Strontium Isotope Study of Coal Utilization By-Products Interacting with Environmental Waters


Sequential leaching experiments on coal utilization by-products (CUB) were coupled with chemical and strontium (Sr) isotopic analyses to better understand the influence of coal type and combustion processes on CUB properties and the release of elements during interaction with environmental waters during disposal. Class C fly ash tended to release the highest quantity of minor and trace elements—including alkaline earth elements, sodium, chromium, copper, manganese, lead, titanium, and zinc—during sequential extraction, with bottom ash yielding the lowest. Strontium isotope ratios (\(^{87}\text{Sr}/^{86}\text{Sr}\)) in bulk-CUB samples (total dissolution of CUB) are generally higher in class F ash than in class C ash. Bulk-CUB ratios appear to be controlled by the geologic source of the mineral matter in the feed coal, and by Sr added during desulfurization treatments. Leachates of the CUB generally have Sr isotope ratios that are different than the bulk value, demonstrating that Sr was not isotopically homogenized during combustion. Variations in the Sr isotopic composition of CUB leachates were correlated with mobility of several major and trace elements; the data suggest that arsenic and lead are held in phases that contain the more radiogenic (high-\(^{87}\text{Sr}/^{86}\text{Sr}\)) component. A changing Sr isotope ratio of CUB-interacting waters in a disposal environment could forecast the release of certain strongly bound elements of environmental concern. This study lays the groundwork for the application of Sr isotopes as an environmental tracer for CUB–water interaction.

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 (FGD) residues (Sajwan et al., 2006). The United States, China, and India alone produce more than 300 Mt/yr of CUB; this is a strong driver for finding value-added products using this material (Asokan et al., 2005). Until the recent economic downturn, the annual production and use of CUB was steadily climbing (ACAA, 2011); about 40% of produced CUB in the United States is used for making bricks, cement, concrete, wallboard, mining materials, adhesives, paint, and as a soil amendment and wood substitute (Yeheyis et al., 2008; ACA, 2011). Although the percentage of CUB used in recycled products has been increasing, the majority is still disposed of in landfills or settling lagoons, where it has the potential to interact with precipitation, runoff, surface water, and groundwater (Yeheyis et al., 2008; Bhattacharyya et al., 2009).

Reliable tests that can determine the extent to which CUB will retain or release potentially toxic metals while interacting with environmental waters under variable pH and redox conditions are critical to the development of new beneficial uses of CUB as well as appropriate long-term storage solutions (Hassett et al., 2005; Véjahlatti et al., 2010). Improved monitoring tools are needed to rapidly detect potential interactions with protected water supplies and to distinguish between different sources, both natural and anthropogenic, which could be contributing to an increase in dissolved metals.

We report an investigation of the mineralogy, geochemistry, and strontium (Sr) isotope systematics of different types of CUB subjected to sequential chemical extractions. Sequential extraction techniques can facilitate identification of various mineral reservoirs in CUB and provide information about the elemental retention and mobility during environmental exposure. Natural isotope compositions of fluids that have interacted with various solid materials can be used to...
identify the source of chemical species in natural and human-impacted waters and to track fluid flow. Strontium isotope ratios (expressed as \(^{87}\text{Sr}/^{86}\text{Sr}\)) are well established as tracers of fluids and water–rock interactions in geologic and environmental systems (Capo et al., 1998; Banner, 2004). Thus, \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios can potentially be used to identify different phases within CUB that could carry toxic trace metals and provide a sensitive technique to track the release of even small amounts of these metals into the environment.

The concentration of \(^{87}\text{Sr}\) in geologic materials increases over long time scales (generally millions to billions of years) as a result of the \(^{87}\text{Sr}\) decay of rubidium (Rb)-87. Natural variations in the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios of different materials reflect the age differences and the Rb/Sr ratios of the geologic sources and can be used to uniquely identify and quantify involvement of these materials in geologic and environmental processes. In general, minerals that are older and have higher Rb/Sr ratios will have higher \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios. Here we report isotope ratios as \(\varepsilon_{\text{Sr}}^{SW}\) values, which is the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio normalized to the present-day seawater \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio:

\[
\varepsilon_{\text{Sr}}^{SW} = 10^4 \left( \frac{^{87}\text{Sr} / ^{86}\text{Sr}_{\text{sample}}}{^{87}\text{Sr} / ^{86}\text{Sr}_{\text{seawater}}} - 1 \right)
\]

The seawater \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio at any given time is uniform across the Earth’s oceans (Faure and Mensing, 2005, p. 437), making it a useful universal normalization ratio. In the case of natural waters, soils, secondary minerals, sediments, and sedimentary rocks (including coal), the \(\varepsilon_{\text{Sr}}^{SW}\) values usually reflect mixtures of isotopically distinct sources of Sr. Continental crust that is exposed to weathering has a rather high average \(\varepsilon_{\text{Sr}}^{SW}\) value of about +100 \((^{87}\text{Sr}/^{86}\text{Sr} \approx 0.716)\), as inferred from the suspended sediment loads of rivers (Goldstein and Jacobsen, 1980). In contrast, the average \(\varepsilon_{\text{Sr}}^{SW}\) value of Sr dissolved in rivers is in the range of ±10 to ±40 (Wadleigh et al., 1985; Goldstein and Jacobsen, 1987), reflecting contributions from more soluble, less radiogenic sources of Sr. The Sr isotopic composition of seawater, and hence marine limestone, varies throughout geologic time over a range of ~35 to +0.5 (Burke et al., 1982). The \(\varepsilon_{\text{Sr}}^{SW}\) values of young oceanic basalts are typically low (~100 to ~60) but can vary considerably in some continental volcanics due to assimilation of crustal materials.

In coal, Sr is a trace element with an average concentration of ~100 mg/kg (Swaine, 1990). Coal utilization by-products are enriched in Sr relative to coal and many other geologic reservoirs with concentrations up to ~3,000 mg/kg (Hurst and Davis, 1981; Hurst et al., 1991). The Sr in CUB is also known to be readily mobilized and biogeochemically available (Hurst and Davis, 1981). Studies of trace element partitioning during coal combustion indicate that Sr is among the group of elements—including barium (Ba), beryllium (Be), cobalt (Co), chromium (Cr), molybdenum (Mo), lead (Pb), and zinc (Zn)—that condense within coal-fired power plants, in contrast to volatile elements such as mercury (Hg) and selenium (Se) (Vejakhti et al. [2010], and references therein).

Previous work on Sr isotopes in CUB focused primarily on the utility of this element as an environmental tracer for airborne fly ash (Hurst and Davis, 1981; Straunghan et al., 1981; Mattigod et al., 1990b; Hurst et al., 1991, 1993). Little data exist on the Sr isotopic compositions of coals, and these are limited to a few samples that were leached in acid (Hurst et al., 1991, 1993; Frost et al., 2002). 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. Hamel et al. (2010), for example, demonstrated that Sr isotope ratios can be sensitive indicators of water–CUB interaction in a CUB-grouted coal mine in West Virginia. The goal of this study is to determine if Sr isotopes can be used to trace the release of potentially toxic trace elements from different CUB components during interaction with natural waters. In particular, we investigate a variety of CUB materials produced from different types of coal and by different combustion techniques to understand how these factors might affect the utility of Sr isotopes as a tracer of CUB in the environment. Strontium isotopes are a conservative tracer in most aqueous environments (Banner, 2004), and a shift in the \(^{87}\text{Sr}/^{86}\text{Sr}\) of a CUB containment outflow could indicate a change in hydrochemical environment or extent of CUB dissolution before detection of reactive metals in the outflow. Moreover, the Sr isotope composition can potentially provide information about the release mechanism and specific phase(s) associated with a given toxic element.

**Materials and Methods**

**CUB Sample Selection and Preparation**

Thirteen samples of CUB comprising 11 fly ashes, 1 bottom ash, and 1 sample of FGD material were subject to sequential extraction. All samples were obtained from the Department of Energy National Energy Technology Laboratory (NETL) in Pittsburgh, PA, with the exception of SRM 1633b fly ash, 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. Three types of fly ash were investigated: ASTM class C and class F fly ashes generated from combustion of pulverized coal, and fly ash produced by a fluidized-bed combustion (FBC) process. The ASTM classification system relates to the characteristics of fly ash that are important for cement manufacture (ASTM International, 2006). For the purposes of this study, the important differences are that class C fly ashes are produced from lignite and sub-bituminous rank coals and have a minimum major oxide \((\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)\) content of 50 wt.%, whereas class F ashes are produced from bituminous and anthracite rank coals with minimum major oxide contents of 70 wt.%. The FBC ashes were selected to investigate the influence of FBC technology on coal ash chemistry. The effects of combustion technology on fly ash chemistry were additionally investigated with two of the class C fly ash samples (CRC 9 w/and CRC 9 w/o) that were produced in the same boiler operating with and without selective catalytic reduction (SCR), an NO\(_x\) emission control technique (Radosevic, 1998). Selected characteristics of the samples are listed in Table 1. Note 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 to 1 kg) were split down to 10- to 100-g aliquots using a coarse riffle splitter. Further division to the final aliquots of 0.5 to 1.0 g was performed at the University of Pittsburgh using a fine-chute riffle splitter.

**X-ray Diffraction**

The major crystalline mineral phases present in the fly and bottom ash samples were determined by X-ray diffraction (XRD) 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 2θ angles from 10° to 80°. Mineralogy was determined using the Philips X’pert Organizer software (X’pert, Philips/PANalytical, Almelo, the Netherlands).

**Sequential Leaching Procedure**

A number of studies have examined the solubility and leaching potential of CUB (Querol et al., 1996, 2001; Sheps-Pelleg and Cohen, 1999; Hassett et al., 2005). Current procedures include serial batch leaching (Kim and Hesbach, 2009), synthetic groundwater leaching (Hassett, 1998), and mine water leaching (Ziemkiewicz et al., 2003), as well as the USEPA-developed toxicity characteristic leaching procedure (USEPA Method 1311; USEPA, 1992). A review of these methods is provided by Kim and Hesbach (2009). However, these procedures often attempt to simulate specific environments to which the CUB may be subjected, in contrast to the procedure used here, which attempts to identify geochemical associations by targeting specific phases in the CUB.

A three-part sequential leaching procedure was performed on the fly ash and bottom ash samples. The steps of the leaching procedure were designed to target elements associated with specific phases, including (i) water-soluble phases, primarily sulfates (e.g., anhydrite, gypsum); (ii) phases soluble in dilute acetic acid (HOAc), specifically carbonate minerals; and (iii) phases soluble in hydrochloric acid (HCl), such as phosphates (e.g., apatite), some oxides, and possibly glass produced during combustion. The leaching solution was added to the sample in a 50-mL polypropylene centrifuge tube, and the mixture was shaken at room temperature for either 8 h (water extractions) or 2 h (HOAc and HCl extractions). The samples were then centrifuged for 10 min and the solutions were filtered through a 0.45-μm 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 HNO₃. Water leachates collected for determination of anions were not acidified and were kept refrigerated at 4°C.

The FGD sample 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 calcium sulfate (gypsum or anhydrite), which is readily water soluble, the full leaching procedure was not performed. Visual inspection of this sample confirmed that all but a few nonsulfate grains had dissolved in the water.

**Chemical Analysis**

For most samples, total (whole-ash) chemical compositions were determined on ~0.1-g aliquots of sample fused in a 10:1 excess of lithium tetraborate. Fly ash standard SRM 1633b was dissolved using the hydrofluoric acid (HF) procedure described in the next section. Elemental concentrations were determined by inductively coupled plasma–optical emission spectroscopy (ICP–OES; PerkinElmer, Optima 3000, Waltham, MA) and inductively coupled plasma–mass spectrometry (ICP–MS; PerkinElmer, Elan DRC II, Waltham, MA) at NETL, with the exception of Sr and sulfur (S) concentrations, which were determined by ICP–OES (Spectroflame Modula, Spectro, Kleve, Germany) at the University of Pittsburgh.

Major elements—aluminum (Al), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), sodium (Na), and silicon (Si)—in the sequential extractions were measured by ICP–OES at the University of Pittsburgh. Minor and trace elements—arsenic (As), boron (B), Ba, cadmium (Cd), Cr, Co, copper (Cu), manganese (Mn), Mo, nickel (Ni), phosphorus (P), Pb, antimony (Sb), Se, Sr, titanium (Ti), vanadium (V), and Zn—were measured by ICP–MS at NETL. In a few cases,
trace elements in the HCl leachate solutions were measured by ICP–OES due to isobaric interferences caused by Cl compounds in the ICP–MS. Major anions in the water leachates \((\text{Cl}^-, \text{F}^-, \text{SO}_4^{2-}, \text{and NO}_3^-)\) were determined by ion-chromatography (ICS 2000, Dionex, Sunnyvale, CA) at the University of Pittsburgh.

**Strontium Isotope Analysis**

For whole-CUB Sr isotope analysis, 0.05- to 0.1-g samples of CUB were digested under clean laboratory conditions in a sequence of concentrated ultra-pure acids including (i) hydrofluoric acid (HF) + aqua regia; (ii) perchloric acid (HClO₄); and (iii) nitric acid (HNO₃). After evaporating to dryness, the samples were redissolved in an HNO₃ solution for aliquoting.

Aliquots of the acid-digested sample solutions and the sequential leaching solutions containing about 3 μg of dissolved Sr were evaporated to dryness in Teflon beakers in a high-efficiency particulate air–filtered hood and redissolved in 3 M HNO₃. The aliquots were then passed through quartz glass columns packed with Sr Resin from Eichrom (Lisle, IL) to separate Sr from the matrix. Approximately 500 ng of Sr was loaded onto Re single filaments with a tantalum oxide activator. Strontium isotopic compositions were measured by multicollector thermal ionization mass spectrometer (Model 262, Finnigan-MAT/Thermo, Bremen, Germany) at the University of Pittsburgh using a multidynamic measurement routine. A total of 100 ratios were measured during each analysis, and instrumental mass fractionation was corrected using \(^{86}\text{Sr}/^{88}\text{Sr} = 0.1194\). The mean \(^{87}\text{Sr}/^{86}\text{Sr}\) value of Sr isotope standard SRM 987 over the period of these analyses was 0.710239 ± 0.000018 \((2\sigma\text{ external reproducibility, } n = 58)\). Our corresponding \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio for seawater is 0.709164.

**Results**

**CUB Mineralogy**

The detection of crystalline phases in CUB materials by XRD is difficult because of the presence of broad, amorphous peaks due to the high proportion of glass phases. Thus, only the most abundant crystalline minerals can be detected, leaving the possibility of minor phases that cannot be determined. The most common minerals observed in the CUB samples were quartz (\(\text{SiO}_2\)) in all of the samples, magnetite (\(\text{Fe}_3\text{O}_4\)) and hematite (\(\text{Fe}_2\text{O}_3\)) in the FBC ashes and some of the class F ashes, mullite (\(\text{Al}_2\text{Si}_2\text{O}_5\)) in the class F ashes and bottom ash, and anhydrite (\(\text{CaSO}_4\)) in the class C and F ashes. Calcite (\(\text{CaCO}_3\)) was also observed in the FBC ashes and one sample each of the class C and F ashes, as well as periclase (\(\text{MgO}\)) in some of the class C fly ash samples.

**CUB Bulk Composition**

The major element compositions of completely dissolved CUB samples (i.e., bulk samples) are provided in Supplemental Table S1. Comparison of our major element values for SRM 1633b with the NIST-certified values (Greenberg et al., 1995) indicates deviations of less than 12% from the certified values. The most likely reasons for the deviations are inhomogeneous splitting of the sample and/or the presence of insoluble solids remaining after HF dissolution, which would not be a problem with the lithium tetraborate fusions used on the other samples. Because SRM 1633b was dissolved using HF, its silicon concentration could not be determined. Certain volatile elements (e.g., As, S, Se) may have been lost during either fusion with lithium tetraborate or HF dissolution procedures, so the reported whole-CUB concentrations of these elements are considered minimum values.

The major element chemistry is quite variable within and between different ash types. In general, class C fly ash has higher concentrations of Ca, Mg, and Na compared with class F fly ash. The two samples of FBC ash have a relatively wide range of major and minor element compositions. The sample of bottom ash (FA 40) is generally similar to the class F ashes, but with significantly lower Ca. The FGD sample consists predominantly of Ca and S, as expected for gypsum or anhydrite.

Concentrations of minor and trace elements in whole-CUB samples are provided in Supplemental Table S2. Our values for SRM 1633b generally agree within 10% of the certified values, with the exception of Pb, for which our measured concentration is 50% lower. The overall distribution of trace elements is similar among the different ash type groups. The largest deviations from this trend are the high concentrations of Ba, P, and Sr in class C ashes; high Mn in class F ashes; the depletion of Pb in bottom ash; and generally low concentrations of P and Zn.

**CUB Leachate Major and Trace Element Concentrations**

The amounts of major elements released from the CUB samples during sequential leaching by H₂O, acetic acid, and hydrochloric acid are provided in Supplemental Table S3 as milligrams of element extracted per gram of original CUB starting material. Figure 1a shows the total amount, averaged for each CUB class, of each major element extracted by the three sequential leaches combined. Element leachability in class C fly ash was generally greater than in class F or FBC fly ash, with higher proportions and total amounts of most elements released during sequential extraction. The average quantities of most major elements

![Fig. 1. Fraction of selected (a) major and (b) trace elements leached from different classes of coal utilization by-products samples by the combined sequential extractions of H₂O + acetic acid + hydrochloric acid leachings. FBC, fluidized-bed combustion.](image-url)
Strontium Isotopes in CUB

We report the Sr isotopic composition of the total CUB acid digests and CUB sequential leaching solutions in Table 2. Isotope ratios are reported as \( \varepsilon^{\text{Sr}}_{\text{SW}} \) values with the in-run 2σ uncertainty shown (external reproducibility is generally better than ± 0.2 units). Isotope ratios for the whole-CUB and all three leachates are shown in Fig. 2. The total range of whole-CUB \( \varepsilon^{\text{Sr}}_{\text{SW}} \) values is +13.5 to +141.6, corresponding to \( \varepsilon^{\text{Sr}}/\varepsilon^{\text{Sr}}_{\text{SW}} \) ratios of 0.71012 to 0.71921. Whole-CUB \( \varepsilon^{\text{Sr}}_{\text{SW}} \) values are, on average, higher in class F ash than in class C ash. All of the CUB samples also show measurable differences between the leachate and the bulk CUB \( \varepsilon^{\text{Sr}}_{\text{SW}} \) values, indicating the presence of multiple sources of isotopically distinct Sr within the CUB. However, there is a wider range of \( \varepsilon^{\text{Sr}}_{\text{SW}} \) values among different Sr reservoirs in class F ash and FBC fly ash than in class C fly ash. The Sr isotope budget in the one sample of bottom ash investigated in this study was similar to that of class F fly ashes but with far less leachable Sr (<1%) removed during sequential extraction.

Different trends are 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 \( \varepsilon^{\text{Sr}}_{\text{SW}} \) values of the various sequential extraction leachates are relatively close to those of the whole ash (Fig. 2). Substantial proportions (64–95%) of the total Sr are also leached from these ashes during sequential extractions with H\(_2\)O, 0.1 M HOAc, and 1 M HCl (Table 2). On the other hand, in class F fly ashes, the \( \varepsilon^{\text{Sr}}_{\text{SW}} \) values of the leachable Sr is markedly lower than the bulk ash \( \varepsilon^{\text{Sr}}_{\text{SW}} \) values. Although different than the bulk value, the \( \varepsilon^{\text{Sr}}_{\text{SW}} \) values of all of the class F ash leachates are similar to each other (Fig. 2).

Table 2. Whole coal utilization by-products (CUB) and CUB sequential leach Sr concentration and isotope data.

<table>
<thead>
<tr>
<th>Sample†</th>
<th>Whole CUB</th>
<th>H(_2)O leach</th>
<th>0.1 M HOAc leach</th>
<th>1 M HCl leach</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{Sr}^\dagger )</td>
<td>( \varepsilon^{\text{Sr}}_{\text{SW}} )§</td>
<td>( \text{Sr}^\dagger )</td>
<td>( \varepsilon^{\text{Sr}}_{\text{SW}} )§</td>
</tr>
<tr>
<td>Class C fly ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA 22</td>
<td>1011</td>
<td>13.90 ± 0.14</td>
<td>150</td>
<td>9.19 ± 0.16</td>
</tr>
<tr>
<td>FA 23</td>
<td>822</td>
<td>13.49 ± 0.11</td>
<td>121</td>
<td>9.90 ± 0.14</td>
</tr>
<tr>
<td>FA 47</td>
<td>2961</td>
<td>36.11 ± 0.14</td>
<td>379</td>
<td>32.91 ± 0.11</td>
</tr>
<tr>
<td>CRC 9 w/</td>
<td>2743</td>
<td>40.70 ± 0.13</td>
<td>478</td>
<td>38.64 ± 0.16</td>
</tr>
<tr>
<td>CRC 9 w/o</td>
<td>2946</td>
<td>39.68 ± 0.13</td>
<td>458</td>
<td>37.26 ± 0.18</td>
</tr>
<tr>
<td>Class F fly ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA 26</td>
<td>359</td>
<td>47.44 ± 0.16</td>
<td>40.8</td>
<td>22.72 ± 0.16</td>
</tr>
<tr>
<td>FA 39</td>
<td>1093</td>
<td>48.10 ± 0.14</td>
<td>88.3</td>
<td>28.58 ± 0.16</td>
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<tr>
<td>FA 44</td>
<td>525</td>
<td>70.32 ± 0.14</td>
<td>21.0</td>
<td>35.93 ± 0.11</td>
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<td>FBC fly ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA 34</td>
<td>363</td>
<td>22.79 ± 0.16</td>
<td>98.5</td>
<td>–7.64 ± 0.13</td>
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<tr>
<td>FA 45</td>
<td>235</td>
<td>141.63 ± 0.14</td>
<td>63.7</td>
<td>8.43 ± 0.10</td>
</tr>
<tr>
<td>Bottom ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA 40</td>
<td>482</td>
<td>69.79 ± 0.17</td>
<td>1.21</td>
<td>31.64 ± 0.21</td>
</tr>
<tr>
<td>FGD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FGD 1</td>
<td>321</td>
<td>–16.75 ± 0.13</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Fly ash standard</td>
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</tr>
<tr>
<td>SRM 1633b</td>
<td>936</td>
<td>51.07 ± 0.14</td>
<td>24.8</td>
<td>28.57 ± 0.13</td>
</tr>
</tbody>
</table>

† FBC, fluidized-bed combustion; FGD, flue-gas desulfurization.
‡ \( \text{Sr}^\dagger \) in whole-CUB is mg/kg; Sr in leachates is mg Sr leached per kg starting material.
§ \( \varepsilon^{\text{Sr}}_{\text{SW}} = 10^{\text{log}(\text{Sr}^{\text{Sample}}/\text{Sr}^{\text{Standard}})} - 1 \); \( \delta^{\text{Sr}}/\delta^{\text{Sr}}_{\text{Standard}} = 0.709164 \). Quoted error is 2σ in-run uncertainty.
Sequential Leaching of CUB

Sequential extractions can help elucidate the modes of occurrence and potential mobility of various major, minor, and trace elements in different types of CUB. Fly ash in contact with natural waters generally produces high-pH conditions that affect the mobility of elements such as As, Mo, and V, whereas contact with low-pH fluids tends to mobilize metals such as Cu, Ni, Pb, and Zn (Kim and Hesbach, 2009). Hassett et al. (2005) also noted differences in empirically determined element mobility based on batch and column leaching studies, and emphasized the role of formation of secondary minerals such as ettringite (hydrated Ca-Al-sulfate hydroxide) in the retention of elements present as oxyanions (e.g., B, As, Cr, Mo, Se, and V).

In Fig. 3, we show the fraction of major elements (Fig. 3a) and selected trace elements (Fig. 3b) in the different CUB classes that were leached by each solution in this study. Generally, no single leaching solution extracted more than half of the total amount of an element from the CUB sample, although in some cases the three leaches together extracted a significant fraction (e.g., > 80% of Ca and Sr leached from class C and FBC ashes).

We were not able to determine whole-CUB concentrations reliably for As, P, S, and Se because of their volatility, and the use of lithium tetraborate during fusion dissolution precluded determination of whole-CUB B concentrations. For most elements, HCl was the most efficient extractant, even following initial leaches by H$_2$O and HOAc (Fig. 3).

Among the major elements in fly ash, Fe, Mg, and Si are essentially water insoluble (Fig. 3a), whereas in class C fly ashes K and Na (probably held in minor chloride salt phases) and Al show slight solubility. Major and minor elements in CUB that were readily leached by water include Ca, Sr, and S. The water-soluble phases carrying these elements in CUB are likely to be sulfate minerals, with anhydrite (CaSO$_4$) being the dominant phase. This interpretation is consistent with the relatively high release of Sr$^{2+}$, which can substitute for eight-coordinated Ca$^{2+}$ in the anhydrite structure, and the low release of Mg$^{2+}$, which does not readily substitute for Ca$^{2+}$ in anhydrite. 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., 1990a).

Selenium and B were also mobilized during the water-leaching step of the sequential leaching procedure (Supplemental Table S3). Selenium is expected to be present as water-soluble selenite and/or selenate (Jackson and Miller, 1998; Huggins et al., 2007; Wang et al., 2007; Shah et al., 2008), whereas B may occur as borate salts (Querol et al., 1996) or as borate complexes substituting into other water-soluble salts that form during combustion as volatilized species condense on the surface of fly ash particles (Eary et al., 1990; Kashiwakura et al., 2009, 2011). The tendency of these elements to form anions when oxidized contributes to their incorporation into surface coatings on fly ash particles or organic complexes.

Minor and trace elements that are water insoluble or only very slightly water soluble are Cr, Cu, Mn, Pb, Ti, and Zn (Fig. 3b). These elements are associated with more refractory phases in coal, such as clay minerals, phosphates, and other detrital minerals (Swaine, 1990; Izquierdo et al., 2011) that are thought to transform in part into aluminosilicate glass and mullite during combustion (Mattigod et al., 1990a).

Dilute acetic acid (HOAc) most likely attacks carbonates in fly ash, as indicated by significant release of Ca, Mg, and Sr (Fig. 3a). This reagent may also dissolve some silicate phases or combustion glass, inferred from the amount of Si extracted during this step. Most elements have their maximum
solubility in HCl, particularly high-field strength elements such as Al and Ti, suggesting that they are bound in more refractory silicate or glass phases. This is supported by the correlation of some of these elements with higher ash contents in coals (Lindahl and Finkelman, 1986). A modest portion (up to 20%) of the leachable fraction of As is released in the water + HOAc leachates of class F and FBC ash, whereas it is almost entirely released (>97%) in the HCl leach of class C and bottom ash (Supplemental Table S3). This suggests that there are fundamentally different modes of occurrence of As in different types of fly ash, which could in part reflect the distribution of As in the feed coal, or different As volatilization and precipitation behaviors during combustion.

**Bulk-CUB Strontium Isotope Systematics**

The modes of occurrence of inorganic elements in coal have considerable impact on their behavior during combustion and transformation to CUB (Ward, 2002). Strontium and other alkaline earth elements have several possible associations in coal, including (i) discrete mineral phases of both detrital and authigenic origin and (ii) cation-bearing organic functional groups (Finkelman, 1981; 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 with high-rank coals (Finkelman, 1981; Benson and Holm, 1985; Lindahl and Finkelman, 1986).

As coal matures, some of the organic matter is destroyed and restructured, 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 relative to authigenic minerals to the inorganic element budget in higher rank coals, while low-rank coals would have more authigenic than detrital mineral matter (Vassileva and Vassilev, 2005). Mattigod et al. (1990b) found that the $^{87}$Sr/$^{86}$Sr ratios (and therefore $\varepsilon_{\text{Sr}}^{\text{SW}}$ values) of dilute HCl leaches of fly ash generally increased with increasing coal rank. This general trend is also seen in our results for class C fly ash (derived from low-rank coals) and class F fly ash (derived from high-rank coals).

In general, minerals that are older and have higher Rb/Sr ratios will have higher $\varepsilon_{\text{Sr}}^{\text{SW}}$ values. Although Rb was not measured in this study, K can serve as a proxy due to its geochemical similarity to Rb in clays and coal mineral matter (Finkelman, 1981; Palmer and Filby, 1984; Spears and Martinez-Tarazona, 1993). There is a positive correlation between K/Sr ratios and $\varepsilon_{\text{Sr}}^{\text{SW}}$ values of whole-CUB samples analyzed in this study (Fig. 4). This correlation most likely reflects the relative importance of detrital mineral inputs to the bulk Sr isotope composition of different types of coal and CUB. Coals with higher abundances of detrital sediments that potentially have high Rb/Sr (and thus K/Sr) ratios should have more radiogenic Sr isotopic compositions than those with dominantly low K/Sr minerals, frequently of authigenic origin (i.e., carbonate and sulfate). In addition, additives such as lime to the coal during the combustion process ultimately end up as CUB and cannot be distinguished from other minerals that were preexisting in the coal itself; these are likely to move the resulting isotopic composition toward values more typical of authigenic sources of Sr (Fig. 4). Strontium isotopes can thus be used to infer sources of mineral matter that end up in CUB.
Isotopic Variations in CUB Leachates

Interpretation of the Sr isotopic composition of CUB and CUB leachates 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 (Fig. 2) must be attributed to the presence of multiple sources of Sr. These sources might include (i) feed-coal mineral matter that has been altered minimally or not at all during combustion; (ii) thermally altered and newly precipitated minerals inheriting the Sr isotopic composition of their precursors; and/or (iii) combustion additives (e.g., limestone sorbent during FBC) that get incorporated into CUB.

Figure 5 shows the plot of the isotopic composition of CUB leachates against the cumulative percentage of Sr progressively extracted during the leaching experiments. Thus, for each sample, the datum with the lowest percentage Sr extracted represents the HCl leach, followed by the HOAc leach, and then the H2O leach. The points plotted at 100% represent the calculated $\varepsilon_{\text{Sr}}^{\text{SW}}$ in the residues, based on the leachate values and the whole-CUB Sr concentrations and isotopic compositions. In most cases (i.e., class C fly ash, class F fly ash, and bottom ash), the shift in leachate isotopic composition, represented by all points in Fig. 5 with <100% Sr extracted, is relatively modest (<4.2 ε units). In contrast, the calculated difference between the residues and leachates in class F fly ashes is 30 to 40 ε units, and up to 10 ε units for class C ashes. The difference in range between class C and class F fly ashes could indicate that (i) class F ashes tend to contain refractory high-$\varepsilon_{\text{Sr}}^{\text{SW}}$ phase(s) that are less abundant in class C ashes, or (ii) class C ashes tend to homogenize to a greater extent during combustion, perhaps due to higher temperatures, more complete burning, or differences in ash fusion temperatures.

The largest shifts in $\varepsilon_{\text{Sr}}^{\text{SW}}$ values during leaching are observed in FBC fly ash (Fig. 5), with differences between different leachates of 23 to 73 ε units, and between leachates and residues of 80 to 285 ε units. Fluidized-bed combustion has several key characteristics that distinguish it from pulverized coal combustion and that could 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 SOx emissions (Goodarzi, 2006). Marine limestone has an average Sr concentration of 2000 mg/kg (Capo et al., 1998) and therefore contributes substantially to the Sr budget of FBC ash. The limestone sorbent serves as a source of Ca that reacts with SOx in the flue gas, forming anhydrite (CaSO4) that ends up in the fly ash. Anhydrite was detected in both FBC ash samples by XRD analysis, and is the probable source of water-soluble Sr in these samples. This is also supported by the $\varepsilon_{\text{Sr}}^{\text{SW}}$ values of the water-soluble fractions of the FBC ashes (Table 2), which are close to or within the range of values for marine limestone (Burke et al., 1982). Calcite, which could be derived from unreacted sorbent, was also detected in the FBC ashes by XRD. However, the presence of calcite in some class C and class F samples investigated in this study indicates that this mineral may also be derived from the original coal mineral matter or as a combustion product. Calcite is commonly found in coals, and remnants of it are observed in low- and high-temperature ashes (Vassilev and Vassileva, 1996). The lower combustion temperature could prevent partial or complete isotopic homogenization of high-$\varepsilon_{\text{Sr}}^{\text{SW}}$ silicate mineral phases, thus preserving the original range of values from the coal mineral matter. Goodarzi (2006) described particles in an FBC ash that consist of quartz and aluminosilicate fragments that are encased in Ca-rich aluminosilicates and Ca- and Fe-oxides, which could effectively armor the interior minerals. The lower boiler temperatures also facilitate the precipitation of soluble CaSO4 in FBC ash by limiting the volatile loss of sulfur during combustion.

The effects of two different coal combustion technologies, selective catalytic reduction and flue-gas desulfurization, on the Sr leaching behavior and isotope systematics of different types of CUB were also investigated in this study. The “matched set” of fly ashes CRC 9 w/ and CRC 9 w/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 expected to be a source of abundant Sr.

One sample of FGD material 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 SOx species from the flue gas is the probable source of Sr in this type of CUB. This is supported by the $\varepsilon_{\text{Sr}}^{\text{SW}}$ value measured in this sample of −16.8,
which is within the expected range of Paleozoic marine limestones (Burke et al., 1982), the most likely source of limestone sorbent. The Sr in FGD material is highly soluble, with nearly 100% extraction in water. Codisposal of this type of CUB with fly ash would have a substantial impact on the Sr isotope geochemistry of waters that encounter this material.

**Strontium Isotope Correlations**

Most CUB leachates analyzed in this study showed a general trend of increasing \( \varepsilon_{\text{SW}} \) with increasing extraction of Sr. This trend mirrors those of many of the major and trace element concentrations. For example, the concentration of Si in the leachates generally increases with \( \varepsilon_{\text{SW}} \) as components are sequentially extracted from class C and class F fly ash (Fig. 6a). This suggests the important contribution of silicate minerals and/or glass to the refractory high \( \varepsilon_{\text{SW}} \) component that is only extracted by stronger solvents (or more prolonged leaching).

To illustrate the correspondence of Sr isotope composition with potentially toxic trace elements released by leaching, the \( \varepsilon_{\text{SW}} \) value of class C and F fly ashes is plotted against As (Fig. 6b). Most show a strong positive correlation between \( \varepsilon_{\text{SW}} \) and As; a similar correlation is seen for Pb (not shown). These results indicate that As and Pb are held in phases that contain the more radiogenic (high-\( \varepsilon_{\text{SW}} \)) component of CUB, or that they are in phases with similar leachability.

Previous work on the Sr isotope systematics of CUB leaching in a field acid mine drainage grouting application (Hamel et al., 2010) also showed a positive correlation between As concentrations and \( \varepsilon_{\text{SW}} \) values. Other trace constituents, including Se and B, are not strongly associated with the high-\( \varepsilon_{\text{SW}} \) phase(s) and thus tend to be solubilized more readily when interacting with aqueous fluids.

**Strontium Isotopes as a Tracer for CUB–Fluid Interaction**

The Sr isotopic composition of coal fly ash has been previously investigated (Mattigod et al., 1990b; Hurst et al., 1993), with particular emphasis on the potential utility of this isotope system as a tracer for atmospheric deposition of fly ash. For the Sr isotope composition to be effectively applied as a tracer for interaction of CUB with environmental fluids, the following conditions should be met: (i) there is a clear difference between the CUB isotope signature and that of the background waters; (ii) the CUB leachates fall within a fairly narrow range of values; (iii) enough Sr is released from CUB to affect the isotopic composition of the background waters; and (iv) the Sr isotopic composition of CUB leachate shows some correlation with elements of environmental interest. We consider these in turn in the following paragraphs.

First, as noted earlier, natural waters such as groundwater and streams can have a wide range of isotopic compositions (\( \varepsilon_{\text{SW}} = -100 \) to +200), depending on the type and age of bedrock and soil in the watershed. However, the Sr isotope composition of any one stream or groundwater system is not expected to vary significantly over timescales of interest for environmental monitoring (generally well less than \( \pm 10 \) ε units; Semhi et al., 2000; Barnett-Johnson et al., 2008). Therefore, under most circumstances, it is probable that the CUB and natural waters will be isotopically distinct from each other. However, this must be tested at any given field site before using Sr isotopes as a tracer.

Second, although the different whole-CUB samples measured in this and previous investigations present a wide range of \( \varepsilon_{\text{SW}} \) values (-30 to +150; Mattigod et al., 1990b; Hurst et al., 1993; Frost et al., 2002), any given feed coal tends to yield fairly similar values, as indicated by the close correspondence of the two “CRC 9” samples (with and without the SCR system on-line). The range is narrower still when only the leachates are considered (rather than the insoluble residue; Fig. 5). Because this represents the fraction of Sr most likely to leach into the environment, it is the most relevant for CUB–water interaction. Fluidized-bed combustion ash tends to yield a much wider range of leachate \( \varepsilon_{\text{SW}} \) values than other CUB measured in this study, so the Sr isotopic composition of CUB leachate at disposal sites dominated by FBC ash may not be as well constrained.

Third, Sr tends to be enriched in CUB relative to average crustal rocks and soils (Hurst and Davis, 1981; Hurst et al., 1991; Depoi et al., 2008). Moreover, as an alkaline earth element, Sr is readily leached from multiple phases of CUB. Both of these factors, when combined with the likely significant
difference between CUB and natural water isotope composition, make Sr isotopes a highly sensitive indicator of interaction between soluble CUB components and background waters interacting with the CUB.

Finally, the limited samples analyzed in this study suggest that variation in the isotopic composition of Sr (\(\varepsilon_{\text{Sr}}\)) is correlated with the release of a number of major and trace elements, including As and Pb. Additional studies (e.g., detailed CUB column extractions) are required to ascertain the extent to which the \(\varepsilon_{\text{Sr}}\) value may forecast the imminent release of elements of environmental concern.

Conclusions

Samples of CUB subjected to a three-step batch leaching procedure show significant differences in Sr isotope composition between the leachate and the bulk CUB values. The presence of unique Sr isotopic reservoirs in a single sample of CUB unequivocally demonstrates that there are multiple sources of distinct Sr in these materials. Thus, Sr isotope composition can be used to understand the origins of the various components in CUB, including geologic sources and mineralization during combustion, as well as the leaching behavior of elements associated with specific CUB phases.

In most cases, the CUB and natural waters will probably be isotopically distinct from each other, as the leachates from any given feed coal tend to yield a narrow range of \(\varepsilon_{\text{Sr}}\) values that are likely to be different from the wide range of potential background isotope compositions. The high concentrations and solubility of Sr in CUB ensures that the leached CUB component will be quantifiable when natural waters interact with CUB. In addition, the isotopic composition of CUB leachate Sr correlates with several major and trace elements, including As and Pb. A changing \(\varepsilon_{\text{Sr}}\) ratio of CUB-interacting waters could forecast the release of certain strongly bound elements of environmental concern.

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