.1789	0.6558	0.9879	0.8413	0.3367	0.3945	0.6561	0.6969	0.6873	0.9681	0.1723	0.9498
V	0.3225	0.2074	0.3287	0.1359	0.0724	-0.2534	0.3282	0.2923	0.1577	-0.0246	0.1580	0.1638	0.2380	0.2976	0.5137	0.3084
W	-0.3160	0.3451	0.9931	0.9825	0.0512	0.6702	0.9953	0.7691	0.1990	0.3528	0.5552	0.6188	0.6765	0.9599	0.1156	0.9183
Yb	-0.1254	0.6957	0.9915	0.8994	0.4626	0.6353	0.9916	0.9174	0.6208	0.5433	0.8892	0.6111	0.6299	0.8749	0.2591	0.8985
Zn	0.1159	0.3168	0.9617	0.0397	0.3537	0.2015	0.9577	0.4683	0.4258	0.2042	0.4096	0.6193	0.1964	0.4091	0.2151	0.3920
Zr	0.4846	0.3853	0.9298	0.3430	0.9365	-0.0235	0.9974	0.3580	0.8782	0.3512	0.6023	0.6326	-0.1299	0.0990	0.2469	0.1969

Table 25 (continued)

Correlation Coefficients of Elemental Concentrations of Fluidized Bed Combustor Ash

	Hf	Hg	In	K	La	Lu	Mg	Mn	Na	Ni	Rb	Sb	Sc	Se	Sm	Sr
Al																
As																
Au																
Ba																
Br																
Ca																
Cd																
Ce																
Co																
Cr																
Cs																
Cu																
Dy																
Eu																
Fe																
Ga																
Hf																
Hg	0.5798															
In	0.3817	0.8787														
K	0.6551	0.3854	0.2182													
La	0.3984	-0.1529	0.0629	0.1367												
Lu	0.4700	-0.1737	-0.0550	0.0689	0.8559											
Mg	0.0414	0.0154	0.0429	0.2942	-0.0118	-0.2254										
Mn	0.1247	0.0659	0.2252	-0.3035	0.3252	0.1446	-0.0089									
Na	0.6316	0.7162	0.4506	0.4907	-0.3395	-0.2527	0.0233	0.0199								
Ni	0.7061	0.8306	0.3688	0.4004	0.1298	0.1807	-0.0909	0.0637	0.6128							
Rb	0.9822	0.6323	0.4424	0.7163	0.2734	0.3433	0.0782	0.0450	0.7194	0.6946						
Sb	0.7406	0.2210	0.3187	0.3101	0.6640	0.7387	-0.0873	0.3313	0.1808	0.3375	0.6712					
Sc	0.5251	0.1950	0.2159	0.7050	0.5617	0.3829	0.1670	0.0267	0.0607	0.4146	0.4820	0.4210				
Se	0.9845	0.5210	0.3715	0.6570	0.4687	0.5455	0.0166	0.0902	0.5792	0.6571	0.9676	0.7966	0.5379			
Sm	-0.0624	-0.1382	0.0628	-0.0283	0.5107	0.2687	0.1689	0.3585	-0.4462	-0.0700	-0.1270	0.2306	0.4404	-0.0535		
Sr	0.4395	-0.1029	0.0514	0.0468	0.8616	0.9118	-0.1925	0.4221	-0.1345	0.2187	0.3594	0.7908	0.4176	0.5643	0.3180	
Ta	0.8080	0.8889	0.4157	0.5304	0.0812	0.1230	-0.0125	0.0447	0.7112	0.9580	0.8192	0.4146	0.4282	0.7566	-0.0985	0.1586
Tb	0.6882	0.2265	0.2080	0.3273	0.7228	0.7083	-0.1399	0.3981	0.1760	0.3556	0.6297	0.7911	0.4233	0.7424	0.1583	0.7502
Th	0.8136	0.4430	0.1934	0.5495	0.5121	0.4784	0.0770	0.3370	0.3680	0.5648	0.7833	0.6825	0.6107	0.8046	0.3703	0.5465
Ti	0.2209	0.2080	0.3278	0.2339	0.3506	0.1537	0.3476	0.4461	-0.1954	0.1525	0.2148	0.2366	0.3074	0.2040	0.1337	0.2397
U	0.6196	-0.0150	0.0643	0.2992	0.9026	0.9344	-0.0914	0.2035	-0.0972	0.3012	0.5137	0.8270	0.5950	0.6937	0.3201	0.9311
V	0.1291	-0.0182	0.1079	0.5065	0.2333	0.0758	0.2516	-0.2033	-0.0915	0.0030	0.1346	0.0867	0.6186	0.1502	0.5331	0.0690
W	0.5094	-0.1372	-0.0147	0.1812	0.8828	0.9750	-0.1856	0.1254	-0.2156	0.2043	0.3927	0.7707	0.4888	0.5933	0.2778	0.9228
Yb	0.8600	0.2335	0.2123	0.4973	0.7261	0.8248	-0.0744	0.0840	0.2287	0.5057	0.7857	0.8699	0.5777	0.9091	0.0974	0.7985
Zn	0.4156	0.3674	0.2353	0.1675	0.4422	0.2446	0.1605	0.3538	0.1909	0.4034	0.3714	0.4044	0.3321	0.4021	0.5007	0.3745
Zr	0.6279	0.9320	0.6645	0.3684	0.0008	-0.0751	0.0080	0.2263	0.6758	0.8735	0.6486	0.3104	0.3450	0.5656	0.0203	0.0313

Table 25 (continued)

Correlation Coefficients of Elemental Concentrations of Fluidized Bed Combustor Ash

	Ta	Tb	Th	Ti	U	V	W	Yb	Zn	Zr
Al										
As										
Au										
Ba										
Br										
Ca										
Cd										
Ce										
Co										
Cr										
Cs										
Cu										
Dy										
Eu										
Fe										
Ga										
Hf										
Hg										
In										
K										
La										
Lu										
Mg										
Mn										
Na										
Ni										
Rb										
Sb										
Sc										
Se										
Sm										
Sr										
Ta										
Tb	0.3967									
Th	0.6515	0.6484								
Ti	0.2066	0.2125	0.1208							
U	0.2749	0.7825	0.6167	0.2951						
V	0.0423	0.0656	0.3266	-0.2361	0.1985					
W	0.1533	0.7472	0.5036	0.2096	0.9698	0.1558				
Yb	0.5386	0.7919	0.7267	0.2171	0.9136	0.1741	0.8635			
Zn	0.3944	0.3192	0.5746	0.2938	0.3943	0.2457	0.2768	0.3790		
Zr	0.9026	0.2890	0.5128	0.2314	0.0859	0.0500	-0.0423	0.3131	0.4566	

Elements Showing Any Significant Pairwise Correlation

Al	∅
As	Au, Cd, Cs, Hf, Rb, Se
Au	As, Ba, Cd, Ce, Co, Ga, La, Lu, Ni, Rb, Sb, Se, Sr, Th, U, W, Zn, Zr
Ba	Au, Cd, Ce, Eu, Ga, La, Lu, Sb, Sr, U, W, Yb
Ca	∅
Cd	As, Au, Ba, Ce, Co, Cs, Dy, Eu, Ga, Hf, Hg, In, La, Lu, Ni, Rb, Sb, Se, Sr, Ta, Tb, Th, U, W, Yb, Zn, Zr
Ce	Au, Ba, Cd, Eu, Ga, Hf, Se, Th, U, Yb
Co	Au, Br, Cd, Cs, Hf, Hg, Ni, Rb, Se, Ta, Zr
Cr	∅
Cs	As, Cd, Hf, Rb, Se, Yb
Cu	∅
Dy	Cd
Eu	Ba, Cd, Ce, Ga, La, Lu, Sr, U, W, Yb
Fe	∅
Ga	Au, Ba, Cd, Ce, Eu, La, Lu, Sb, Sr, Tb, Th, U, W, Yb
Hf	As, Cd, Ce, Co, Cs, Rb, Se, Ta, Th, Yb
Hg	Br, Cd, Co, In, Ni, Ta, Zr
In	Cd, Hg
K	∅
La	Au, Ba, Cd, Eu, Ga, Lu, Sr, U, W
Lu	Au, Ba, Cd, Eu, Ga, La, Sr, U, W, Yb
Mg	∅
Mn	∅
Na	∅
Ni	Au, Br, Cd, Co, Hg, Ta, Zr
Rb	As, Au, Br, Cd, Co, Cs, Hf, Se, Ta
Sb	Au, Ba, Cd, Ce, Ga, Rb, U, Yb

Sc	Ø
Se	As, Au, Cd, Co, Cs, Hf, Th, Yb
Sm	Ø
Sr	Au, Ba, Cd, Eu, Ga, La, Lu, U, W
Ta	Br, Cd, Co, Hf, Hg, Ni, Rb, Zr
Tb	Cd, Ga
Th	Au, Cd, Ce, Hf, Se
Ti	Ø
U	Au, Ba, Cd, Ce, Eu, Ga, La, Lu, Sb, Sr, W, W, Yb
V	Ø
W	Au, Ba, Cd, Eu, Ga, La, Lu, Sr, U, Yb
Yb	Ba, Cd, Ce, Cs, Eu, Ga, Hf, Lu, Sb, Se, U, W
Zn	Au, Cd
Zr	Au, Br, Cd, Co, Hg, Ni, Ta

Elements Shwoing a Significant Pairwise Correlation at the $\alpha \geq 0.8$ Level

Al	In
As	Au, Br, Cd, Ce, Co, Cs, Hf, K, Na, Rb, Sb, Se, Th, Yb
Au	As, Ba, Br, Cd, Ce, Co, Cs, Dy, Eu, Ga, Hf, Hg, In, La, Lu, Ni, Rb, Sb, Se, Sr, Ta, Tb, Th, U, W, Yb, Zn, Zr
Ba	Au, Ca, Cd, Ce, Cs, Dy, Eu, Ga, Hf, La, Lu, Sb, Se, Sr, Tb, Th, U, W, Yb
Br	As, Au, Cd, Co, Cs, Hf, Hg, K, Na, Ni, Rb, Se, Ta, Th, Zr
Ca	Ba, Ce, Eu, Ga, La, Lu, Sr, U, W, Yb
Cd	As, Au, Ba, Br, Ce, Co, Cs, Dy, Eu, Ga, Hf, Hg, In, La, Lu, Ni, Rb, Sb, Se, Sr, Ta, Tb, Th, U, W, Yb, Zn, Zr
Ce	As, Au, Ba, Ca, Cd, Co, Cs, Dy, Eu, Ga, Hf, La, Lu, Rb, Sb, Sc, Se, Sr, Ta, Tb, Th, U, W, Yb
Co	As, Au, Br, Cd, Ce, Cs, Hf, Hg, K, Na, Ni, Rb, Se, Ta, Th, Yb, Zr
Cr	Cs, Hf, Na, Rb, Se
Cs	As, Au, Ba, Br, Cd, Ce, Co, Cr, Eu, Ga, Hf, Hg, K, Na, Ni, Rb, Sb, Sc, Se, Ta, Tb, Th, U, W, Yb, Zr
Cu	Dy, In, La, Sc, Sr, U
Dy	Au, Ba, Cd, Ce, Cu, Eu, Ga, La, Lu, Sb, Sr, U, W, Yb
Eu	Au, Ba, Ca, Cd, Ce, Cs, Dy, Ga, Hf, La, Lu, Sb, Sc, Se, Sr, Tb, Th, U, W, Yb
Fe	K, Sc
Ga	Au, Ba, Ca, Cd, Ce, Cs, Dy, Eu, Hf, La, Lu, Rb, Sb, Sc, Se, Sr, Tb, Th, U, W, Yb
Hf	As, Au, Ba, Br, Cd, Ce, Co, Cr, Cs, Eu, Ga, Hg, K, Na, Ni, Rb, Sb, Se, Ta, Tb, Th, U, Yb, Zr
Hg	Au, Br, Cd, Co, Cs, Hf, In, Rb, Na, Ni, Ta, Zr
In	Al, Cd, Cu, Hg, Zr
K	As, Br, Co, Cs, Fe, Hf, Rb, Sc, Se, Th
La	Au, Ba, Ca, Cd, Ce, Cu, Dy, Eu, Ga, Lu, Sb, Sc, Sr, Tb, U, W, Yb
Lu	Au, Ba, Ca, Cd, Ce, Dy, Eu, Ga, La, Sb, Se, Sr, Tb, U, W, Yb

Mg	∅
Mn	∅
Na	As, Br, Co, Cr, Cs, Hf, Hg, Ni, Rb, Se, Ta, Zr
Ni	Au, Br, Cd, Co, Cs, Hf, Hg, Na, Rb, Se, Ta, Th, Zr
Rb	As, Au, Br, Cd, Ce, Co, Cr, Cs, Ga, Hf, K, Na, Ni, Sb, Se, Ta, Tb, Th, Yb, Zr
Sb	As, Au, Ba, Ca, Cd, Ce, Cs, Dy, Eu, Ga, Hf, La, Lu, Rb, Se, Sr, Tb, Th, U, W, Yb
Sc	Ce, Cs, Cu, Eu, Fe, Ga, K, La, Se, Th, U, V, Yb
Se	As, Au, Ba, Br, Cd, Ce, Co, Cr, Cs, Eu, Ga, Hf, K, Na, Ni, Rb, Sb, Sc, Sr, Ta, Tb, Th, U, W, Yb, Zr,
Sm	∅
Sr	Au, Ba, Ca, Cd, Ce, Cu, Dy, Eu, Ga, La, Lu, Sb, Se, Tb, Th, U, W, Yb
Ta	As, Au, Br, Cd, Co, Cs, Hf, Hg, Na, Ni, Rb, Se, Th, Zr
Tb	Au, Ba, Cd, Ce, Cs, Eu, Ga, Hf, La, Lu, Rb, Sb, Se, Sr, Th, U, W, Yb
Th	As, Au, Ba, Br, Cd, Ce, Co, Cs, Eu, Ga, Hf, K, Ni, Rb, Sb, Sc, Se, Sr, Ta, Tb, U, Yb, Zn
Ti	∅
U	Au, Ba, Ca, Cd, Ce, Cs, Cu, Dy, Eu, Ga, Hf, La, Lu, Sb, Sc, Se, Sr, Tb, Th, W, Yb
V	Sc
W	Au, Ba, Ca, Cd, Ce, Cs, Dy, Eu, Ga, La, Lu, Sb, Se, Sr, Tb, U, Yb
Yb	As, Au, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Eu, Ga, Hf, La, Lu, Rb, Sb, Sc, Se, Sr, Tb, Th, U, W
Zn	Au, Cd, Th
Zr	Au, Br, Cd, Co, Cs, Hf, Hg, In, Na, Ni, Rb, Se, Ta

correlations (such as for Dy, In, Tb, and Zn) to as high as twenty-seven (Cd). It should be noted that Au and Cd concentrations were measured only for Run II. Thus, no calculations were possible for Table 24 and the results in Tables 26 and 27 may not be truly representative.

In general, the concentrations of alkali metals; Na, K, Rb, and Cs; appear to correlate fairly well with each other with the exception of sodium and potassium, which do not appear to be related. Magnesium does not correlate with any other element, but the concentrations of the other alkaline earths do correlate with each other. The rare earth elements (Ce, Dy, Eu, La, Lu, Tb, Th, U, and Yb) appear to be associated both with each other and with the same main group or transition elements (especially Ba, Cd, Ga, Sb, Sc, Se, Sr, and W); about half of the rare earth elements also correlate well with Ca and Hf. The statistical analysis also suggests that elements from the middle of the first transition (V, Cr, Mn, Fe) are not strongly associated with many other elements.

It is postulated that limestone added to the bed to control SO_2 emissions crumbles into fine particles after sulfation. As a result, elements such as Ca, Ce, La, Mg, Mn, Sn, and Sr, which occur naturally in the stone, are concentrated in the smallest particles. The behavior of Th and U, generally found to be coal associated, is not well understood since these elements were also found in highest concentration in the smaller sized material.

The independence of the concentrations of Al, Fe, Na, Sc, and Yb to particle size considerations is believed due to those elements not being vaporized during combustion. These lithophiles occur in the refractory matrix of the coal ash and this behavior is not unexpected, although sodium might be expected to volatilize fairly readily.

The behavior of potassium, which is possibly present in the form of $K_2S_2O_7 - K_2SO_4$ was unique in that it was large-particle associated. This is believed to be primarily the result of agglomeration of smaller particles, although this could not be confirmed based on the available information.

The application of the different surface techniques to the analysis of fluidized bed samples provided limited information. For example, it was unexpected that K, Ba, F, Na, and possibly Mn were not observed in addition to those elements reported in Table 15. Based on the available bulk analysis data and the relative Auger sensitivities, measurable signals would be expected for all five of the aforementioned elements. While possible surface depletion may have occurred, the observed inverse dependence of concentrations on particle size and temperature (for both bag house and cyclone material) makes this unlikely. Spectral interference (in the Auger analysis) between Ba, F, Mn, and the stronger Fe lines is perhaps the most logical explanation for the failure to detect these elements, especially given the poor S/N of this energy region. In the case of potassium, interferences may arise from calcium or there may be charged-induced migration into the bulk sample from the surface. A similar phenomenon may be occurring with sodium. Migration of alkali metals has been observed in insulating materials (Coburn, 1976; McCaughan and Kushner, 1974) so the migration of K and Na is not surprising in fluidized bed particles.

Studies by Mazza, et al. (1978), who employed X-ray powder diffraction to identify the crystalline phases in fluidized bed ash samples, indicated that the amount of anhydrite ($CaSO_4$) was greatest in the bag house samples. The lime (CaO , $Ca(OH)_2$), calcium aluminosilicate, and quartz (SiO_2) materials were enriched in the bed material. Analysis of sized aerosol samples indicated elevated calcium and sulfur concentrations and enhanced Ca-S associations in the fine particles. The finding of the

highest CaSO_4 concentrations in the bag house samples is consistent with this trend.

The results of the X-ray photoelectron (XPS) studies of the Morgantown samples suggest that CaSO_4 is a major constituent of the sample surface. Low resolution scans indicate that Fe, O, Ti, Ca, Mo, Mg, S, and Si are all present. Molybdenum is found in the mask used to support the sample. The number of elements detected by XPS is slightly larger than the number found using Auger spectrometry.

The chemical form of the detectable elements appears to be mainly that of the oxide. Agreement between the observed Al 2p, Si $2p_{3/2}$ and Ti $2p_{3/2}$ binding energies and the reference energies of the respective oxides is good. However, the Ti $2p_{3/2}$ line of the titanates also occurs in the same energy region, 458.5 to 459.0 eV. Their presence, and that of other Al and Si species, cannot be completely discounted. The breadth of the Fe $2p_{3/2}$ line is indicative of more than one chemical environment, and although the low peak intensity prevented accurate determination of position, the estimated binding energy is not inconsistent with that of the oxides. The position and intensities of the Ca $2p_{3/2}$, S 2p and O 1s peaks suggest that CaSO_4 is a major constituent of the sample surface. The binding energy of the Ca $2p_{3/2}$ electrons is 2 eV higher than normal for the oxide. Considering the most simple and probable species, calcium-binding energies are greatest for sulfates and halides. Since halogens were not detected, the presence of CaSO_4 is most likely.

In summary, the results of both the Auger and XPS analyses provided little information concerning trace metal surface concentrations. The elements which were found on the surface were the same as those expected for the bulk material. The concentrations determined by INAA confirm that these elements are generally not found in smaller particles, as would be

predicted. The surface concentrations of sodium and potassium were generally not detectable, suggesting that they were not enhanced on the surface. This conclusion is subject to the limitations previously discussed.

The results of the leaching experiments were, in many respects, very similar to those previously discussed for the surface analyses: The most leachable elements were those commonly classified as "bulk" elements. Figures 7 to 11 provide evidence that most anionic species in FBC ash are readily released by leaching. Regardless of collection temperature and location (Cyclone 1 at 910°F, Cyclone 2 at 640°F or the bag house at 490°F), the pattern appears to be very consistent with the bulk of the leachable anions being solubilized during the first twenty to forty minutes. A possible exception is nitrate, where the lowest levels observed were at the detection limits of the instrument. The general order of decreasing concentration was $\text{SO}_4^{2-} \gg \text{F}^- > \text{Cl}^- > \text{NO}_3^-$. With the important exception of sulfate, Cyclone 1 yielded the largest amount of anion per sample weight leached while the bag house yielded the least. Once the initial most soluble material was leached, the material being released with time rapidly became constant. The 100-fold larger sulfate concentration over that of some of the other species indicates that the fluidized bed is absorbing SO_2 quite efficiently. It is important to point out that most of the sulfate is concentrated in the bag house material--in the smallest particles. This result is entirely consistent with the work reported by Crow and Seale (1978) who found that the CaSO_4 concentration of fluidized bed fly ash increased with decreasing particle size.

The plasma emission data given in Tables 20 to 22 are shown graphically in Figures 12 to 14. Although PES is capable to detecting a total of eighteen elements, only B, Si, Al, Ca, and K were present at a concentration

above the detection limits of the instrument. Detection limits for the instrument for the eighteen elements examined are given in Table 6. As can be seen in Table 6, the detection levels for potassium and sodium are 0.04 $\mu\text{g/ml}$ and 0.4 $\mu\text{g/ml}$, respectively, suggesting that the water accessible concentrations of those two corrosion suspect species is relatively low.

The leaching profile for silicon is shown in Figure 14. Clearly, there is no dependence of concentration with time for this species as was the case with the anionic species. Within the limits of the measurements, the profile is constant; an expected result for a species that is the primary matrix material of most fly ash. The profiles of barium and calcium, shown in Figures 12 and 13, respectively, again show that the initial leachable surface is much higher in these two elements than is the surface exposed by the leaching process. This is somewhat surprising, especially for calcium in view of the large amount of calcium that is initially present in the fluid bed. As before, the concentrations of both the calcium and barium appear to level out and reach a relatively constant level; however, the time scale is slightly longer than for the anions.

The results of this study suggest, but do not confirm several aspects of fluidized bed combustor behavior. First, the damage to the stainless steel impactor plates during sample collection indicates that corrosion can indeed occur in the fluidized bed system. As in the case of corrosion in more well established combustion systems, temperature and sulfur dioxide concentrations appear to be crucial. Thus, the only occurrence of corrosion was under high temperature--low limestone feed rate conditions. The low limestone feed rate would probably lead to higher SO_2 concentrations in contact with the plates.

Second, the lower temperatures found in the fluidized bed systems

lead to rather anomalous trace element behavior when compared to that found in the literature for conventional power plants. A surprisingly large number of elements appear to increase in concentration with a decrease in particle size even though it is unlikely they could volatilize at the temperature of the FBC. Likewise, elements that might be expected to volatilize are inconsistent in their behavior. Undoubtedly, this behavior is at least partially related to the influence of the limestone, which, although it does not appear to be a significant flue gas component, must adsorb or otherwise influence the distribution of elements in the fly ash.

Third, calcium does not follow an inverse size dependence trend nor does potassium. Sodium, however, does show such a trend. The leaching data indicates that sulfate is found mainly in the smallest particles. These results suggest that sodium sulfate is the most likely corrosive agent in the flue gas stream since it is the smallest size fraction which will be most prevalent. However, the rapidity with which the temperature falls would suggest that corrosion from Na_2SO_4 will only occur over a relatively short distance. Within or near the combustor itself, where the large particle associated potassium-sulfur compound could form, however, the leaching data suggest that the amount of sulfate on large particles is minimal when compared to that on small particles. Most likely the corrosion of the impactor plates was a direct result of small particle (Na_2SO_4) attack.

Suggestions for Additional Work

The results of this study leave a considerable number of questions both in the area of trace metal-particle size association and in the area of corrosion in fluidized beds. Some of these are:

1. Do the observed particle size-concentration trends reflect a specific result of a given set of operating conditions and/or type of coal and limestone?

2. What is the influence of temperature on corrosion? Especially important is the temperature range from 800°F and higher.
3. What is the effect of limestone feed rate and/or SO_2 concentration on the corrosion process? What, if measurable is the amount of SO_3 that is present?
4. How representative is the relatively small combustor used in this study of larger systems?
5. Is it possible to identify the mechanism whereby trace elements become particle associated given that it appears to differ considerably from conventional combustion systems? How does limestone affect this partitioning?

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