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Rare Earth Element Distribution in Fly Ash Derived from the Fire Clay Coal, Kentucky

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ABSTRACT

Fly ash was collected from individual mechanical and electrostatic precipitator (ESP) hoppers at a 130-MW pulverized-coal utility unit burning a southeastern Kentucky moderate- to high-S Pennsylvanian Fire Clay coal. The fly ash particle size is generally similar within each row of the mechanical and ESP hoppers, with the mean particle diameter decreasing from >36 μm in the mechanical hoppers to 6 μm in the last ESP row. Rare earth element (REE)–bearing phases occur within fine minerals and, possibly, as part of the fly ash glass phase. Transmission electron microscopy was used to identify Y-Ce-Nd-La–bearing regions within a glassy matrix. Y- and U-bearing zircons were also found in the fly ash. Total REE plus yttrium (REY) occupies a narrow range from 719 to 775 ppm, showing an overall lack of partitioning of the REY elements with respect to particle size and temperature in ash collection systems. The heavy REE increase and the light REE/heavy REE ratio decreases from the mechanical hoppers through ESP rows.

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Keywords: lanthanides; critical materials; coal combustion

1. Introduction

The chemistry of a fly ash is, fundamentally, the product of the input fuel and the design and operating conditions of the boiler and ash collection system. In addition to coal, in some cases, the fuel can contain other components, such as biomass, petroleum coke, or chopped tires. Nonfuel contaminants can enter the fuel and ash stream anywhere from the mine to the preparation plant to the pulverizer to the boiler to the ash collection system. In most cases, though, when we think of fly ash chemistry, we are considering it to be directly related to the coal or coal blends fed to the boiler. For a fly ash from an Si-Al–rich mineral assemblage from a moderate- to high-S high volatile A bituminous coal, such as that studied here, the parent material leaving the boiler is, therefore, a SiO2-Al2O3 > Fe2O3 >> CaO-MgO-P2O5-K2O-Na2O melt with volatile inorganic trace elements (e.g., Hg), refractory minerals such as quartz, partially melted to baked rock fragments, inertinite macerals, and thermoplastic melts of (mainly) vitrinite, all in a CO2 >> SO2-H2O–rich flue gas.

The typical coal feed to a bituminous coal–fed utility boiler in the eastern United States consists of a blend of many coals, so the fly ash chemistry cannot be traced back to a single coal. In this study, as with two previous studies (Sakulpitakphon et al., 2000; Mardon and Hower, 2004), arrangements were made for the utility unit to burn a single-seam/single-mine feed coal, in this case exclusively consisting of the Fire Clay coal from central eastern Kentucky. The Fire Clay coal is known to be relatively enriched in rare earth elements (Hower et al., 1999, 2015, 2016a; Mardon and Hower, 2004).

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2. Sampling and Methods

Fly ash was collected at a utility 130-MW pulverized coal unit—plant I in our code—burning a southeastern Kentucky moderate- to high-S Pennsylvanian coal. As noted above, special arrangements had been made for the unit to burn a feed coal exclusively consisting of the Fire Clay coal from central eastern Kentucky. Additionally, within the discussion, we will consider examples from a southeastern US utility boiler (plant W) exclusively burning the Fire Clay coal and a midwestern US utility boiler burning a subbituminous Powder River Basin coal.

Moisture, ash, and carbon analyses (the latter from the ultimate analysis) were conducted at the University of Kentucky Center for Applied Energy Research (CAER). Major oxides and minor element concentrations were quantified by X-ray fluorescence at the CAER following procedures outlined by Hower and Bland (1989). Mercury was analyzed on the whole sample using a LECO AMA254 absorption spectrometer. The rare earth elements (REE) + yttrium (REY) were extracted from the fly ash samples by heated digestion with a 1:1 HF:HNO₃ acid mixture followed by analysis by inductively couple plasma mass spectrometry (Agilent Technologies 7700) in the Department of Civil and Environmental Engineering at Duke University (procedures after Taggart et al., 2016). The accuracy of this analysis method was tested on fly ash National Institute of Standards and Technology standard reference material (NIST SRM 1633c) that was digested and analyzed in parallel with the samples for this study. Average recoveries of individual REY elements were 89.3–103.4% of the reference concentrations (for Dy, Eu, La, Lu, Sc, and Tb) and information mass concentrations (for Ce, Nd, Sm, and Yb) for SRM 1633c.

Fly ash petrology was performed on epoxy-bound pellets prepared to a final 0.05-μm alumina polish using ×50 reflected-light, oil-immersion optics on Leitz Orthoplan microscopes at the CAER following procedures described by Hower (2012).

Selected samples were examined by powder X-ray diffraction (XRD) at CAER. If required, the samples were ground by hand in a ceramic mortar and pestle just before XRD analysis. The powdered samples were then dry mounted in aluminum holders. The samples were scanned at 8–60° 2θ with copper K-α radiation on a Philips X’Pert diffractometer (model PW3040-PRO) operating at 45 kV and 40 mA. Crystalline substances or “minerals” were identified in the diffractograms with an International Centre for Diffraction Data (Newtown Square, PA) powder diffraction database.

Particle size analysis was conducted on a Cilas 1090 laser particle size analyzer at the CAER using the liquid-dispersion mode. The instrument has a measurement range of 0.04–500 μm.

Surface area of ash samples was measured using a Coulter SA 3100 surface area and pore analyzer based on the Brunauer–Emmett–Teller model of nitrogen sorption at 77 K. Differential scanning calorimetry–thermogravimetric analysis (DSC-TGA) was conducted on monazite grains at the CAER. A 10°C/min ramp was used in the heating of the monazite. For further thermal testing, splits of the same monazite sample were heated to 1400°C in a Carbolite oven at the CAER.

Laser ablation inductively couple plasma mass spectrometry (LA-ICP-MS) was conducted in the University of Kentucky Department of Plant and Soil Sciences on a Agilent Technologies 7500 ICP-MS equipped with a Teledyne-CETAC Technologies 213-nm λ-frequency quintupled neodymium-doped yttrium aluminum garnet laser. For the analyses conducted here, three laser bursts using a 100-μm spot size were used. Epoxy-bound particulate samples prepared as for petrographic analyses, as above, were used in the study. The standardization used glasses with nominal concentrations of 5, 50, or 500 mg/kg each of Sc, Y, La, Ce, Pr, Nd, and Sm (NIST SRMs 610, 612, and 614). The matrix composition and homogeneity of the measured sample differs from that of the standards, so the measured values must be considered to be semiquantitative.

![Fig. 1. Cumulative particle size percentages for fly ash from mechanical hoppers and from three rows of ESP hoppers.](image)

<table>
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<tr>
<th>Sample no.</th>
<th>93951</th>
<th>93953</th>
<th>93954</th>
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<td>9</td>
<td>10</td>
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<td>Diameter 10% (μm)</td>
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<td>10.58</td>
<td>1.68</td>
<td>1.87</td>
<td>1.43</td>
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<td>Diameter 50% (μm)</td>
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<td>Diameter 90% (μm)</td>
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<td>65.47</td>
<td>67.96</td>
<td>29.46</td>
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<td>25.93</td>
<td>25.49</td>
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<td>Mean diameter (μm)</td>
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<td>37.69</td>
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<td>9.69</td>
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<tr>
<td>Surface area (m²/g)</td>
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<td>12.738</td>
<td>13.195</td>
<td>9.962</td>
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Note: BET = Brunauer–Emmett–Teller; Mech = mechanical; ESP = electrostatic precipitator.
Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy analysis was conducted using a Helios NanoLab 660 DualBeam focused ion beam (FIB)/SEM and transmission electron microscopy (TEM) was run on a JEOL 2010F at the University of Kentucky Electron Microscopy Center. Both particulate samples and polished epoxy-bound pellets were used for analysis. TEM was also conducted on a JEOL 2100 field thermionic emission analytical electron microscope equipped with a silicon drift detector–based energy-dispersive spectroscopy (EDS) system for chemical mapping at the Virginia Tech National Center for Earth and Environmental Nanotechnology Infrastructure (NanoEarth), Blacksburg, VA.

High-resolution TEM (HR-TEM) was carried out at the National Institute for Occupational Safety and Health laboratory in Cincinnati, OH. The fly ash sample was deposited onto a carbon support film on a Cu TEM grid. TEM observations were made using an FEI Tecnai TF20 transmission electron microscope at 200 kV. Energy-dispersive X-ray spectroscopy analysis was carried out using an EDAX Genesis spectrometer.

<table>
<thead>
<tr>
<th>Sample no.</th>
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<td>Glass</td>
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<td>83.0</td>
<td>90.0</td>
<td>37.6</td>
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<td>0.0</td>
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<td>0.0</td>
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<tr>
<td>Sulfide</td>
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<td>0.0</td>
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<td>0.0</td>
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<tr>
<td>Crystalline silicate</td>
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<tr>
<td>Lime</td>
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<td>0.0</td>
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<tr>
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<td>Isotropic coke</td>
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<td>4.4</td>
<td>3.4</td>
<td>3.0</td>
<td>0.5</td>
<td>44.4</td>
<td>38.0</td>
<td>18.8</td>
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<tr>
<td>Anisotropic coke</td>
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<td>6.0</td>
<td>6.4</td>
<td>5.9</td>
<td>8.5</td>
<td>7.0</td>
<td>10.0</td>
<td>5.2</td>
<td>12.8</td>
</tr>
<tr>
<td>Inertinite</td>
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<td>0.8</td>
<td>0.8</td>
<td>2.0</td>
<td>4.0</td>
<td>0.5</td>
<td>6.4</td>
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<td>2.4</td>
</tr>
<tr>
<td>Unburned coal</td>
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<td>0.0</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Note: Mech = mechanical; ESP = electrostatic precipitator.
3. Results and Discussion

The flue gas temperature at the collection points was not determined in this study. In the investigation of another, albeit larger, unit at the same power plant, Mardon and Hower (2004) reported temperatures of 235°C at the entrance to the mechanical collection hoppers, 203°C at the exit of the latter hoppers, and <150°C at the exit of the electrostatic precipitator (ESP) hoppers.

3.1. Particle size and surface area

The fly ash particle size is generally similar within each row of the mechanical and ESP hoppers (Figure 1; Table 1). The largest deviation is seen in the third-row ESPs where the size distributions for the coarser portions of the ash deviate significantly. Overall, the mean particle diameter decreases from >36 μm in the mechanical row to an average of <13 μm, <10 μm, and 6 μm in the first through third ESP rows, respectively. Although single pictures do not tell the whole story of the petrology and particle size distribution, the contrast between Figures 2A–D show that the ESP fly ashes tend to have a greater abundance of fine particles, as was seen in Figure 1 and Table 1. The coarser particles are preferentially separated by the cyclones associated with the mechanical hoppers. In any case, the first row of any ash collection system would tend to have a coarser particle distribution than the more distant rows. In general, as the particle size decreases, the sample surface area increases.

3.2. Petrology

Much of the inorganic fraction of the fly ash is dominated by glass, with carbons and spinel being important constituents in some of the ashes (Table 2; Figure 2). The microscopic carbons are present as inertinite, derived directly from the feed coal (Figures 2A and 2B).
and from isotropic (Figures 2B and 2D) and anisotropic (Figure 2A) carbons derived from the melting and repolymerization of vitrinite.

The more-or-less rectangular mineral in the center of Figure 2C has a shape and color similar to pure monazite. Monazite, zircon, and other REE-bearing minerals are known to occur in the feed coal (Hower et al., 1999, 2016a), but with a few exceptions (Figure 2C), they are scarce at the scale of optical petrology. Thus, we question what happens to these minerals during the combustion process and ash collection. Zircon is known to degrade to zirconia (ZrO₂-t) and cristobalite between 1285°C and 1720°C (Quercia et al., 2007). Among other potential REY mineral sources, the elemental composition plays a role in determining the melting temperature: Er-xenotime melts at 1896°C up to Y-xenotime at 1995°C, Sm-monazite melts at 1916°C up to La-monazite at 2072°C, and natural monazite melts at 2057°C (Hikichi and Nomura, 1987). All of the latter temperatures are much higher than the 1400–1500°C of a pulverized-fuel boiler.

Considering heat-induced fragmentation as a possible means of size reduction, a double-screened monazite sample undergoes very little weight loss to 1400°C (by DSC-TGA at a heating ramp of 10°C/min) (Figure 3A), as expected, but shows a substantial size reduction, in part to submicron particles (Figures 3B and 3C). One mechanism of fragmentation is the expansion of gas within the REE-bearing minerals. The decay series of Th and U, trace constituents of REE minerals, include both Ra and He. Radon, a relatively short-lived way station, is not likely to be a major contributor to the gas content of the REE-bearing minerals. Helium, a stable noble gas, is produced through α decay at several steps in the decay of ²³⁸U and ²³²Th. Zeitler et al. (1987) found that fluorapatite shows complete retention of radiogenic He. Helium closure temperature increases from 300°C for LaPO₄ to 410°C for GdPO₄ (Farley, 2007), as supported by observations that He diffusion is faster in light REE (LREE) phosphates than in heavy REE (HREE) phosphates (Cherniak et al., 2009; Cherniak and Watson, 2013). Natural zircon and xenotime show slower He diffusion than synthetic phosphates. Monazite structure phosphates of La, Ce, Pr, Nd, Sm, Gd and Eu are more He retentive, with He retention temperatures 300°C higher than zircon structure phosphates (Farley, 2007; Cherniak and Watson, 2013). Helium trapped in monazite expands the crystal lattice; with an increase in temperature, unit cell volume decreases from relaxation of the monazite lattice with the diffusion of Ge (Seydoux-Guillaume et al., 2002). Zircon He closure occurs at about 170–190°C (Reiners et al., 2004). Zircon He diffusion has been correlated to α damage of crystal lattice (Guenther et al., 2013).

### 3.3. Mineralogy

The XRD analyses of the fly ash samples are all dominated by glass and carbons. Among the minerals that were noted in the whole ashes, quartz is more abundant than mullite in most fly ashes. Quartz and mullite are found in approximately equal amounts in the third-row ESP fly ashes. Magnete and hematite are found in trace amounts in sample 93951 (whole ash), 93953 (mechanical separation hopper), and 92956 (first-row ESP).

Further mineralogic analysis was conducted on sample 92953 with the TEMs at the University of Kentucky and at Virginia Tech. Figures 4 and 5 show a complex particle with several mineral phases within the glass. Ti-rich minerals, both as cubic grains and as a bladed mineral, are associated with an Al-Si bladed mineral (mullite?) (Figure 5A) and nanoscale Fe-rich minerals (Figure 5B).

As noted in section 3.2, detection of REY-bearing particles in the fly ash is difficult, but rare occurrences have been noted. TEM examination after FIB extraction of a thin, 10 × 10-μm block (Figures 6A and 6B) and ion-milling of the block to <90 nm thick demonstrated that the region is a mix of glass and nanoscale minerals, with no definitively identifiable minerals. Elemental analysis of the polished section of sample 93953 shows a submicron La-Ce–bearing region in the glassy matrix (Figure 6C). SEM-EDS analysis at the University of Kentucky also demonstrated the presence of Y and Nd in the particle.

Zircons and Zr-rich areas (not definitively crystalline) were observed in the fly ash (Figure 7). Yttrium and U seem to be present in particle 4 as well as in some other grains (not illustrated). The Y peak on the shoulder of the stronger Zr peak makes a definitive identification difficult. Other regions, such as particle 6, have strong Zr and Si peaks, but small, perhaps nonexistent, Y peaks. As noted above, zircon can begin to decompose at boiler temperatures. It is also possible that the REY signature of zircons (and other REY-bearing minerals) can vary within the coal. For example, the Fire Clay coal, the source coal for this fly ash, has both volcanic- and detrital-derived minerals, including zircon. The whole-sample REY distributions of the volcanic tonstein and the detrital-influenced basalt coal lithotype are different (Hower et al., 2016a): an average LREE/HREE = 7.89 (n = 13) for the tonstein vs. 6.47 (n = 6) for the basalt lithotype for samples in a six–7.5'-quadrangle area in central eastern Kentucky (J.C. Hower and C.F. Eble, personal communication, 2016).

Comparisons in the relative ease of REY extraction from Power River Basin (PRB) coal-derived fly ashes vs. Central Appalachian...
Fig. 5. Individual and combined (A) Si, Al, and Ti (individual maps in the latter order in column on left) and (B) Al, Fe, and Ti (individual maps in the latter order in column on left) element maps for grain in Figure 4. Scale = 1 μm.

Fig. 6. (A) Scanning electron microscopy (SEM) image of fly ash glass (in box) with Ce-La-Nd-bearing phases. Scale = 5 μm. (B) SEM image of the same particle as seen from the reverse side of the focused ion beam (FIB) lift-out specimen. Scale = 1 μm. C/combined Ce, La, and Y elemental map of particle in panel B. Scale = 1 μm. Column on the left includes, from top to bottom, the Y map, La map, and Ce map.
Fig. 7. Spectra of two Zr-bearing grains. Top spectrum (particle 4) has a strong Zr signal, with indications of Y and U signals. The bottom spectrum (particle 6) has a strong Zr signal, with a marginal to nonexistent Y signal and no apparent U signal.

Fig. 8. Left: Image of Ca-Al-Si-rich particle (lower center) (scale = 20 μm); right: elemental spectrum. Sample 93927.
coal-derived fly ashes have been made by Taggart et al. (2016). Because the ashes in this study are among the Appalachian coals considered in the latter study, some of the fundamental differences should be noted. Whereas the Appalachian-derived fly ashes are dominated by Si-Al glass, the PRB-derived fly ashes tend to be dominated by Ca-Al-Si–rich glass and minerals (Figure 8), some with Ca-S–rich (possibly Ca sulfate) rims tens to hundreds of nanometers thick (Figure 9). The greater ease of dissolution of the PRB-derived fly ash is likely related to this fundamental difference in the glass and mineral chemistry.

3.4. Chemistry

3.4.1. Coal chemistry

The chemistry of the feed coal is given in Table 3. The coal has 2.23% total sulfur, placing it at the lower end of the high-S category, albeit relatively high for an Eastern Kentucky coal. The > 15% Fe$_2$O$_3$ is largely a function of the pyrite in the feed coal [0.82% pyritic sulfur ($S_{py}$)]. The 769 mg/kg total REE and 897 mg/kg REY (both ash basis) are higher than most Central Appalachian feed coals but also represent a diminished REE concentration from the Fire Clay seam section, including the REE-enriched tonstein, because beneficiation removes the REE-rich rock (Hower et al., 2015).

3.4.2. Fly ash chemistry

3.4.2.1. Major oxides and minor elements

The chemistry of the fly ash is given in Table 4. As expected for a Central Appalachian coal source, the major oxides are dominated by SiO$_2$ and Al$_2$O$_3$, with 7.5–9.9% Fe$_2$O$_3$ and lesser amounts of the other major oxides. Only SO$_3$ exhibits a significant increase from the mechanical rows to the third-row ESP, an expected trend given the relative volatility of SO$_3$, the cooler flue gas temperature, and the greater surface area (smaller particles) of the fly ash in the back end of the ESP compared with the mechanical hoppers.

Among the minor elements analyzed, exclusive of the REE and Hg, the V, Cr, Cu, Zn, As, Ba, Pb, Ga, and Se concentrations show significant increases from the mechanical hoppers to the third-row ESP, with Mn, Co, Ni, Sr, and Mo having more muted increases. Zinc and As exhibit the most significant increases in concentration, from < 100 mg/kg in the mechanical hoppers to 311 mg/kg and 566 mg/kg, respectively, in the third-row ESP fly ashes. All of the latter trends are in accordance with behavior reported by Sakulpitakphon et al. (2000), Mardon and Hower (2004), and Hower et al. (2006), among others. Distributions of Se through ash collection systems do not always seem to follow the pattern expected of such a volatile element (Hower and Robertson, 2004; Mardon and Hower, 2004; Hower et al., 2009). Despite the large difference in Se concentration between the two third-row ESP samples, there appears to be no reason to suspect anomalous behavior of Se in this sample suite.

3.4.2.2. Mercury

Mercury is an element of concern in coal combustion. The behavior of Hg in ash collection systems is more complex than for the volatile trace elements discussed above, with Hg capture by fly ash being a function of the speciation of the Hg, the flue gas temperature ($T$), and the amount, type, and surface area of the fly ash carbon (Hower et al., 2010). Specifically, Hg capture increases with a decrease in flue gas $T$ and increases with an increase in the amount of carbon. The distribution of Hg vs. carbon is shown in Figure 10. For all of the ESP rows, each individual row more or less seeing the
Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>MA no.</th>
<th>Ash M</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
<th>Ssulf</th>
<th>Organic S</th>
<th>Cl</th>
<th>HV</th>
<th>LREE</th>
<th>HREE</th>
<th>LREE/HREE</th>
<th>LREE plus yttrium</th>
<th>HREE plus yttrium</th>
<th>REY total</th>
<th>Critical</th>
<th>Uncritical</th>
<th>Excessive</th>
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<td>14.18</td>
<td>3.09</td>
<td>5.95</td>
<td>5.05</td>
<td>1.45</td>
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Note: MA = materials analysis; CAER = University of Kentucky Center for Applied Energy Research; XRF = X-ray fluorescence; ICP-MS = inductively couple plasma mass spectrometry; REE = rare earth elements; Mois = moisture; VC = volatile; C = carbon; H = hydrogen; N = nitrogen; S = sulfur; O = oxygen; Cl = chlorine; HV = heating value; REY = rare earth elements (Yttrium); LREE = light rare earth elements; MREE = medium rare earth elements; HREE = heavy rare earth elements; LREY = light REE plus yttrium; MREY = medium REE plus yttrium; HREY = heavy REE plus yttrium; LREE/HREE = light rare earth elements to heavy rare earth elements.

3.4.2.3. Rare earth elements

REE are commonly divided into the LREE and HREE fractions from La through Sm and Eu through Lu, respectively (Seredin and Dai, 1996; Hower et al., 1999; Mardon and Hower, 2004; among others). When Y is included in the distributions (REY), the suite can be divided into light, medium, and heavy fractions: LREY (La through Sm plus Y), MREY (Eu through Dy plus Y), and HREY (Ho through Lu plus Y) (Seredin and Dai, 2012). Seredin and Dai (2012; summary by Hower et al., 2016b) further divided the REY into economic categories, based on the known abundances vs. the industrial needs at the time of their writing, as follows: critical (Y, Nd, Eu, Tb, Dy, and Er), uncritical (La, Pr, Sm, and Gd), and excessive (Ce, Ho, Tb, Yb, and Lu) REY.

The total REY occupies a narrow range from 719 to 775 mg/kg, confirming previous observations about the overall lack of partitioning of the REY elements with respect to particle size and temperature in ash collection systems (Mardon and Hower, 2004; Hower et al., 2013; Liu et al., 2017). The HREE increases from the mechanical throughput ESP hoppers, leading to a decrease in LREE/HREE in the same direction. Similar LREE/HREE trends were noted by Mardon and Hower (2004) for another unit burning Fire Clay coal and by Hower et al. (2013) for several other Kentucky units burning blends of several coals. The critical REY increases from about 241 mg/kg in the mechanical hoppers to 278–298 mg/kg in the ESP hoppers.

Particle-to-particle variations in REY content exist. As noted above, REY concentrations are associated with REE minerals such as monazite, Y-bearing minerals such as zircon (Figure 7) and xenotime (not observed in this study but seen in other Central Appalachian coal-derived fly ashes), and fine minerals, and perhaps as fine particle dispersion in glass (Figure 6). Not all minerals in the fly ash contain REE, as noted with the minerals seen in Figure 5. Similarly, not all of the glass contains REE, as observed in the LA-ICP-MS analyses. Semiquantitative La, Ce, and Nd concentrations in the plant W fly ash particles showed a range from 0 mg/kg up to about 75, 120, and 70 mg/kg, respectively (the whole ash contains 744 mg/kg REY; sample SCEGWS01-02; U.S. Department of Energy–National Energy Technology Laboratory, 2015).

Not all of the REE occur within the glass or as free minerals. Amorphous carbon with nanoscale metal inclusions can be found surrounding Al-Si glass particles in bituminous coal-derived fly ashes (Hower et al., 2008; Wilcox et al., 2015). Both the carbon (Figure 11) and the fine inclusions, here demonstrated to include REE particles (Figure 12), occur in the plant I fly ash. In addition to the Ce and Nd shown in Figure 12, Y, Pr, and Sm have been observed in the plant I amorphous carbons.

4. Conclusions

A 130-MW pulverized-coal unit at a Kentucky power plant burning, for the sake of this study, the Fire Clay coal from a single mine was investigated, with particular emphasis on the distribution and mode of occurrence of rare earth elements in the fly ash.

The major oxides in the fly ash are dominated by SiO2 and Al2O3, followed by 7.5–9.9% Fe2O3, with lesser amounts of the
Table 4

| Sample MA no. | Type   | Row Bin | Ash % | Moist | C | S | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | Na₂O | K₂O | P₂O₅ | TiO₂ | SO₃ | REE (ppm) | LREE/HREE | LREE Total | MREE Total | HREE Total | REE Total |
|---------------|--------|---------|-------|-------|---|---|------|-------|-------|-----|-----|------|-----|------|------|-----|----------|-----------|-----------|-----------|-----------|-----------|----------|
| 93952         | 73824  | Silo 5  | 94.12 | 0.08  | 6.93 | 8.02 | 53.57 | 30.01 | 8.66  | 7.17 | 1.40 | 0.33 | 0.03 | 0.03 | 0.10 | 0.18 | 1.91  | 3.72   |
| 93953         | 73826  | Mech 1  | 5     | 9.44   | 0.99  | 8.72 | 10.59 | 9.31  | 30.02 | 9.27 | 1.40 | 0.33 | 0.03 | 0.03 | 0.10 | 0.18 | 1.91  | 3.72   |
| 93954         | 73827  | Mech 1  | 1     | 9.13   | 0.88  | 8.95 | 9.61  | 9.30  | 30.02 | 9.27 | 1.40 | 0.33 | 0.03 | 0.03 | 0.10 | 0.18 | 1.91  | 3.72   |
| 93955         | 73828  | Mech 1  | 1     | 9.13   | 0.88  | 8.95 | 9.61  | 9.30  | 30.02 | 9.27 | 1.40 | 0.33 | 0.03 | 0.03 | 0.10 | 0.18 | 1.91  | 3.72   |
| 93956         | 73829  | Mech 1  | 1     | 9.32   | 0.23  | 9.25 | 9.17  | 9.31  | 30.02 | 9.27 | 1.40 | 0.33 | 0.03 | 0.03 | 0.10 | 0.18 | 1.91  | 3.72   |
| 93957         | 73830  | Mech 1  | 1     | 9.32   | 0.23  | 9.25 | 9.17  | 9.31  | 30.02 | 9.27 | 1.40 | 0.33 | 0.03 | 0.03 | 0.10 | 0.18 | 1.91  | 3.72   |
| 93958         | 73831  | Mech 1  | 1     | 9.32   | 0.23  | 9.25 | 9.17  | 9.31  | 30.02 | 9.27 | 1.40 | 0.33 | 0.03 | 0.03 | 0.10 | 0.18 | 1.91  | 3.72   |
| 93959         | 73832  | Mech 1  | 1     | 9.32   | 0.23  | 9.25 | 9.17  | 9.31  | 30.02 | 9.27 | 1.40 | 0.33 | 0.03 | 0.03 | 0.10 | 0.18 | 1.91  | 3.72   |
| 93960         | 73833  | Mech 1  | 1     | 9.32   | 0.23  | 9.25 | 9.17  | 9.31  | 30.02 | 9.27 | 1.40 | 0.33 | 0.03 | 0.03 | 0.10 | 0.18 | 1.91  | 3.72   |

Note: MA = materials analysis; CAER = University of Kentucky Center for Applied Energy Research; XRF = X-ray fluorescence; ICP-MS = inductively-coupled plasma mass spectrometry; REE = rare earth elements; Mois = moisture; silo = fly ash silo; mech = mechanical fly ash; ESP = electrostatic precipitator; LREE = light REE; MREE = medium REE; HREE = heavy REE; REE Total = total REE plus yttrium.
other major oxides. Vanadium, Cr, Cu, Zn, As, Ba, Pb, Ga, and Se increase in concentration from the hotter to the cooler ends of the ash collection system. Manganese, Co, Ni, Sr, and Mo exhibit less significant increases in the same direction. Within each fly ash collection row, Hg capture is greater at higher levels of fly ash carbon. As observed in other studies, the total REE do not show much variation with flue gas temperature or with the bulk particle size of the fly ash. The heavy REE do increase from the mechanical hoppers to the ESP hoppers, the direction of decrease in flue gas temperature, leading to a decrease in the LREE to HREE ratio in the same direction. Not all REY-bearing minerals have equal concentrations of the elements, as seen in varying Y concentrations in zircons in this study. Variations in REE concentrations between glass particles were also noted. In a fly ash from another power plant, semiquantitative measurements of La, Ce, and Nd concentrations in glass particles ranged from 0 ppm to 75, 120, and 70 ppm, respectively. Amorphous carbon, generally best observed using HR-TEM, surrounds Al-Si glass particles in this and

![Fig. 10. Mercury vs. carbon for fly ashes from the mechanical separation and from the three ESP rows.](image)

![Fig. 11. Left: Al-Si glass fly ash particle surrounded by amorphous carbon. The approximate extent of the carbon is shown by the dashed line. Right: Amorphous carbon within the area of the box shown on the left image. Scale = 40 nm for both images.](image)

![Fig. 12. Neodymium and Cerium in carbon within the same area shown in the right image of Figure 11. The apparent high concentrations of Nd and Ce coincident with the Al-Si glass do not necessarily imply that the Nd and Ce are within the glass. With high-resolution transmission electron microscopy (HR-TEM) imaging, the x–y locations of elements in the glass, on the surface of the glass, and in the carbon surrounding the glass are all recorded. Three-dimensional mapping of elements was not attempted. Scale = 40 nm.](image)
other bituminous coal–derived fly ashes. The amorphous carbon contains nanoscale inclusions containing Y, Ce, Nd, Pr, and Sm.

The fly ash is dominated by glass and carbons, with quartz and mullite being among the more important mineral phases and lesser amounts of magnetite and hematite. Titanium minerals were observed in the TEM studies. From investigations of the source coal and from rare views in the fly ash using optical microscopy, we know that REY-bearing minerals such as zircon and monazite are present in the fly ash. Based on thermal gravimetric analyzer experiments, it was demonstrated that monazite will shatter at boiler temperatures (1400°C), accounting for the general lack of monazite observations at the scale of optical microscopy. Although La-/Ce-rich regions of glass and fine minerals were detected in TEM examination of the fly ash, definitive REE-bearing minerals were not found. Yttrium-bearing zircons were detected.

Rare earth elements and yttrium, therefore, occur in this fly ash at scales ranging from REY-bearing minerals and glass to fine nanoparticles embedded within the amorphous carbon surrounding the glassy particles.

Acknowledgments

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This work also used shared facilities at the Virginia Tech National Center for Earth and Environmental Nanotechnology Infrastructure (NanoEarth), a member of the National Nanotechnology Coordinated Infrastructure (NNCI), supported by NSF (ECCS 1542100). Michael Hochella, Christopher Winkler, Debora Berti, and Mitsu Murayama assisted us at Virginia Tech. Tristana Duvallet, Robert Jewell, and Aaron Owen assisted with thermal studies at the CAER. Wencal Zhang, University of Kentucky Mining Engineering, supplied the monazite used in the thermal studies.

This work was supported by National Science Foundation grants CBET-1510965 and CBET-1510861 to Duke University and the University of Kentucky, respectively, and U.S. Department of Energy–National Energy Technology Laboratory (US DOE-NETL), 2015. Collected samples spreadsheet v051515. https://edx.netl.doe.gov/dataset/integrated-sample-databases/resource_download/8489de5e-8a20-4a6c-97e7-c2b4ca9b5928, accessed 24 May 2017.

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