# STRONTIUM ISOTOPE SYSTEMATICS AND GEOCHEMISTRY OF COAL UTILIZATION BY-PRODUCTS

by

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A.B., University of Chicago, 2004

Submitted to the Graduate Faculty of

Arts and Sciences in partial fulfillment

of the requirements for the degree of

Master of Science

University of Pittsburgh

2007

UNIVERSITY OF PITTSBURGH

Faculty of Arts and Sciences

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UTILIZATION BY-PRODUCTS**

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Coal combustion for energy generation creates large quantities of solid coal utilization by-products (CUB), including fly ash, bottom ash, and flue gas desulfurization products. These materials are either used in environmental and industrial applications or stored adjacent to power plants. The development of new techniques to track and understand the behavior of CUB in the environment is essential to the safe utilization of coal. In this research, sequential leaching techniques are coupled with strontium (Sr) isotope analysis to investigate the influence of coal type and combustion process on the geochemical characteristics of CUB. Sequential leaches of water, acetic acid, and hydrochloric acid were carried out on a variety of CUB types. Systematic differences in $^{87}Sr/^{86}Sr$ ratios were observed (1) among different types of CUB, and (2) between leachates and their corresponding bulk CUB values. These differences can help elucidate the origins of the inorganic components of coal, as well as the transformations that occur during combustion. In addition, this study demonstrates for the first time that there are multiple sources of Sr in coal that remain isotopically distinct during combustion. The degree of isotopic homogenization induced during the formation of CUB appears to be controlled by the feed coal chemistry and the particular combustion technology used. The Sr isotope data, when combined with major and trace element results, suggest that a greater fraction of Sr is bound in detrital minerals in higher-rank coals, while authigenic minerals and organic complexes comprise the dominant form of Sr in lower-rank coals. Investigation of CUB produced from fluidized bed

combustion (FBC) also demonstrates that the combustion process can strongly impact the behavior of the inorganic components of coal during utilization. The association of potentially toxic trace elements with certain soluble Sr-bearing phases in CUB make Sr isotopes a promising tool to trace the release of these species during interactions with water. Application of Sr isotopes to studies of coal and CUB could facilitate the development of better disposal techniques by serving as a robust tracer of CUB in the environment.

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# 1.0    INTRODUCTION

The combustion of coal for energy generation results in the production of several types of coal utilization by-products (CUB), primarily fly ash, bottom ash, and flue-gas desulfurization residues (FGD) (Sajwan et al. 2006). Whether CUB is used in industrial and agricultural processes, or disposed of in landfills and settling lagoons, assessment of the potential environmental hazard of this material is essential for safe coal utilization. The geochemical behavior of CUB is influenced considerably by factors such as the combustion conditions and feed coal properties. Both the chemistry of the feed coal and the mode of occurrence of geochemical constituents in the coal are recognized as important factors in determining how an element or compound will behave during all stages of coal utilization (Finkelman 1994).

This thesis includes a study of the geochemistry and Sr isotope systematics of different types of CUB using sequential leaching. Sequential leaching techniques facilitate chemical fractionation of various mineral reservoirs in CUB and provide information about the elements that might be leached from these different reservoirs during environmental exposure. The addition of Sr isotopes represents a powerful tool to understand the origins of the various components in CUB, including geologic sources and behavior during combustion. This novel technique of combined sequential leaching and Sr isotope analysis is applied to CUB derived from different types of coal and by different combustion technologies in order to investigate the

effects of these variables on the geochemical properties of CUB. The use of Sr isotopes as an environmental tracer of CUB is also addressed.

# 2.0    BACKGROUND


## 2.1    SR ISOTOPES IN COAL AND CUB


Strontium (Sr) isotopes are increasingly used as tracers in geological and environmental systems (Capo et al. 1998, and references therein, Bullen and Kendall 1998). The concentration of $^{87}$Sr in geologic materials increases over long time scales (generally millions of years) as a result of the beta-decay of $^{87}$Rb, at a rate that depends on the Rb/Sr ratio of the material. Natural variations in the $^{87}$Sr/$^{86}$Sr ratios of different materials, caused by age differences and parent-daughter fractionation of Rb-Sr during geologic processing, can be used to identify the unique sources of Sr. In coal, Sr is a trace element with an average concentration of ~100 ppm (Swaine 1990). CUB are enriched in Sr relative to coals and many other geologic reservoirs with concentrations up to ~3000 ppm (Hurst et al. 1991). The Sr in CUB is also known to be readily mobilized and biogeochemically available (Hurst et al. 1991). As such, previous work on Sr isotopes in CUB has focused primarily on the utility of this element as an environmental tracer (Hurst and Davis 1981, Straughan et al. 1981, Hurst et al. 1991). There has also been an investigation of Sr isotopic variability among fly ash samples generated from different coal types in order to determine the implications of source coal on the utility of this tracer (Mattigod et al. 1990a). Very few data exist on the Sr isotopic compositions of coals, and these are limited to one

or two samples that have been leached in acid (Hurst et al. 1991, Frost et al. 2002). More work on Sr isotopes in CUB and coal is clearly warranted.

While Sr is not an element of great environmental concern, intrinsic variations in its isotopic composition could be used elucidate the modes of occurrence of this element in coal and CUB, as well as the effects of the combustion process on its geochemical behavior. Additionally, the behavior of other elements in coal and CUB that might be environmentally harmful if not properly mediated during coal utilization could potentially be better understood if they have mineralogical and geochemical affinities with Sr. The ability of Sr isotopes to distinguish the various fractions of CUB that might carry toxic trace metals potentially makes this system useful as an environmental tracer. The leaching behavior and isotope systematics of Sr in CUB can provide useful information about the sources and fate of Sr and other associated elements during coal utilization.

## 2.2    CUB GEOCHEMISTRY AND CLASSIFICATION

The factors that contribute to the inorganic chemistry of coal are complex and numerous, depending largely on the specific conditions in the peat-forming environment (Swaine 1990). These can include the inputs of various detrital minerals of different origins, the chemistry of ground and surface waters that infiltrate the peat swamp, intrusion of seawater, air-fall inputs from volcanic ash, and other variables (Swaine 1990). There are also factors that can arise following the deposition and burial of peat that influence the chemistry of coal, including the maturation level reached by the coal and the precipitation of authigenic minerals, usually in cleats and fractures of coal beds (Swaine 1990). As such, elements of interest in coal can occur

in multiple forms and from diverse origins that are difficult to determine. As mentioned above, this has direct implications for understanding the geochemistry of CUB.

In this study, class C and class F fly ashes, as defined by the American Society for Testing and Materials (ASTM), were investigated, along with ashes produced by fluidized bed combustion (FBC), a bottom ash, and a flue gas desulfurization (FGD) product. The ASTM classification system is designed to determine suitable fly ash samples for cement manufacture, while the samples for this study were chosen to represent diverse geologic origins. For the purpose of this study, the important characteristics of this classification include (1) the sum of major oxide ($SiO_2 + Al_2O_3 + Fe_2O_3$) concentrations and (2) the rank of coal burned to produce the ash. Class C fly ash is produced from lignite and sub-bituminous coal and has minimum major oxide content of 50 wt.%, while class F ash is produce from bituminous and anthracite coal with a minimum major oxide content of 70 wt.%.

## 3.0    MATERIALS AND METHODS

### 3.1    CUB SAMPLES

Thirteen samples of CUB were chosen for this study, including eleven fly ashes, one bottom ash, and one sample of FGD material. All of the samples except one fly ash were obtained from the collection at the Department of Energy, National Energy Technology Laboratory (NETL) in Pittsburgh, PA. The sample of SRM 1633b fly ash is a standard reference material obtained from the National Institute of Standards and Technology (NIST). The samples were chosen to represent a diverse range of CUB materials generated from different fuel sources and combustion technologies, including five class C and four class F fly ashes, two FBC fly ashes, a bottom ash, and a FGD product. Two of five class C fly ashes are considered a "matched set" produced in the same boiler operating with and without selective-catalytic reduction (SCR), a $NO_x$ emission control technique. Selected sample characteristics of the samples are listed in Table 1. It should be noted that some of the fly ash samples do not meet the strict definition of ASTM class C and F, specifically in elevated loss on ignition (LOI) and moisture content. The ash samples obtained from NETL (originally ~0.2-1kg) were split down to 10-100g aliquots of using a course riffle splitter. Further division to the final aliquots of ~0.5-1.0 g was carried out at the University of Pittsburgh using a fine-chute riffle splitter.

## 3.2    ANALYTICAL PROCEDURES


### 3.2.1    CUB Chemical Analysis and Sequential Leaching Procedure


The total (whole-ash) chemical compositions of the CUB samples were determined by NETL staff technicians on ~0.1g aliquots of sample fused in a 10:1 excess of lithium tetraborate, with elemental analysis by inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectroscopy (ICP-MS) at NETL Pittsburgh. Two exceptions are the Sr and S concentrations, which were determined by ICP-OES at the University of Pittsburgh. For these analyses, 0.05-0.1g samples of CUB were digested under clean-lab conditions in a series of concentrated ultra-pure acids including, (1) hydrofluoric acid (HF) + aqua regia, (2) perchloric acid ($HClO_4$), and (3) nitric acid ($HNO_3$).

A three part sequential leaching procedure, illustrated in Figure 1, was performed on the fly and bottom ash samples. The steps of the leaching procedure were designed to target elements associated with specific phases including: (a) water-soluble phases, primarily sulfates and some carbonate; (b) dilute acetic acid (HOAc) soluble phases, specifically carbonate; and (c) phases that are soluble in hydrochloric acid (HCl) such as phosphates, some oxides, and possibly aluminosilicate glass. The leaching solution was added to the sample in a 50mL polypropylene centrifuge tube and the mixture was shaken at room temperature for a specified time (Fig. 1). The samples were then centrifuged for ~10 minutes and the solutions were filtered through a 0.45μm cellulose acetate filter. The next leaching solvent was then added to the residue and the process repeated. Aliquots of the water leachate taken for elemental and Sr isotopic analysis were acidified with concentrated $HNO_3$ to ~2%. Water leachates collected for determination of

major anions by ion-chromatography (IC), using a Dionex ICS 2000 ion-chromatograph at the University of Pittsburgh, were not acidified and were kept refrigerated at ~4$^o$C.

Major elements in the sequential extractions were measured by ICP-OES at the University of Pittsburgh and minor and trace elements were measured by ICP-MS at NETL, Pittsburgh. There are a few exceptions where trace elements were measured by ICP-OES in the HCl leaching solutions due to isobaric interferences cause by Cl$^-$ in the ICP-MS.

The sample of FGD was leached in ultra-pure water for ~30 min and then filtered as described for the other CUB leachates. As the majority of this CUB material was assumed to be gypsum, which is readily water-soluble, the full leaching procedure was omitted. Visual inspection of this sample confirmed that all but a few grains (most likely silicate inclusions) had dissolved in the water.

### 3.2.2 Strontium Isotope Analysis

Aliquots of the acid-digested samples and sequential leaching solutions typically containing ~3μg of Sr, when available, were evaporated to dryness in acid washed Teflon$^®$ beakers in a HEPA-filtered hood and re-dissolved in 3N HNO$_3$. These aliquots were then passed through quartz glass columns packed with SrSpec$^®$ resin to separate Sr from the solution. Around 500 ng of Sr was loaded onto Re single filaments with a tantalum oxide (Ta$_2$O$_5$) activator. The Sr isotopic compositions were measured on a Finnigan MAT 262 multicollector thermal ionization mass spectrometer (TIMS) using a multi-dynamic measurement routine. A total of 100 ratios was measured during each analysis, and instrumental mass fractionation was corrected using $^{86}$Sr/$^{88}$Sr = 0.1194. The mean value of standard SRM 987 over the period of these analyses was 0.71024 with a 2σ external reproducibility of ±20ppm.

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### 3.2.3   X-ray Diffractometry (XRD)

The major crystalline mineral phases present in the fly and bottom ash samples were determined by XRD on a Philips X'pert diffractometer at the University of Pittsburgh. Samples were ground if necessary and "back-packed" to ensure random orientation of the minerals. Peak intensities were measured for $2\theta$ angles from 10-80$^{\text{o}}$.

**Table 1.** CUB sample characterization

| Sample | CUB Type | Combustor Type | ASTM Class | Moisture % | LOI % |
|--------|----------|----------------|------------|------------|-------|
| FA 22 | FA | PC | Class C | 0.36 | 3.06 |
| FA 23 | FA | PC | Class C | 0.82 | 8.53 |
| FA 47 | FA | PC | Class C | 0.08 | 0.32 |
| CRC 9 w/ | FA | PC w/SCR | Class C | 0.29 | 2.75 |
| CRC 9 w/o | FA | PC w/o SCR | Class C | 0.48 | 5.44 |
| FA 26 | FA | PC | Class F | 3.00 | 18.74 |
| FA 39 | FA | PC | Class F | 0.45 | 0.91 |
| FA 44 | FA | PC | Class F | 41.60 | 10.03 |
| SRM 1633b | FA | Unknown | Class F | - | - |
| FA 34 | FA | FBC | n/a | 0.82 | 8.01 |
| FA 45 | FA | FBC | n/a | 0.00 | 4.24 |
| FA 40 | BA | PC | n/a | 0.00 | 7.40 |
| FGD 1 | FGD | n/a | n/a | - | - |

FA = Fly Ash, BA = Bottom Ash, FGD= Flue Gas Desulfurization Product,
PC = Pulverized Coal, FBC = Fluidized Bed Combustor,
SCR = Selective Catalytic Reduction, n/a = Not Applicable, (-) = No Data

| ~0.5 g Whole CUB Sample | |
|---|---|

↓

| **Extract sulfates and some carbonate** |
|---|
| Sample + 50ml water, shake 8 h at room temp. |

↓

| Centrifugation and filtration, residue let stand over night | → | Aliquots taken for elemental and Sr isotope analysis |
|---|---|---|

↓

| **Extract carbonate and some glass** |
|---|
| Residue + 50ml 0.1N HOAc, shake for 2 h at room temp |

↓

| Centrifugation and filtration | → | Aliquots taken for elemental and Sr isotope analysis |
|---|---|---|

↓

| **Extract phosphates, some oxides and some glass** |
|---|
| Residue + 40ml 1N HCl, shake for 2 h at room temp. |

↓

| Centrifugation and filtration | → | Aliquots taken for elemental and Sr isotope analysis |
|---|---|---|

**Figure 1.** Flow chart of sequential leaching procedure. The phases extracted at each step are shown in bold.

# 4.0    RESULTS

## 4.1    XRD AND CUB MINERALOGY

The detection of crystalline phases in CUB materials by XRD is difficult because of large amorphous peaks due to the high proportion of glass phases. As such, only the most abundant crystalline minerals can be detected, leaving the possibility that there are minor phases that cannot be determined. Minerals identified by XRD diffraction patterns of the CUB samples investigated in this study are reported in Table 2. The most common minerals observed in the CUB samples were quartz ($SiO_2$) in all the samples, magnetite ($Fe_3O_4$) and hematite ($Fe_2O_3$) in the FBC ashes and some of the class F ashes, mullite ($Al_6Si_2O_{13}$) in the class F ashes and bottom ash, and anhydrite ($CaSO_4$) in the class C and FBC ashes. Calcite ($CaCO_3$) was also observed in the FBC ashes and one sample each of the class C and F ashes, as well as periclase ($MgO$) in some of the class C fly ash samples.

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| Class C Fly Ash | Class F Fly Ash | FBC Fly Ash |
|:---:|:---:|:---:|
| Quartz ($SiO_2$) | Quartz | Quartz |
| Anhydrite ($CaSO_4$) | Mullite ($Al_6Si_2O_{13}$) | Anhydrite |
| Calcite ($CaCO_3$) | Calcite | Calcite |
| Periclase (MgO) | Magnetite ($Fe_3O_4$) | Magnetite |
| | Hematite ($Fe_2O_3$) | Hematite |

**Table 2.** Crystalline phases in coal fly ash identified by XRD

## 4.2    BULK CUB CHEMICAL COMPOSITION

Chemical compositions of the totally dissolved CUB samples (bulk CUB samples) are presented in Tables 3 and 4. The major element chemistry is quite variable within and between different groups of ash type. On average, class C fly ash has higher concentrations of Ca, Mg, Na, and S compared to class F fly ash, which has higher Al, Fe, K, Si and Ti concentrations. The two samples of fluidized bed-combustion (FBC) ash have substantially different chemical compositions from each other. Sample FA 34 has the highest Ca and Fe contents, but with extremely low Si compared to the other fly ash samples, while FA 45 is chemically similar to class F ash but with more Ca. The sample of bottom ash (FA 40) consists mainly of Al and Si,

and the flue-gas desulfurization (FGD) sample is predominantly Ca and S, as expected for gypsum.

The concentrations of minor and trace elements are similar between the different ash type groups. However, class C ash has notably higher average concentrations of Ba, Sr and P than the other ash types, which could be due to higher carbonate contents (Vassileva and Vassilev, 2005) and/or the presence of Sr and Ba bearing phosphate minerals (Brownfield et al. 1999).

**Table 3.** Bulk CUB major element concentrations, wt.%[a]

| Sample | Al | Ca | Fe | K | Mg | Na | S[b] | Si | Ti |
|---|---|---|---|---|---|---|---|---|---|
| *Class C* | | | | | | | | | |
| FA22 | 7.25 | 7.49 | 4.06 | 0.85 | 1.32 | 1.86 | 0.38 | 27.23 | 0.61 |
| FA23 | 5.55 | 13.66 | 3.09 | 0.56 | 1.13 | 2.02 | 3.34 | 20.10 | 0.50 |
| FA47 | 9.67 | 14.16 | 4.38 | 0.51 | 3.00 | 1.11 | - | 19.94 | 0.94 |
| CRC 9 w/ | 8.56 | 17.20 | 5.44 | 0.61 | 3.73 | 1.49 | 1.66 | 13.81 | 0.86 |
| CRC 9 w/o | 8.37 | 17.10 | 5.60 | 0.52 | 3.80 | 1.54 | 1.16 | 12.97 | 0.84 |
| *Class F* | | | | | | | | | |
| FA26 | 9.80 | 1.80 | 24.37 | 0.98 | 0.37 | 0.26 | 0.50 | 19.23 | 0.55 |
| FA39 | 13.27 | 3.95 | 6.42 | 1.97 | 1.06 | 0.31 | 0.36 | 23.71 | 1.14 |
| FA44 | 13.74 | 0.61 | 5.39 | 2.13 | 0.54 | 0.30 | 0.13 | 26.68 | 1.18 |
| SRM 1633b | 14.37 | 1.39 | 8.06 | 1.71 | 0.49 | - | 0.18 | - | 0.74 |
| *FBC ash* | | | | | | | | | |
| FA34 | 5.99 | 18.25 | 13.53 | 0.76 | 0.32 | 0.27 | 4.26 | 11.08 | 0.31 |
| FA45 | 12.86 | 6.60 | 5.11 | 2.37 | 0.86 | 0.32 | 1.18 | 22.95 | 1.23 |
| *Bottom ash and FGD* | | | | | | | | | |
| FA40 | 15.31 | 0.46 | 3.91 | 1.75 | 0.42 | 0.14 | 0.15 | 26.17 | 1.09 |
| FGD 1 | 1.85 | 18.67 | 0.17 | 0.06 | 0.14 | - | 14.87 | - | 0.02 |

[a]Concentrations determined by ICP-OES following lithium tetraborate fusion except S in ash samples

[b]Sulfur in ash samples determined by ICP-OES following HF digestion

**Table 4.** Bulk CUB minor and trace element concentrations, ppm[a]

| Sample | As | Ba | Cd | Co | Cr | Cu | Mn | Ni | P | Pb | Se | Sr[b] | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Class C* | | | | | | | | | | | | | |
| FA22 | 29 | 1520 | <DL | <DL | 53 | 71 | 155 | 37 | 686 | <DL | 4 | 1011 | 46 |
| FA23 | 44 | 999 | <DL | <DL | 55 | 42 | 155 | 35 | 735 | <DL | 3 | 822 | 33 |
| FA47 | 31 | 6900 | <DL | 32 | 62 | 140 | 155 | 56 | 6822 | 117 | 11 | 2961 | 142 |
| CRC 9 w/ | 34 | 6543 | <DL | 50 | 96 | 319 | 206 | 81 | 7602 | 81 | <DL | 2743 | <DL |
| CRC 9 w/o | 34 | 6784 | <DL | 46 | 79 | 281 | 178 | 83 | 8169 | 68 | <DL | 2946 | <DL |
| *Class F* | | | | | | | | | | | | | |
| FA26 | 44 | 469 | 1.1 | 33 | 114 | 53 | 465 | 124 | 644 | 12 | 1 | 359 | 34 |
| FA39 | 128 | 1540 | 0.3 | 45 | 167 | 178 | 465 | 91 | 441 | 83 | 26 | 1093 | 168 |
| FA44 | 113 | 1400 | 2.0 | 55 | 157 | 140 | 310 | 103 | 429 | 53 | 22 | 525 | 80 |
| SRM 1633b | 124 | 685 | <DL | 62 | 196 | 93 | 125 | 126 | 2377 | 34 | <DL | 936 | 220 |
| *FBC ash* | | | | | | | | | | | | | |
| FA34 | 106 | 268 | <DL | 31 | 87 | 108 | 155 | 126 | 175 | 65 | 20 | 363 | 333 |
| FA45 | 56 | 613 | 1.5 | 8 | 141 | 66 | 310 | 40 | 205 | 59 | 24 | 235 | 50 |
| *Bottom ash and FGD* | | | | | | | | | | | | | |
| FA40 | 0.7 | 693 | 0.2 | 47 | 155 | 79 | 232 | 102 | 321 | 16 | 0.4 | 482 | 45 |
| FGD 1[c] | <DL | 117 | <DL | <DL | 15 | 9 | 44 | <DL | 44 | <DL | <DL | 321 | 24 |

[a]Concentrations determined by ICP-OES and ICP-MS following lithium tetraborate fusion, unless otherwise noted

[b]Strontium in ash samples determined by ICP-OES following HF digestion

## 4.3    SEQUENTIAL LEACHING EXPERIMENTS

The results of the sequential leaching experiments are presented in Tables 5 and 6. In general, class C fly ash was more soluble than class F or FBC fly ash, with higher proportions and total amounts of most elements released during sequential extraction (Figs. 2, 3 and 4). The average amounts of major elements (Al, Ca, Fe, Mg, Na, K, Si and S) leached from class C fly ash were approximately an order of magnitude higher than those leached from class F fly ash, with intermediate amounts released from FBC ash. Sulfur, occurring predominately as $SO_4$, is a notable exception, with the highest soluble quantity found in the FBC ashes. The total amounts of Cl and $NO_3$ leached into water were similar for the different fly ash types, while class C ash had slightly higher quantities of water soluble F. In general, the amounts of minor and trace elements leached during sequential extraction were highest in the class C fly ash, with the exception of arsenic (As) and molybdenum (Mo). However, the differences between the amounts of minor and trace elements leached from the various types of fly ash are generally less pronounced than for major elements, except for Ba, B, P, Sr and Ti, which leached approximately ten times higher quantities from the class C ash compared to the other ash types. Leachates from the single sample of bottom ash used in this study contained the lowest amounts of all elements during the sequential extraction. Among fly ash samples, in general, class C fly ash was the most soluble, followed by FBC ash and then class F ash.

For some elements (As, Cd, Cr, P, S, and Se) the total quantity extracted appears to exceed the amount measured in the whole CUB sample (Figs. 2, 3 and 4). This analytical artifact

could be caused by either contamination during the sequential leaching procedure or by yields of less than 100% during total sample digestion. Because our blank levels in the leaching procedure are low, this artifact is mostly likely a result of volatile behavior of these elements during alkali fusion or evaporation of HF solutions. In the case of boron, whole CUB concentrations could not be determined due to the use of lithium tetraborate flux in the fusion procedure and the known volatility of B during acid digestion (Leeman et al. 1991).

**Table 5.** Major elements in CUB sequential leach extractions, μg element per g CUB leached[a]

| Sample | Al | Ca | Fe | K | Mg | Na | S$_{tot}$ | Si | Cl[b] | F[b] | SO$_4$[b] | NO$_3$[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **DI Water Leach** | | | | | | | | | | | | |
| *Class C* | | | | | | | | | | | | |
| FA 22 | 272 | 22377 | 3.7 | 25 | <DL | 291 | 2605 | 194 | 3322 | 107.4 | 8168 | 137 |
| FA 23 | 242 | 23482 | 1.6 | 190 | <DL | 2592 | 40345 | 524 | 6302 | 180.2 | 43944 | 396 |
| FA 47 | 4090 | 11638 | 2.3 | 24 | <DL | 204 | 1559 | 73 | 2387 | 209.4 | 4834 | 74 |
| CRC 9 w/ | 7040 | 21111 | 3.4 | 572 | <DL | 2277 | 9104 | 16 | 2901 | 101.4 | 17064 | 376 |
| CRC 9 w/o | 6095 | 14134 | 3.1 | 743 | <DL | 2288 | 3758 | 31 | 4357 | 446.8 | 10089 | 95 |
| *Class F* | | | | | | | | | | | | |
| FA 26 | 534 | 4026 | 1.1 | 58 | 17 | 129 | 1886 | 137 | 2347 | 6.4 | 5240 | 200 |
| FA 39 | 405 | 8801 | 4.1 | 38 | 11 | 70 | 3581 | 375 | 3023 | 45.5 | 11323 | 276 |
| FA 44 | <DL | 1056 | 1.3 | 121 | 81 | 99 | 1090 | 0 | 2804 | 15.6 | 3404 | 536 |
| SRM 1633b | 35 | 2162 | <DL | 117 | 10 | 53 | 1699 | 0 | 3316 | 23.6 | 5585 | |
| *FBC Ash* | | | | | | | | | | | | |
| FA 34 | <DL | 66289 | 2.4 | 64 | 8.1 | 9.4 | 40545 | 203 | 3087 | 83.1 | 97547 | |
| FA 45 | 137 | 23776 | 1.5 | 165 | <DL | 39 | 12041 | 626 | 1787 | 74.7 | 36832 | 902 |
| *Bottom Ash* | | | | | | | | | | | | |
| FA 40 | 11 | 95 | 3.8 | 4.4 | 12 | 19 | 147 | 7 | 3320 | <DL | 446 | 273 |
| | | | | | | | | | | | | |
| **0.1 N HOAc Leach** | | | | | | | | | | | | |
| *Class C* | | | | | | | | | | | | |
| FA 22 | 1460 | 25589 | 828 | 61 | 5226 | 321 | 1558 | 4921 | | | | |
| FA 23 | 1311 | 80595 | 2079 | 92 | 4582 | 1092 | 26283 | 4441 | | | | |
| FA 47 | 468 | 35884 | 8.9 | 59 | 5551 | 329 | 952 | 10352 | | | | |
| CRC 9 w/ | 3909 | 52849 | 268 | 342 | 8723 | 970 | 5069 | 14538 | | | | |
| CRC 9 w/o | 2869 | 45985 | 170 | 265 | 5830 | 1077 | 4608 | 10976 | | | | |
| *Class F* | | | | | | | | | | | | |
| FA 26 | 269 | 3990 | 59 | 30 | 608 | 25 | 95 | 618 | | | | |
| FA 39 | 713 | 14220 | 26 | 74 | 1082 | 47 | 619 | 2106 | | | | |
| FA 44 | 395 | 359 | 27 | 70 | 32 | 9.2 | 30 | 164 | | | | |
| SRM 1633b | 828 | 1694 | 25 | 152 | 131 | 21 | 66 | 615 | | | | |
| *FBC Ash* | | | | | | | | | | | | |
| FA 34 | 2660 | 77900 | 902 | 116 | 1013 | 17 | 16780 | 7090 | | | | |
| FA 45 | 1573 | 21901 | 163 | 219 | 4328 | 48 | 1605 | 3553 | | | | |
| *Bottom Ash* | | | | | | | | | | | | |
| FA 40 | 25 | 8 | 8.2 | 2.3 | <DL | <DL | 6.9 | <DL | | | | |
| | | | | | | | | | | | | |
| **1 N HCl Leach** | | | | | | | | | | | | |
| *Class C* | | | | | | | | | | | | |
| FA 22 | 12173 | 13485 | 9399 | 1081 | 2675 | 4141 | 115 | 16456 | | | | |
| FA 23 | 11622 | 10637 | 7548 | 990 | 2208 | 4813 | 480 | 15729 | | | | |
| FA 47 | 34129 | 61886 | 18144 | 1145 | 14540 | 4163 | 512 | 35513 | | | | |
| CRC 9 w/ | 43929 | 80629 | 26601 | 2908 | 15929 | 6845 | 1347 | 55874 | | | | |
| CRC 9 w/o | 43358 | 88175 | 28058 | 2239 | 18423 | 7650 | 2101 | 53971 | | | | |
| *Class F* | | | | | | | | | | | | |
| FA 26 | 785 | 1851 | 1569 | 49 | 201 | 43 | 83 | 1327 | | | | |
| FA 39 | 6424 | 6488 | 5096 | 449 | 1175 | 123 | 662 | 6848 | | | | |
| FA 44 | 1038 | 415 | 633 | 80 | 90 | 26 | 30 | 669 | | | | |
| SRM 1633b | 2660 | 1715 | 1123 | 175 | 173 | 31 | 72 | 2121 | | | | |
| *FBC Ash* | | | | | | | | | | | | |
| FA 34 | 7904 | 22528 | 9304 | 464 | 456 | 136 | 940 | 9520 | | | | |
| FA 45 | 6901 | 7883 | 1266 | 465 | 439 | 192 | 44 | 8070 | | | | |
| *Bottom Ash* | | | | | | | | | | | | |
| FA 40 | 71 | 14 | 289 | 4.3 | <DL | 8.7 | 40 | 17 | | | | |

[a]Measured by ICP-OES unless otherwise indicated
[b]Measured by ion-chromatography

**Table 6.** Minor and trace elements in CUB sequential leach extractions, µg g⁻¹ CUB leached[a]

| Sample | As | B[b] | Ba[b] | Cd | Cr | Co | Cu | Mn | Mo | Ni | P[b] | Pb[c] | Sb[c] | Se[c] | Sr[b] | Ti[b] | V[c] | Zn[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **DI Water Leach** | | | | | | | | | | | | | | | | | | |
| **Class C** | | | | | | | | | | | | | | | | | | |
| FA 22 | <DL | 760 | 35.9 | <DL | 7.38 | 0.02 | 0.03 | <DL | 2.59 | <DL | <DL | 0.01 | 0.12 | 3.99 | 149.6 | <DL | 1.40 | 1.00 |
| FA 23 | <DL | 689 | 18.8 | <DL | 6.67 | 0.04 | 0.09 | 0.08 | 2.81 | <DL | <DL | 0.41 | 0.21 | 2.61 | 120.9 | <DL | 5.11 | 2.08 |
| FA 47 | <DL | 97 | 373.0 | <DL | 4.73 | 0.01 | 0.16 | <DL | 1.64 | <DL | <DL | <DL | 0.11 | 2.89 | 379.2 | <DL | 1.93 | 1.06 |
| CRC 9 w/ | <DL | 203 | 159.3 | <DL | 8.78 | 0.04 | 0.13 | 0.01 | 8.18 | <DL | <DL | 0.05 | 0.13 | 9.37 | 477.7 | <DL | 2.29 | 1.40 |
| CRC 9 w/o | <DL | 122 | 123.4 | <DL | 9.73 | 0.05 | 0.22 | 0.04 | 11.58 | <DL | <DL | 0.05 | 0.14 | 8.34 | 458.5 | <DL | 2.32 | 1.39 |
| **Class F** | | | | | | | | | | | | | | | | | | |
| FA 26 | 4.44 | 59 | 4.4 | <DL | 0.73 | 0.01 | 0.14 | 0.04 | 2.45 | <DL | <DL | 0.02 | 0.05 | 5.53 | 40.8 | <DL | 9.06 | 1.81 |
| FA 39 | 3.35 | 46 | 7.5 | <DL | 5.89 | 0.20 | 0.78 | 1.60 | 4.97 | 1.73 | <DL | 4.77 | 0.44 | 3.45 | 88.3 | <DL | 8.93 | 9.34 |
| FA 44 | 3.91 | 14 | 17.8 | <DL | <DL | 0.03 | 0.07 | 0.21 | 5.97 | 0.26 | <DL | 0.02 | 0.27 | 4.22 | 21.0 | <DL | 4.94 | 1.34 |
| SRM 1633b | <DL | 19 | 2.0 | <DL | <DL | <DL | 0.32 | 0.04 | 3.20 | <DL | <DL | 0.01 | 0.15 | 1.13 | 24.8 | <DL | 2.79 | 1.24 |
| **FBC Ash** | | | | | | | | | | | | | | | | | | |
| FA 34 | 0.18 | 35 | 7.4 | <DL | 0.71 | 0.11 | 0.06 | <DL | 4.77 | <DL | <DL | 0.08 | <DL | 1.83 | 98.5 | <DL | 2.84 | 2.03 |
| FA 45 | 0.61 | 9.0 | 2.4 | <DL | 3.17 | 0.03 | 5.84 | 0.11 | 2.77 | 0.35 | <DL | 0.82 | 0.02 | 1.98 | 63.7 | <DL | 5.94 | 5.34 |
| **Bottom Ash** | | | | | | | | | | | | | | | | | | |
| FA 40 | <DL | 4.3 | 1.7 | <DL | <DL | 0.09 | 0.54 | 2.42 | <DL | 0.38 | <DL | 0.01 | <DL | <DL | 1.2 | <DL | <DL | 2.68 |
| **0.1 N HOAc Leach** | | | | | | | | | | | | | | | | | | |
| **Class C** | | | | | | | | | | | | | | | | | | |
| FA 22 | 0.45 | 470 | 106.9 | 0.31 | 11.49 | 0.82 | 6.09 | 27.21 | 0.16 | 3.54 | 35 | 0.85 | 0.46 | 1.47 | 183.6 | 9.6 | 2.36 | 10.71 |
| FA 23 | 0.94 | 393 | 53.5 | 0.22 | 11.29 | 0.91 | 3.18 | 48.67 | 0.59 | 3.80 | 50 | 0.24 | 0.70 | 3.59 | 196.2 | 3.4 | 13.24 | 8.73 |
| FA 47 | 1.79 | 165 | 344.1 | 0.41 | 7.41 | 2.28 | 9.22 | 3.61 | 0.17 | 6.08 | 339 | 0.27 | 0.10 | <DL | 819.4 | <DL | 5.23 | 18.06 |
| CRC 9 w/ | 0.19 | 393 | 118.1 | 1.10 | 6.88 | 4.32 | 20.92 | 15.23 | 0.04 | 10.81 | 76 | 0.64 | 0.21 | <DL | 643.4 | 9.2 | 0.98 | 49.80 |
| CRC 9 w/o | 0.26 | 356 | 105.0 | 0.93 | 6.20 | 4.04 | 20.26 | 14.87 | 0.06 | 9.76 | 72 | 1.13 | 0.23 | <DL | 563.0 | 4.3 | 1.19 | 47.08 |
| **Class F** | | | | | | | | | | | | | | | | | | |
| FA 26 | 1.11 | 28 | 14.4 | 0.04 | 1.25 | 0.27 | 0.91 | 30.89 | 0.01 | 1.25 | 7 | 0.34 | 0.03 | <DL | 25.1 | 1.9 | 2.50 | 2.68 |
| FA 39 | 14.63 | 81 | 50.0 | 0.20 | 11.00 | 0.85 | 5.40 | 14.90 | 1.00 | 1.70 | 95 | 0.08 | 0.45 | <DL | 138.9 | <DL | 11.70 | 8.20 |
| FA 44 | 15.12 | 7.5 | 136.4 | 0.10 | 1.22 | 0.52 | 5.98 | 2.33 | 0.27 | 1.22 | 44 | 0.30 | 0.25 | 0.84 | 22.7 | 22.9 | 4.97 | 4.87 |
| SRM 1633b | 28.11 | 28 | 38.8 | 0.16 | 3.05 | 0.59 | 5.49 | 3.05 | 1.50 | 1.73 | 365 | 0.40 | 0.68 | 0.56 | 37.4 | 1.0 | 10.26 | 7.01 |
| **FBC Ash** | | | | | | | | | | | | | | | | | | |
| FA 34 | 4.95 | 610 | 11.0 | 0.15 | 2.00 | 1.15 | 7.40 | 28.60 | 0.78 | 3.80 | 25 | 1.40 | 0.97 | <DL | 65.9 | 10.8 | 6.20 | 33.00 |
| FA 45 | 13.85 | 19 | 10.7 | 0.01 | 1.46 | 0.31 | 2.05 | 12.57 | 0.35 | 0.53 | 12 | 0.20 | 0.30 | 5.75 | 31.6 | 1.8 | 6.53 | 5.46 |
| **Bottom Ash** | | | | | | | | | | | | | | | | | | |
| FA 40 | <DL | 4.6 | 0.8 | <DL | 0.05 | 0.01 | 0.45 | 0.25 | 0.00 | 0.05 | <DL | 0.01 | <DL | <DL | 0.3 | 0.4 | <DL | 0.75 |
| **1 N HCl Leach** | | | | | | | | | | | | | | | | | | |
| **Class C** | | | | | | | | | | | | | | | | | | |
| FA 22 | 16.35 | 183 | 391.5 | 0.25 | 14.15 | 1.84 | 13.52 | 39.92 | 1.73 | 5.97 | 632 | 12.89 | 0.52 | 4.40 | 310.5 | 1114 | 46.44 | 12.35 |
| FA 23 | 22.18 | 135 | 314.4 | 0.30 | 16.59 | 2.25 | 19.06 | 41.07 | 1.26 | 7.56 | 553 | 19.88 | 0.53 | 3.12 | 267.9 | 1119 | 28.44 | 9.36 |
| FA 47 | 35.13 | 304 | 3352.1 | 0.52 | 27.83 | 12.43 | 62.97 | 43.65 | 3.95 | 26.01 | 7483 | 33.46 | 1.26 | 2.43 | 1454.0 | 2996 | 103.12 | 62.16 |
| CRC 9 w/ | 43.54 | 509 | 3666.0 | 1.05 | 34.58 | 13.31 | 121.49 | 82.67 | 5.82 | 27.19 | 6711 | 55.01 | 2.61 | 5.82 | 1472.7 | 5902 | 229.16 | 177.29 |
| CRC 9 w/o | 40.58 | 618 | 2227.0 | 0.92 | 30.22 | 12.70 | 109.05 | 67.45 | 4.96 | 28.91 | 7190 | 46.28 | 2.35 | 11.09 | 1671.5 | 5223 | 187.88 | 158.98 |
| **Class F** | | | | | | | | | | | | | | | | | | |
| FA 26 | 23.14 | 19 | 13.7 | 0.01 | 3.57 | 0.34 | 2.57 | 40.86 | 0.74 | 1.57 | 96 | 0.53 | 0.11 | <DL | 20.8 | 88 | 7.21 | 1.08 |
| FA 39 | 93.28 | 40 | 280.2 | 0.13 | 24.48 | 2.78 | 20.43 | 53.28 | 9.92 | 5.28 | 781 | 8.80 | 1.30 | 9.12 | 211.9 | 578 | 81.92 | 20.91 |
| FA 44 | 75.13 | 10 | 156.2 | 0.08 | 8.60 | 1.03 | 6.49 | 6.33 | 3.41 | 2.60 | 212 | 3.25 | 1.10 | 5.68 | 25.7 | 115 | 16.31 | 4.76 |
| SRM 1633b | 81.79 | 14 | 75.9 | 0.08 | 12.52 | 1.11 | 6.99 | 7.15 | 8.46 | 3.01 | 687 | 7.15 | 1.76 | 3.25 | 100.3 | 223 | 33.85 | 9.18 |
| **FBC Ash** | | | | | | | | | | | | | | | | | | |
| FA 34 | 42.88 | 66 | 63.0 | 0.13 | 9.44 | 4.10 | 15.28 | 18.08 | 3.49 | 10.40 | 274 | 14.88 | 0.74 | <DL | 98.9 | 442 | 62.00 | 80.24 |
| FA 45 | 45.38 | 7.6 | 54.4 | 0.01 | 2.81 | 0.58 | 5.30 | 14.50 | 0.78 | 1.31 | 174 | 4.83 | 0.30 | 1.40 | 41.3 | 150 | 32.40 | 2.11 |
| **Bottom Ash** | | | | | | | | | | | | | | | | | | |
| FA 40 | 6.13 | 2.3 | 3.2 | <DL | 0.96 | 0.05 | 1.67 | 4.94 | 0.08 | 0.21 | 9 | 0.64 | 0.02 | <DL | 0.7 | 6.7 | <DL | 2.63 |

[a]Measured by ICP-MS, unless otherwise indicated
[b]Measured by ICP-OES
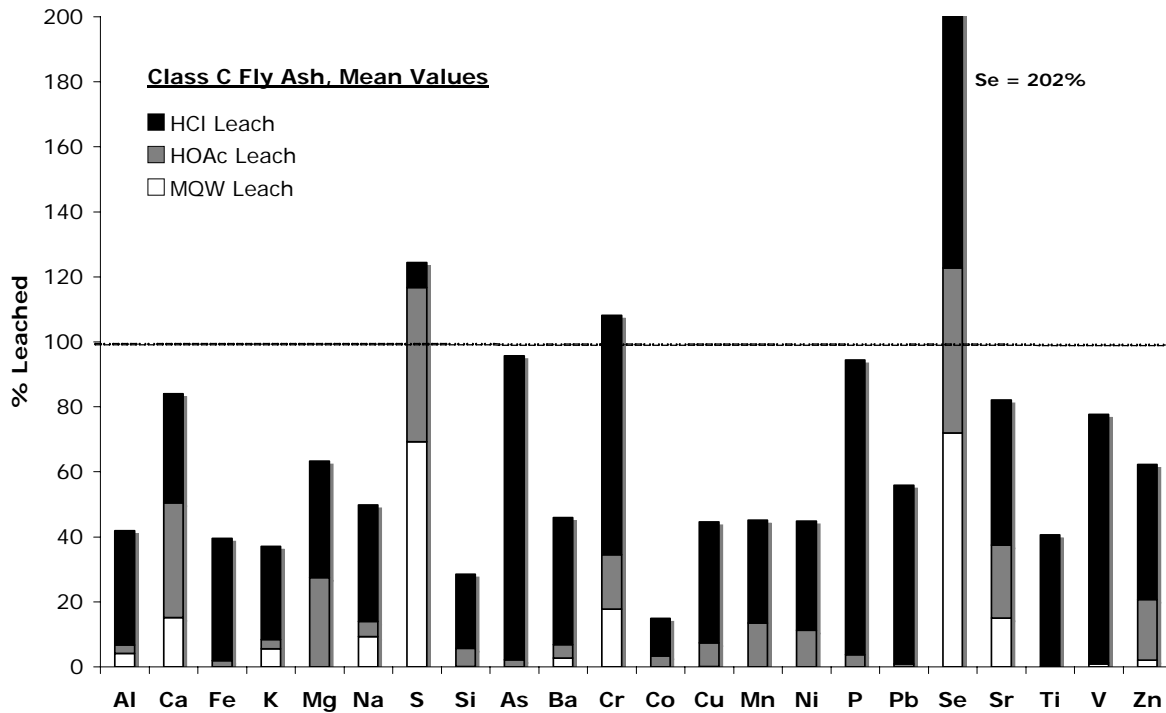[c]Water and HOAc leachates measured by ICP-MS, HCl leachates measured by ICP-OES (see text for details)

**Figure 2.** Percent of elements leached during each step of sequential extraction of class C fly ash. Each value represents the average percent of the element leached from the five class C samples in the indicated solvent. The total bar height represents the average cumulative percent leached from the five samples during the entire sequential extraction.
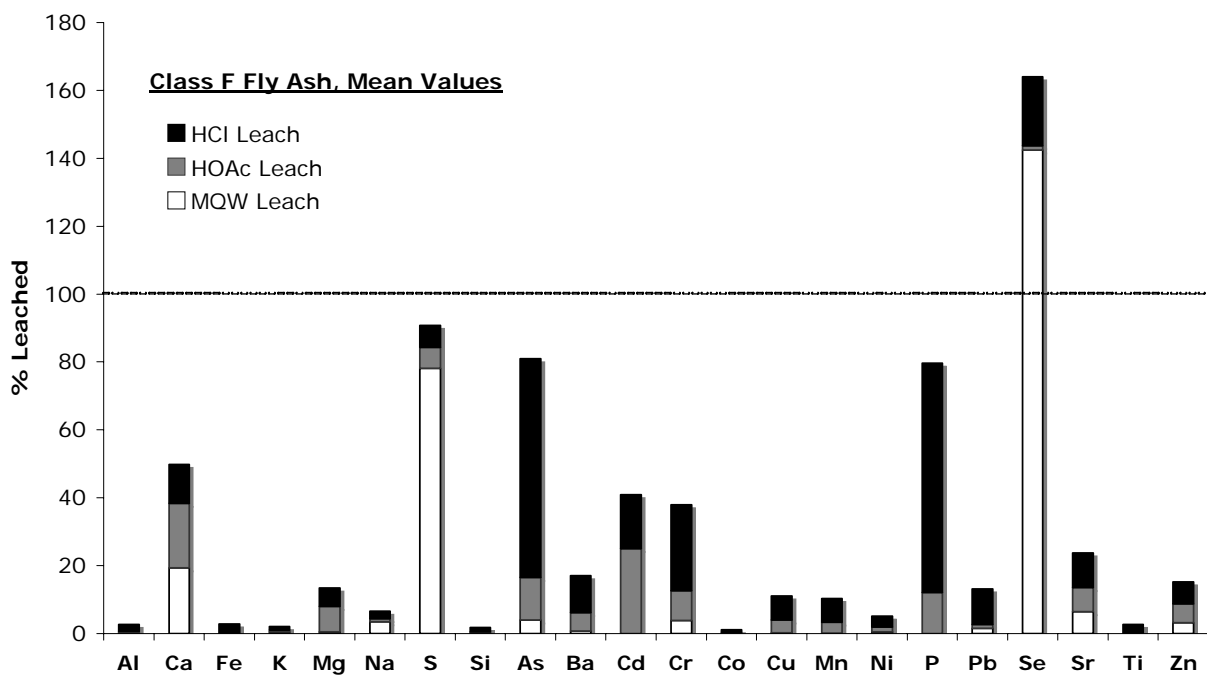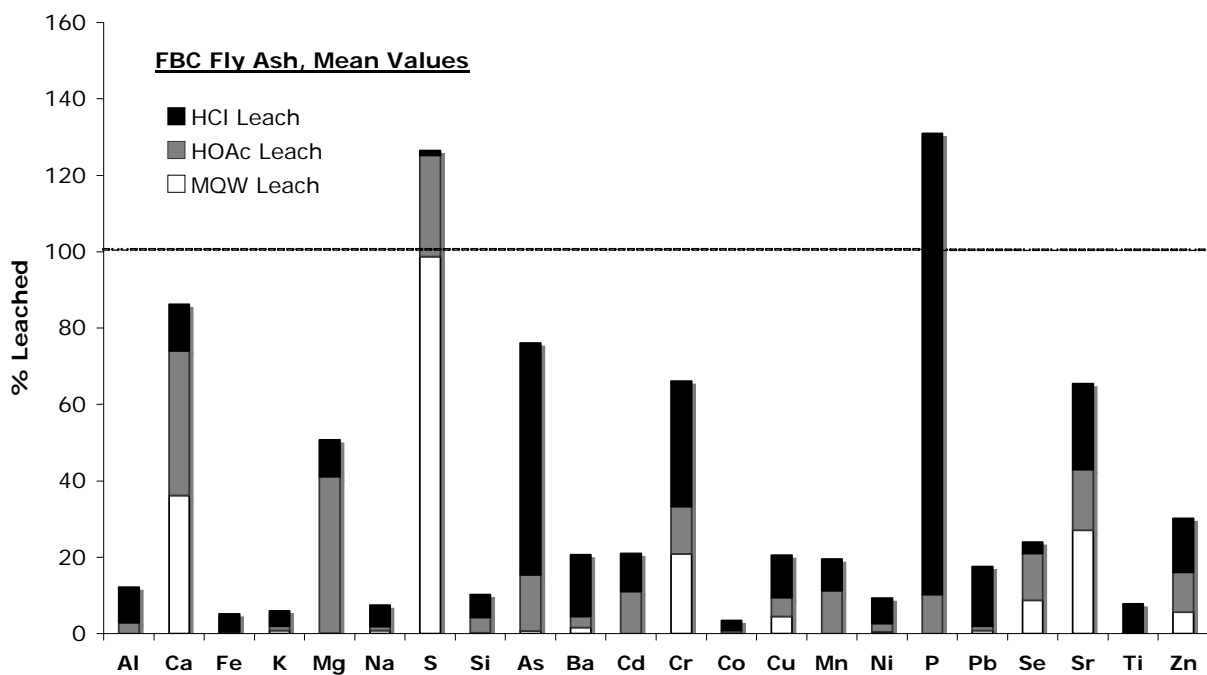
**Figure 3.** Percent of elements leached during each step of sequential extraction of class F fly ash. Each value represents the average percent of the element leached from the four class F samples in the indicated solvent. The total bar height represents the average cumulative percent leached from the four samples during the entire sequential extraction.

**Figure 4.** Percent of elements leached during each step of sequential extraction of FBC fly ash. Each value represents the average percent of the element leached from both FBC samples in the indicated solvent. The total bar height represents the average cumulative percent leached from both samples during the entire sequential extraction.

## 4.4    STRONTIUM ISOTOPES

The $^{87}Sr/^{86}Sr$ ratios of the sequential leaching solutions and total CUB acid digestions are presented in Tables 7 and 8 and Figure 5. Whole CUB $^{87}Sr/^{86}Sr$ ratios are, on average, higher in class F ash than in class C ash. Certain samples also show significant differences between the leachate and the whole CUB $^{87}Sr/^{86}Sr$ ratios, indicating the presence of multiple sources of isotopically distinct Sr.  This is not surprising, given the complexities of coal formation and the processes that contribute to the inorganic chemistry of coal.  Although $^{87}Sr/^{86}Sr$ of leachates from all samples are distinct from the values of their corresponding whole-ash, the variability of the different Sr isotopic reservoirs is much more pronounced in class F and FBC fly ash than in class C fly ash. The geochemical behavior of Sr in the one sample of bottom ash investigated in this study was similar to that of fly ash but with far less Sr (<1%) leached during sequential extraction.

Three different trends were observed in the Sr leaching behavior and isotope systematics of the three types of fly ash investigated in this study.  In class C fly ash, the $^{87}Sr/^{86}Sr$ ratios of the various Sr reservoirs as inferred from sequential extraction are relatively close to that of the whole ash (Fig. 5).  Substantial proportions (64-95%) of the total Sr were also leached from these ashes during sequential extraction with water, 0.1N HOAc and 1N HCl (Table 8).  On the other hand, in class F fly ashes the $^{87}Sr/^{86}Sr$ ratios of the various reservoirs of leachable Sr are markedly lower than the whole ash $^{87}Sr/^{86}Sr$ ratios, although all of the leachates are isotopically

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similar to each other (Fig. 5). A smaller fraction of the total Sr (13-40%) was sequentially leached from the class F fly ashes compared to the class C ashes (Table 8). The widest range and highest variability of $^{87}Sr/^{86}Sr$ ratios among different reservoirs of leachable Sr is observed in the FBC ashes (Fig. 5). In these samples, the $^{87}Sr/^{86}Sr$ ratios of the soluble Sr fractions increase with increasingly aggressive solvents, approaching the whole ash values. Over 50% of the total Sr was leached from both FBC fly ash samples during the sequential extraction (Table 8).

**Table 7.** Bulk CUB strontium data

| Sample Name | [Sr] ppm | $^{87}Sr/^{86}Sr$ |
|---|---|---|
| *Class C* | | |
| FA22 | 1011 | 0.710150 ± 10 |
| FA23 | 822 | 0.710121 ± 8 |
| FA47 | 2961 | 0.711725 ± 10 |
| CRC 9 w/ | 2743 | 0.712050 ± 9 |
| CRC 9 w/o | 2946 | 0.711978 ± 9 |
| *Class F* | | |
| FA26 | 359 | 0.712528 ± 11 |
| FA39 | 1093 | 0.712575 ± 10 |
| FA44 | 525 | 0.714151 ± 10 |
| SRM 1633b | 937 | 0.712786 ± 10 |
| *FBC Ash* | | |
| FA34 | 363 | 0.710780 ± 11 |
| FA45 | 235 | 0.719208 ± 10 |
| *Bottom Ash* | | |
| FA 40 | 482 | 0.714113 ± 12 |

**Table 8.** CUB sequential extraction strontium data

| Sample Name | Water Leach | | 0.1 N HOAc Leach | | 1 N HCl Leach | |
|---|---|---|---|---|---|---|
| | % Sr leached | $^{87}Sr/^{86}Sr^a$ | % Sr leached | $^{87}Sr/^{86}Sr^a$ | % Sr leached | $^{87}Sr/^{86}Sr^a$ |
| *Class C* | | | | | | |
| FA22 | 15 | 0.709816 ± 11 | 18 | 0.709851 ± 11 | 31 | 0.710019 ± 8 |
| FA23 | 15 | 0.709866 ± 10 | 24 | 0.709875 ± 8 | 33 | 0.710092 ± 8 |
| FA47 | 13 | 0.711498 ± 8 | 28 | 0.711570 ± 12 | 49 | 0.711795 ± 10 |
| CRC 9 w/ | 17 | 0.711904 ± 11 | 23 | 0.712119 ± 11 | 54 | 0.712095 ± 11 |
| CRC 9 w/o | 16 | 0.711806 ± 13 | 19 | 0.712029 ± 8 | 57 | 0.711986 ± 10 |
| *Class F* | | | | | | |
| FA26 | 11 | 0.710775 ± 11 | 7 | 0.710732 ± 10 | 6 | 0.710924 ± 10 |
| FA39 | 8 | 0.711191 ± 11 | 13 | 0.711183 ± 12 | 19 | 0.711339 ± 12 |
| FA44 | 4 | 0.711712 ± 8 | 4 | 0.711726 ± 7 | 5 | 0.711902 ± 11 |
| SRM 1633b | 3 | 0.711190 ± 9 | 4 | 0.711118 ± 11 | 11 | 0.711069 ± 9 |
| *FBC Ash* | | | | | | |
| FA34 | 27 | 0.708622 ± 9 | 18 | 0.709246 ± 10 | 27 | 0.710300 ± 6 |
| FA45 | 27 | 0.709762 ± 7 | 13 | 0.710708 ± 14 | 18 | 0.714904 ± 8 |
| *Bottom Ash and FGD* | | | | | | |
| FA 40 | 0.25 | 0.711408 ± 15 | 0.05 | 0.711359 ± 27 | 0.14 | 0.711608 ± 36 |
| FGD 1 | 97 | 0.707976 ± 9 | | | | |

[a]Quoted error is 2σ in-run uncertainty; estimated external reproducibility is ±20 ppm.
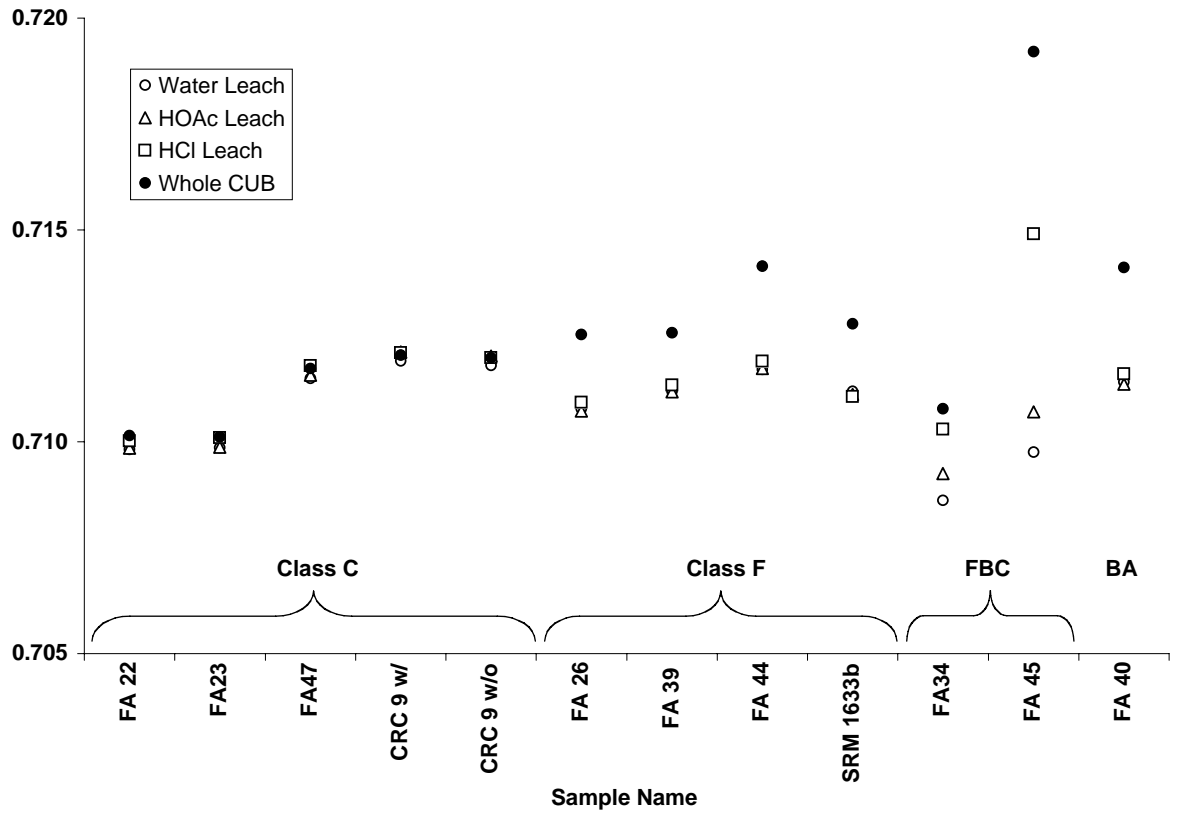Mean value for SRM 987 is 0.71024.

**Figure 5.** Strontium isotopic composition of bulk CUB and sequential extractions. The $^{87}Sr/^{86}Sr$ ratios of leachable Sr are similar to the bulk CUB values for class C fly ash, while the $^{87}Sr/^{86}Sr$ ratios of leachable Sr are markedly lower than the bulk CUB values for class F fly ash. The leachable Sr from FBC fly ash has variable $^{87}Sr/^{86}Sr$ ratios that approach bulk CUB values with increasing aggressiveness of the solvent.

# 5.0    DISCUSSION

## 5.1    STRONTIUM LEACHING AND ISOTOPE SYSTEMATICS IN CUB

### 5.1.1    CUB Geochemistry: Coal to Combustion

The decay of rubidium-87 ($^{87}$Rb) leads to the accumulation of radiogenic $^{87}$Sr in Rb-bearing mineral phases. Although Rb was not measured in this study, potassium (K) can serve as a proxy due to its geochemical similarity to Rb in clays and coal mineral matter (Finkelman 1980, Palmer and Filby 1984, Spears and Martinez-Tarazona 1993). The relationship between K concentrations and the $^{87}$Sr/$^{86}$Sr ratio of CUB is demonstrated in Figure 6, where the $^{87}$Sr/$^{86}$Sr ratios of whole-CUB samples are shown to be positively correlated with K/Sr ratios. This relationship demonstrates the relative importance of detrital mineral inputs to the bulk Sr isotope composition of different types of coal and CUB.

Calcium (Ca) plays an integral role in determining the geochemistry of CUB produced from different coal types and by different combustion processes. The primary difference between the major element chemistry of class C and class F fly ash is the higher concentrations of Ca found in class C ash. Limestone, or other Ca-rich sorbents, are also used for the capture of S during fluidized-bed combustion (FBC). Strontium is geochemically similar to Ca and therefore a particularly useful element for investigating the effects of coal type and combustion process on

the geochemistry of CUB. Many Ca-bearing phases are also readily soluble (e.g., anhydrite and calcite) and contribute substantially to the leachable portion of CUB. The fraction of soluble Sr in CUB is related to the Ca contents (Fig. 7.), demonstrating the important association of these two elements.

The modes of occurrence of chemical components in coal have considerable impact on their behavior during combustion (Ward 2002). Previous work suggests that Sr and other alkaline earth elements have several possible associations in coal, including (1) discrete mineral phases of both detrital and authigenic origin and (2) cation-bearing organic functional groups (Finkelman 1980, Lindahl and Finkelman 1986, Swaine 1990). It has been proposed that alkaline earth elements have a stronger association with organic matter in low-rank coals compared to high-rank coals (Finkelman 1980, Benson and Holm 1985, Lindahl and Finkelman 1986), as the concentrations of alkaline earth elements show an inverse relationship with increasing rank (Lindahl and Finkelman 1986). In this study, a similar relationship is observed between class C fly ash, derived from combustion of lignite or sub-bituminous coal, and class F fly ash, derived from bituminous or anthracite coal. As coal matures, some of the organic matter is destroyed causing the release and potential removal of any associated inorganic elements by fluids (Lindahl and Finkelman 1986). This would have the effect of increasing the contribution of detrital mineral matter to the inorganic element budget in higher rank coals. However, some authors also note that the degree of organic affinity of Sr and other alkaline earth elements can be highly variable in bituminous coals (Finkelman 1980, Querol et al. 2001). Alkali elements are also reported to have similarly varying modes of occurrence among different coal ranks (Huffman and Huggins 1986). Overall, it is likely that the association of inorganic elements

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Interpretation of the Sr isotopic composition of CUB requires consideration of both the feed coal chemistry and the combustion conditions. Because Sr isotope mass fractionation is negligible during most natural processes (and corrected for during measurement), the observation of isotopically distinct Sr reservoirs in a single CUB sample must be attributed to the presence of multiple sources of Sr. These sources might include: (1) mineral matter associated with the feed coal; (2) combustion additives (e.g., limestone sorbent during fluidized-bed combustion) that are preserved during combustion; and/or (3) thermally altered and newly precipitated minerals inheriting the Sr isotopic composition(s) of their precursors.
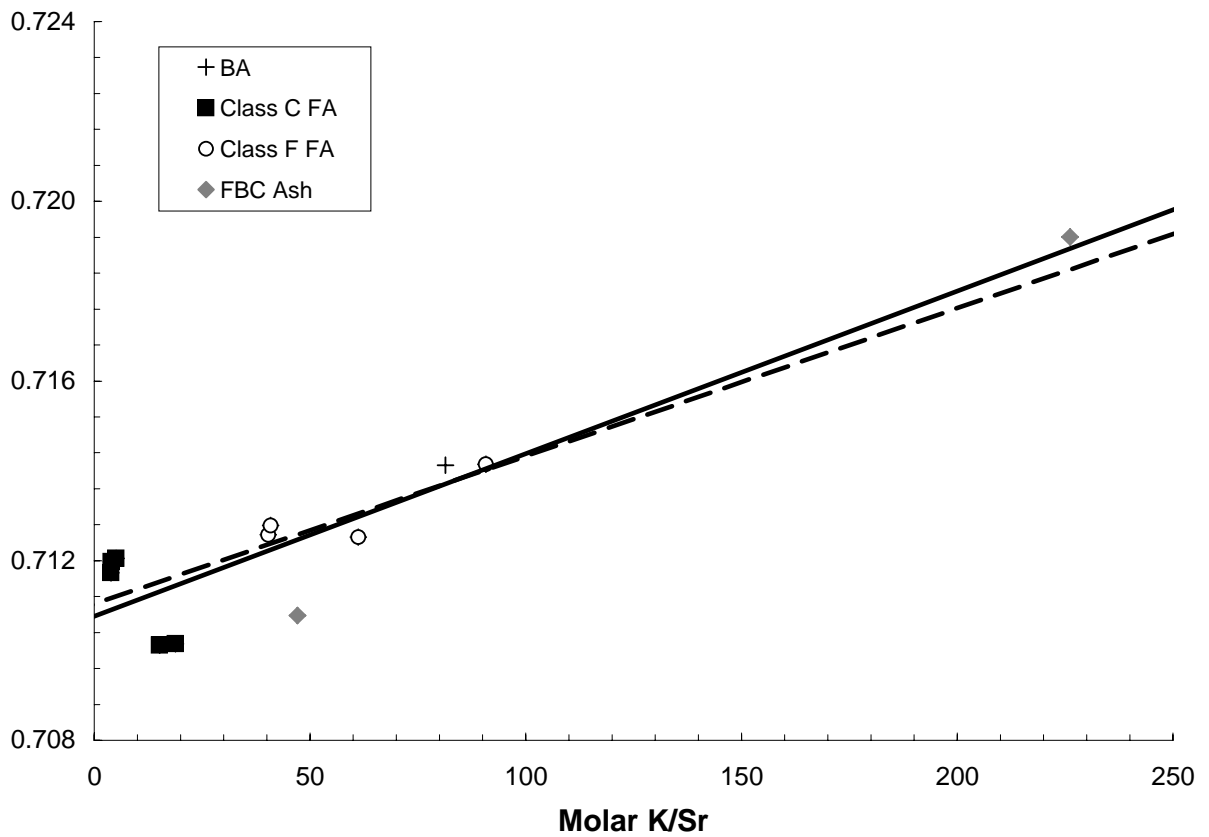
**Figure 6.** $^{87}$Sr/$^{86}$Sr ratios vs. molar K/Sr for bulk CUB samples. When all of the samples are considered there is a positive correlation between these parameters demonstrating the effect of K (and therefore Rb) bearing minerals on the Sr isotopic composition of CUB (solid line, $R^2 = 0.85$). A positive correlation is still observed when the FBC ash samples are excluded (dashed line, $R^2 = 0.61$).
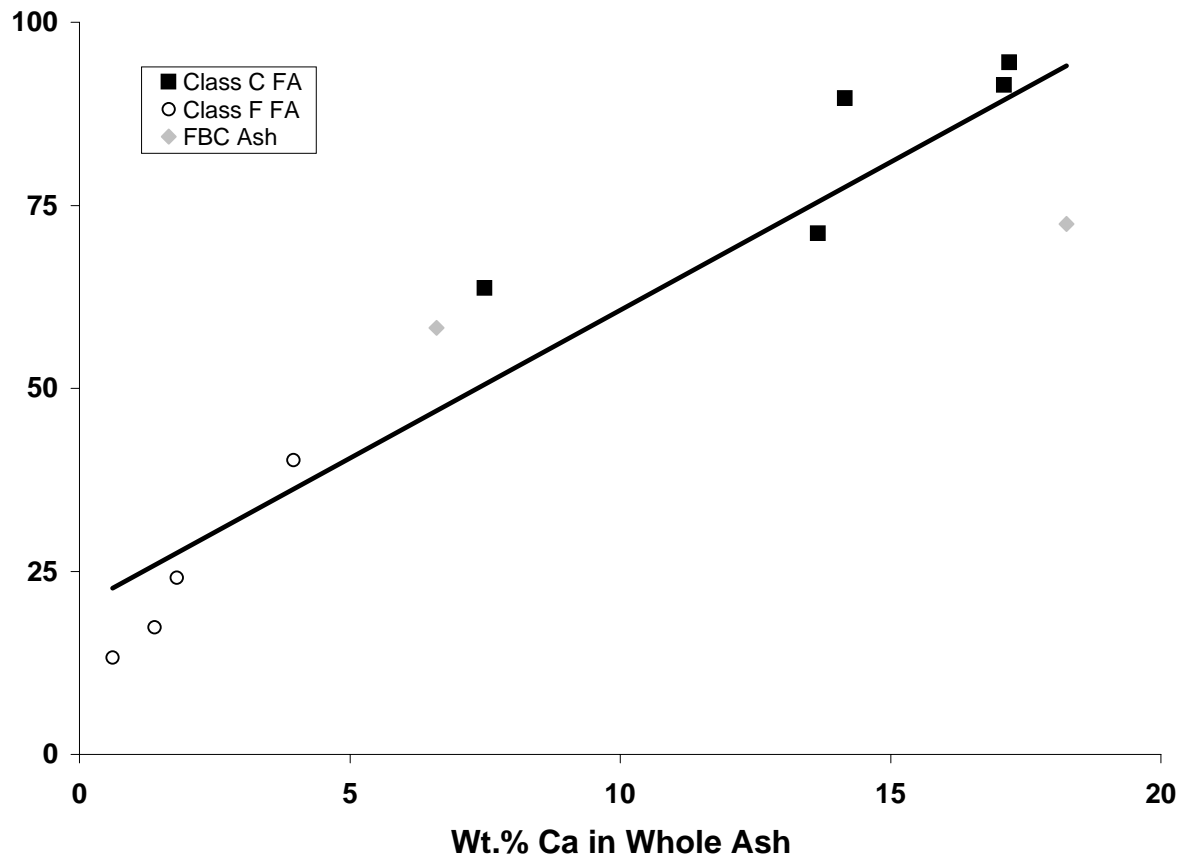
**Figure 7.** Wt.% calcium in whole ash vs. cumulative % strontium leached during sequential extraction. The positive correlation ($R^2 = 0.87$) of these variables demonstrates the important association of these two elements in CUB.

### 5.1.2　Comparison Of Different Types of Fly Ash

*Class C Fly Ash*

The distinct trends in the leaching behavior of Sr observed between class C and F fly ashes can be explained in part by the relative importance of the various Sr sources in different types of coal. During coal combustion, inorganic elements that have a high degree of organic affinity are expected to volatilize and react in the flue gas more readily those that are associated with refractory mineral phases (Miller and Schobert 1994). The high solubility of Sr and relatively restricted range of $^{87}Sr/^{86}Sr$ ratios found within the sequential extractions of class C fly ash are most likely a result of the dominance of organically associated Sr and Ca in the low-rank coals that are burned to produce this type of CUB. The volatilized alkaline earth elements produced during the combustion of low-rank coals react with S in the flue gas to form sulfates, primarily anhydrite ($CaSO_4$), in which Sr is readily incorporated (Miller and Schobert 1994). The presence of anhydrite in all of the class C fly ashes investigated in this study was confirmed by XRD analysis (Table 2). The relative influence of this soluble and isotopically equilibrated phase on the Sr isotopic budget of a given fly ash should increase with higher proportions of organically associated alkaline earth elements. Organically bound calcium that has been volatilized can also act as a fluxing agent for aluminosilicate minerals during coal combustion, allowing these refractory minerals to react more readily in the flue-gas (Miller and Schobert 1994). There is also evidence that high contents of authigenic minerals in low-rank coals break down during combustion, forming alkaline and alkaline earth oxides that react with silicate phases at relatively low temperatures (Vassileva and Vassilev 2006). Furthermore, the

importance of this process is limited in higher-rank coals due to the greater contribution of refractory phases to the inorganic matter (Vassileva and Vassilev 2006). Thus, the high Ca content of class C fly ashes could contribute to the isotopic homogenization of Sr-bearing phases in these samples. Isotopic homogeneity caused by the coincidental similarity of the Sr isotopic compositions of all of the minerals in a coal cannot be ruled out, but this is unlikely in most pre-Cenozoic coals.

### Class F Fly Ash

The relative leachability and variability of Sr isotopic reservoirs found within class F fly ash are markedly different than those of class C fly ash. The essentially bimodal distribution of $^{87}Sr/^{86}Sr$ ratios between the soluble and insoluble fractions of class F fly ash is consistent with the occurrence of both organically associated and mineral-bound Sr in higher rank coals. The small but significant differences in $^{87}Sr/^{86}Sr$ ratios that are observed between the various leachable fractions are likely explained by the presence of multiple modes of occurrence of Sr in the coals that produce class F fly ash. The organically bound fraction of Sr in high-rank coals would be volatilized and condensed in new mineral phases during combustion as described previously for low-rank coals. The Sr that is bound in authigenic phases such as calcite and gypsum are transformed to other readily soluble phases such as lime (CaO) and anhydrite (Mattigod et al. 1990b), inheriting the isotopic composition of the parent minerals. The Sr associated with more refractory phases, most likely detrital minerals, does not readily react and mix with the volatilized organically bound Sr during combustion, thus preserving the $^{87}Sr/^{86}Sr$ ratio of the parent material as well. One of the important findings of this study is that CUB can retain significant isotopic heterogeneity during combustion, despite core burning temperatures

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reaching as high as 1800°C (Mackowsky 1982). Either the duration of the combustion is too short, or portions of the feed coal in the boiler do not reach maximum temperatures.

It was previously noted that mineral-bound elements, rather than those associated with organic functional groups, generally make up a greater proportion of the inorganic component of high-rank coals. As the detrital minerals in high-rank coals are also the primary carriers of K and therefore Rb, it is likely that this component will have more radiogenic Sr associated with it. The relatively high $^{87}Sr/^{86}Sr$ ratios of the whole ash material compared to those of the leachable Sr in class F fly ash reflects the greater importance of the detrital mineral components in the overall Sr budget of high-rank coals and the CUB produced from their combustion.

### *FBC Fly Ash*

The geochemical characteristics of CUB can be strongly influenced by the particular combustion process used. Fluidized-bed combustion has several key characteristics that distinguish it from pulverized coal combustion, and these are likely to have important impacts on the geochemistry of ash produced by this process. These include lower combustion temperatures, longer boiler residence times, and the addition of limestone, or other Ca-rich sorbent with the feed coal to mitigate $SO_x$ emissions (Goodarzi 2006). Marine limestone has an average of 2000 ppm Sr (Faure 2005) and therefore contributes substantially to the Sr budget of FBC ash. The limestone sorbent serves a source of calcium that reacts with S in the flue gas, forming anhydrite that ends up in the fly ash. Anhydrite was detected in both FBC ash samples by XRD analysis (Table 2), and is the likely source of water-soluble Sr in these samples. This is also supported by $^{87}Sr/^{86}Sr$ ratios of the water-soluble fractions of the FBC ashes, which are close to the values of seawater (and therefore limestone) throughout geologic time (~0.707-0.709; Burke et al. 1982). Calcite was also detected in the FBC ashes by XRD (Table 2), which could be derived from

leftover sorbent. However, the presence of calcite in two other fly ash samples investigated in this study (Table 2), one class C and one class F, indicates that this mineral might also be derived from the original coal mineral matter or as a combustion product. The presence of Sr reservoirs with intermediate leachability and $^{87}Sr/^{86}Sr$ ratios that characterizes the FBC ashes can be explained by the addition of limestone and longer boiler residence time experienced by this type of fly ash during combustion. The prolonged heating allows some of the more refractory minerals (with higher $^{87}Sr/^{86}Sr$ ratios) to react with the limestone (lower $^{87}Sr/^{86}Sr$ ratios) possibly creating new phases with variable solubility and Sr isotopic compositions that represent mixtures of these components. Goodarzi (2006) describes particles in an FBC ash that consist of quartz and aluminosilicate fragments that are encased in Ca-rich aluminosilicates and Ca and Fe oxides. Although FBC boiler temperatures are too low to completely melt silicates ($<1000^{o}$ C), the addition of Ca from the limestone sorbent might act as a fluxing agent, as described above (Miller and Schobert 1994), thereby lowering the melting point of these phases and allowing them to react more readily during combustion. The lower boiler temperatures also facilitate the precipitation of soluble $CaSO_4$ in FBC ash by limiting the volatile loss of sulfur during combustion. Rousseau et al. (1997) suggest three ways that trace elements can be incorporated into fly ash during combustion, including (1) association with unaltered coal mineral matter, (2) dissolution of trace element-bearing minerals into molten particles, and (3) volatilized elements in the gas reacting with molten phases. The latter processes might be expected to be especially important during FBC, because the reaction of vapor and molten phases is intentionally induced as a means of S control, and prolonged boiler residence times would allow a higher degree of interaction between molten and solid phases. At the same time, the lower temperatures would preclude complete isotopic homogenization.

### 5.1.3 Selective Catalytic Reduction And Flue-Gas Desulfurization

In addition to fluidized-bed combustion, the effects of other coal combustion technologies, including selective catalytic reduction and flue-gas desulfurization, on the Sr leaching behavior and isotope systematics of different types of CUB are investigated in this study. The "matched set" of fly ashes CRC 9w/ and CRC 9w/o, derived from the same boiler operating with and without SCR, demonstrates the negligible impact of this process on the geochemistry of Sr in fly ash. The leaching behavior and isotope systematics of Sr are very similar in these two samples, with slight but measurable differences most likely caused by feed coal variability rather than as a result of the process. This is not surprising, as the added reductant, typically ammonia or urea, is not a carrier of Sr.

One sample of FGD gypsum was also included in this study. As Sr is thought to be quantitatively partitioned into the fly and bottom ash during coal combustion (Llorens et al. 2001), the limestone sorbent used to remove $SO_x$ from the flue gas is the likely source of Sr in this type of CUB. This is supported by the $^{87}Sr/^{86}Sr$ ratio measured in this sample of 0.70798, which is within the expected range of marine limestones (Burke et al. 1982). The Sr in FGD gypsum is highly soluble with nearly 100% extraction in water. Co-disposal of this type of CUB with fly ash would have a substantial impact on the Sr geochemistry of waters that encounter this material.

## 5.2    SEQUENTIAL LEACHING OF CUB

Sequential extractions can help elucidate the modes of occurrence and potential mobility of various major, minor and trace elements in the different types of CUB. Despite the considerable variability in leaching behavior between CUB samples of the same type, trends in the relative mobility of different elements in different CUB types can still be investigated.

### 5.2.1    Water Soluble Fraction

In general, the order of relative leachability of different elements is quite similar between the various types of fly ash. Several major elements that have relatively high proportions of the leachable amounts associated with the water-soluble fraction of fly ash include Ca, K, Na, and S. The water-soluble forms of these elements are presumed to be sulfate minerals, with $CaSO_4$ (anhydrite) being the dominant phase. There are also some minor and trace elements that are readily mobilized during the water-leaching step of the sequential leaching procedure, including B, Cr, Mo, Se, and Sr. These elements are also assumed to be associated with sulfate phases, and possibly borates or other salts (Querol et al. 1996) that form during combustion as volatilized species condense on the surface of fly ash particles (Eary et al. 1990). This could possibly be attributed to the organic association of these elements in coals allowing them to readily volatilize during combustion, as was previously described for Sr. The tendency of these elements, with the exception of Sr, to form anions when oxidized might also contribute to their incorporation in surface coatings on fly ash particles. Some of these elements could also be associated with authigenic minerals in coals, including gypsum and carbonates, which are thought to transform into relatively soluble species such as anhydrite and alkaline earth oxides during combustion

(Mattigod et al. 1990b). Among the major elements, Fe, Mg and Si are basically water-insoluble in fly ash (Figs. 2-4). Minor and trace elements that are water-insoluble, or only very slightly water-soluble are P, Ti, Cu, Mn, Pb, As, Ni, Co, Sb, Cd, V and Zn (Figs. 2-4). These elements are associated with more refractory phases in coal, such as clay minerals, phosphates, and other detrital minerals (Swaine 1990) that are thought to transform into the aluminosilicate glass and mullite during combustion (Mattigod et al. 1990b).

### 5.2.2  Acetic Acid- and Hydrochloric Acid-Soluble Fractions

Dilute acetic acid (HOAc) presumably attacks carbonates and was also found to dissolve silicate phases that could be slightly acid soluble, such as glass, inferred by the substantial portion of leachable Si found during this extraction step. Most elements in all types of fly ash are more soluble in HOAc and HCl as compared to water. There are, however, a few exceptions, including S, B, Mo, and Se in class C and F fly ash (Fig. 2), which can be interpreted as having an affinity for incorporation in sulfates or other salts precipitated during combustion. Several other elements (notably Ca, Mg, B, Sr, Zn, Cu, Mn, Cr, Ni, Co, Sb and Cd) are relatively HOAc-soluble in class C and class F fly ash, indicating association with carbonates, or possibly glass. Others are predominantly soluble in HCl (Al, Fe, P, Ti, V, and Pb), suggesting that they are bound in more refractory phases. This is supported by the correlation of some of these elements with higher ash contents in coals (Lindahl and Finkelman 1986). Arsenic is the only element that is leached in higher quantities from class F and FBC ashes compared to class C. Some portion of the leachable fraction of As is released in the water and HOAc leachates of class F and FBC ash, whereas it is almost entirely in the HCl leach in class C ash. This suggests that there are

fundamentally different modes of occurrence of arsenic in different types of fly ash, which could

in part reflect the distribution of As in coal.

# 6.0    STRONTIUM ISOTOPES AS A TRACER OF FLY ASH

The use of Sr isotopes as a tracer of CUB is largely dependent on site-specific factors, particularly the $^{87}Sr/^{86}Sr$ ratios and Sr concentrations of surrounding soils, sediments and waters. Differences in the leachability and Sr isotope systematics of the various types of fly ash also has important implications for the use of this element as an environmental tracer of CUB. The evolution of the Sr isotopic composition of leachate released from the different types of fly ash during progressive dissolution is shown as the cumulative $^{87}Sr/^{86}Sr$ ratio of mobilized Sr plotted against the cumulative percent of total Sr released (Figs., 8-10). In class F fly ash, only a small fraction of the total Sr would be released, possibly limiting the utility of this tracer for long-term applications (Fig. 8). Strontium isotopes are probably most suitable as a tracer of class C fly ash, which releases a large portion of its Sr as well as higher total amounts of this element during leaching (Fig. 9).  In addition, the homogeneity of the $^{87}Sr/^{86}Sr$ ratio in successive extractions would provide more reliable tracking of the fly ash contribution to a mixed-source water-solid interaction. Although a substantial fraction of the Sr is readily leached from the FBC ash, the large variability of the $^{87}Sr/^{86}Sr$ ratios in the leachate as the ash dissolved could limit the utility of Sr isotopes as a unique tracer of this type of CUB (Fig .10).  However, in certain situations, the change in isotopic composition over time could provide information about the extent to which an FBC ash site has been "leached out." If the conditions are favorable, monitoring

$^{87}$Sr/$^{86}$Sr ratios of waters that are interacting with CUB could provide quantitative information about the contributions of the CUB to ground and surface water chemistry.
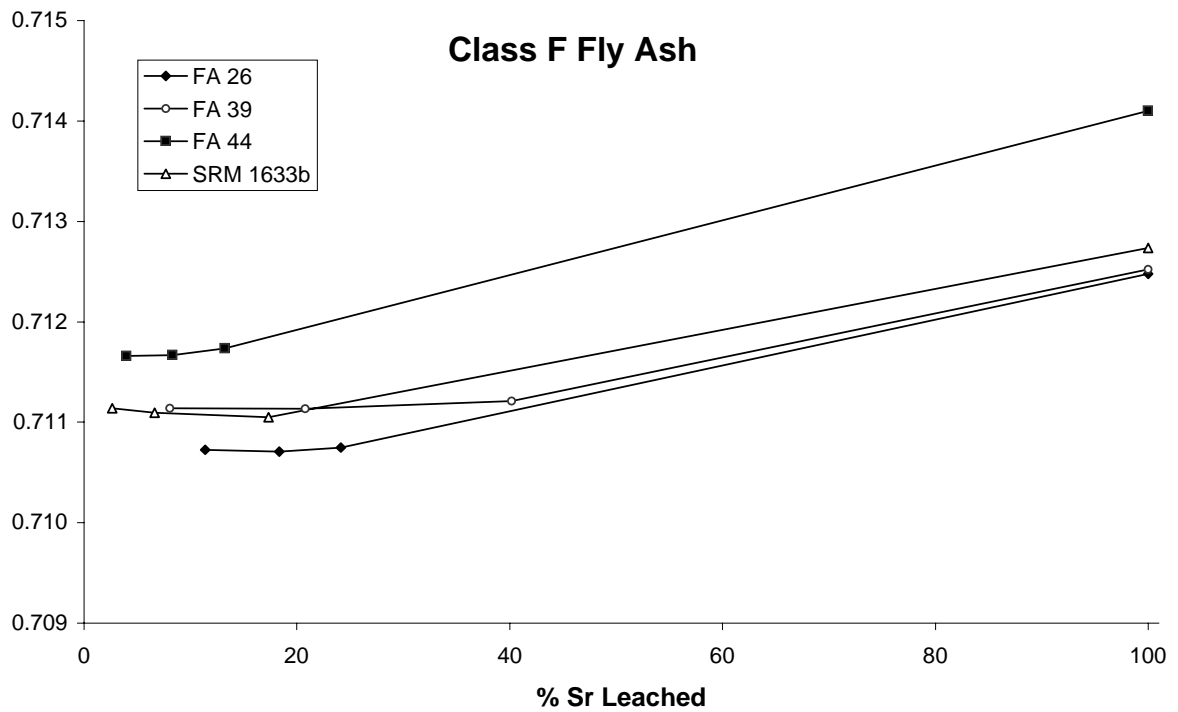


**Figure 8.** Cumulative % strontium leached vs. cumulative $^{87}$Sr/$^{86}$Sr ratio of class F fly ash leachate. From left to right, the data points represent the total fraction of Sr leached and the isotopic composition in the combined leachate after each additional sequential extraction step. The points plotted at 100% Sr leached are the total dissolution data.
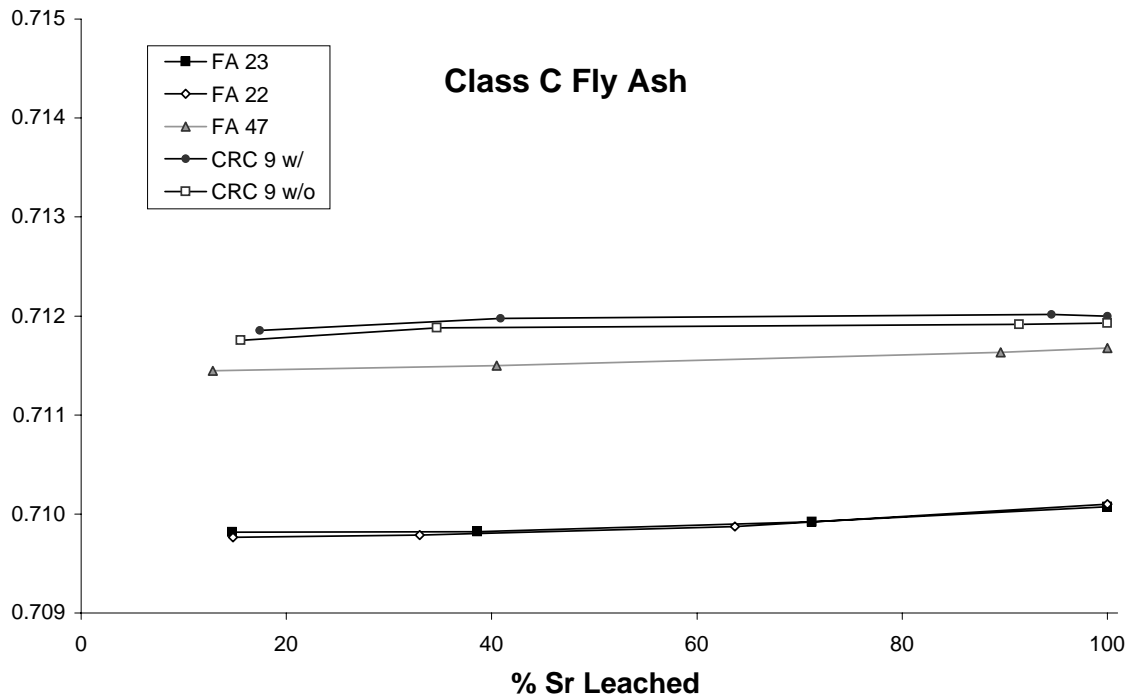
**Figure 9.** Cumulative % strontium leached vs. cumulative $^{87}Sr/^{86}Sr$ ratio of class C fly ash leachate. From left to right, the data points represent the total fraction of Sr leached and the isotopic composition in the combined leachate after each additional sequential extraction step. The points plotted at 100% Sr leached are the total dissolution data.
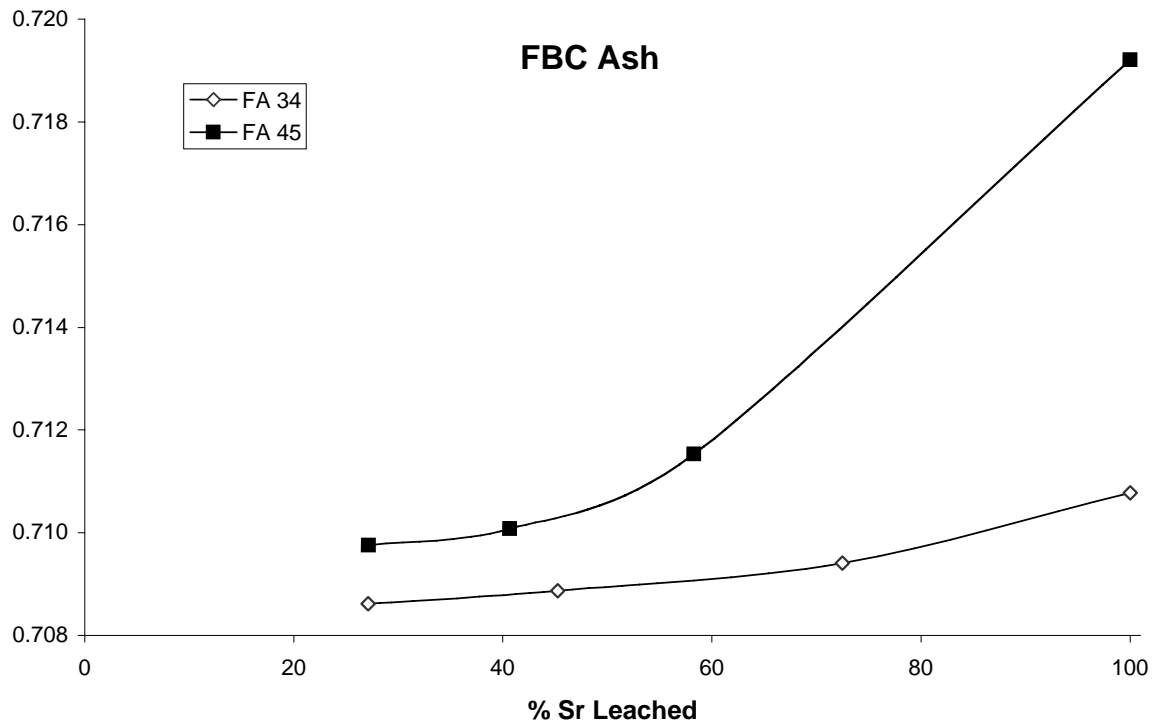
**Figure 10.** Cumulative % strontium leached vs. cumulative $^{87}Sr/^{86}Sr$ ratio of FBC fly ash leachate. From left to right, the data points represent the total fraction of Sr leached and the isotopic composition in the combined leachate after each additional sequential extraction step. The points plotted at 100% Sr leached are the total dissolution data.

## 7.0    CONCLUSIONS


This study presents an investigation of the Sr isotope systematics and geochemistry of coal utilization by-products (CUB). Sequential leaching experiments were coupled with elemental and Sr isotope analyses to isolate specific geochemical reservoirs in the CUB and to understand the behavior of different minerals and associated elements during coal utilization. Several different types of CUB were investigated to better understand the influence of coal characteristics and combustion processes on the geochemical properties of CUB. The utility of Sr isotopes as an environmental tracer of CUB was also addressed.

Higher total quantities and a larger fraction of many elements were leached from class C and FBC fly ash as compared to class F fly ash. This is most likely a result of the presence of more soluble Ca-bearing phases in these ashes. Several elements that are potentially detrimental to the environment were readily leached from fly ash in water (B, Cr, Mo, Se and F) and dilute acetic acid (Zn, Cu, Mn, Cr, Ni, Co, Sb and Cd). Other potentially toxic elements (V and Pb) were only found to be soluble in HCl.

The presence of unique Sr isotopic reservoirs with varying degrees of solubility in a single sample of CUB unequivocally demonstrates the presence of multiple sources of isotopically distinct Sr in these materials. Moreover, information about strontium sources, the relative importance of these sources in different types of coal, and the way in which they are affected during combustion can be inferred from the Sr isotopic systematics of CUB sequential

extractions. The leaching behavior and Sr isotope systematics of class F fly ash, derived from higher rank coals, demonstrates that isotopic equilibration of various minerals in coal does not necessarily occur during combustion, despite the high temperatures reached in the boiler. However, the trends in the leachability and Sr isotope systematics observed in sequentially extracted class C fly ash suggests that isotopic homogenization can occur during combustion, possibly due to the specific chemistry of the feed coal. Investigation of fluidized-bed combustion (FBC) ash demonstrates that the particular combustion process can affect the chemical and mineralogical characteristics of CUB through the input of materials other than coal, and through the combustion parameters such as boiler temperature, residence time, etc.

Sequential leaching of various types of coal fly ash and other CUB can provide useful information on the geochemical behavior of these materials in the natural environment. Differences in the geochemistry of Sr between various types of fly ash could also have implications on the use of this isotope system as a tracer for the interaction of CUB with soils and waters. It may also be possible to interpret the modes of occurrence and behavior of other elements in coal and CUB that are associated with Sr, although more work, such as studies of both feed coal and the ash it produces, are clearly needed. Understanding the Sr isotope systematics of CUB will aid in future applications of other isotopic tools (e.g., Pb, Nd, U, Cd, Se and B) to understand coal combustion processes and track CUB-water interaction in the environment.

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