Appendix A: Leaching Results for Rare Earth Elements, Yttrium, and Scandium in Samples from Coal Combustion Facilities D, I, KSU, and W

1. Introduction

Many rare earth elements (REEs) have valuable applications in electronics and a variety of products from the aerospace, defense, and clean energy industries. The REEs are lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Some coal-combustion byproducts have been identified as potentially valuable sources of REEs excluding Pm. All isotopes of Pm are short-lived radionuclides and they would not be present in coal-combustion byproducts.

Although not REEs, scandium (Sc), and yttrium (Y) are often included in studies that identify and possibly recover REEs from coal-combustion byproducts. As part of a study to evaluate the recovery of REEs, Y, and Sc (REYSc), ash samples were collected and evaluated from four coal-combustion facilities, identified as plants D, I, KSU, and W. Plants D, I, and KSU are located in Kentucky, and plant W is in the eastern US outside of Kentucky. All four facilities utilize eastern US bituminous coal.

2. Sample Descriptions

The coal ash samples utilized in this study are listed in Table A1. The plants I and W samples were fly ashes, the KSU sample was a stoker ash, and the plant D samples included a composite of 20 ash pond samples and five fly ashes. The plant D fly ashes were collected in 2002. All of the other samples are from 2016. The plants I and W fly ashes, the KSU stoker ash, and the plant D composite pond ash were also water separated into carbon-rich, magnetic, non-magnetic fine (-200 mesh), and non-magnetic coarse (+200 mesh) fractions.

One possible source of REEs is the eastern Kentucky Fire Clay Coal (Hower et al. 1999). This coal is known to contain above average concentrations of REEs compared with other coals and the Earth's crust. The REEs probably originated from a volcanic ash that was deposited in the peat that eventually became the coal.

3. Methodology

3.1 Powder X-ray Diffraction

The phases detected in the ashes and their fractions by powder X-ray diffraction (XRD) are listed in Table A2. The X-ray diffractograms for the samples are show in Appendix B.

Except for hand grinding the samples to the required fineness with a ceramic mortar and pestle, the XRD samples were analyzed as-received. With the exception of the KSU fine (-200 mesh) non-magnetic fraction, the samples were dry mounted in aluminum holders using the back-loaded method described in Appendix B3 of PANalytical (2005). The quantity of the KSU fine non-magnetic sample was too small to fill the aluminum holder. The sample was mixed with ethanol and mounted on a quartz plate.

All of the samples were scanned at 7-60º 2θ with copper K-α radiation on a Philips X'Pert diffractometer (model PW3040-PRO) operating at 45 kilovolts (kV) and 40 milliamps (mA). The scans had a 0.0167113º step size, 60.325 sec/step, and a scan speed of 0.035182º/step. The scans used 0.04 rad Soller slits, a nickel filter, a 5.5 mm AS slit, a 1/2º fixed slit, a 1/4º divergence slit and a 10 mm mask. Minerals and other crystalline substances in the diffractograms were identified with an International Centre for Diffraction Data (ICDD, Newtown Square, Pennsylvania, USA) powder diffraction (PDF) database. In qualitative XRD, crystalline substances are grouped into major, minor and trace categories.

4. Beneficiation (Separation)

As shown in the flow diagram in Figure A1, tap water was used to separate the four bulk ashes into carbon-rich, magnetic, non-magnetic coarse (+200 mesh), and non-magnetic fine (-200 mesh) fractions. The mass percentages of the oversized (+60 mesh) samples for the D, I, KSU and W ashes were 9.6%, 0.5%, 0.0%, and 0.4%, respectively. Due to the generally small quantities, the oversized fractions were not leached. Except for the oversized (+60 mesh) samples, the mass percentages of the fractions when compared with their bulk parent ash are shown in Table A1.

The separation and analysis of the different ash components could reveal whether particular REYSc elements are concentrated by size, carbon content or magnetic properties.

This information may provide insights into the phase distributions of the elements in the samples and how best to commercially extract them.

5. REYSc Chemistry of the Solid Ashes

Tables A3-A6 and 6 in the main text summarize the REYSc concentrations in the solid ash samples listed in Table A1. The REYSc concentrations in the ashes were determined with ASTM D6357. ASTM D6357 is a digestion method that uses hydrofluoric acid and aqua regia to dissolve solid samples so that they may be analyzed with inductively coupled plasma spectrometry (ICPS) or inductively coupled plasma mass spectrometry (ICPMS).

Figure A1. A flow diagram of the beneficiation (separation) of the bulk ashes into carbon-rich, magnetic, oversized (+60 mesh), non-magnetic coarse (+200 mesh), and non-magnetic fine (-200 mesh) fractions.
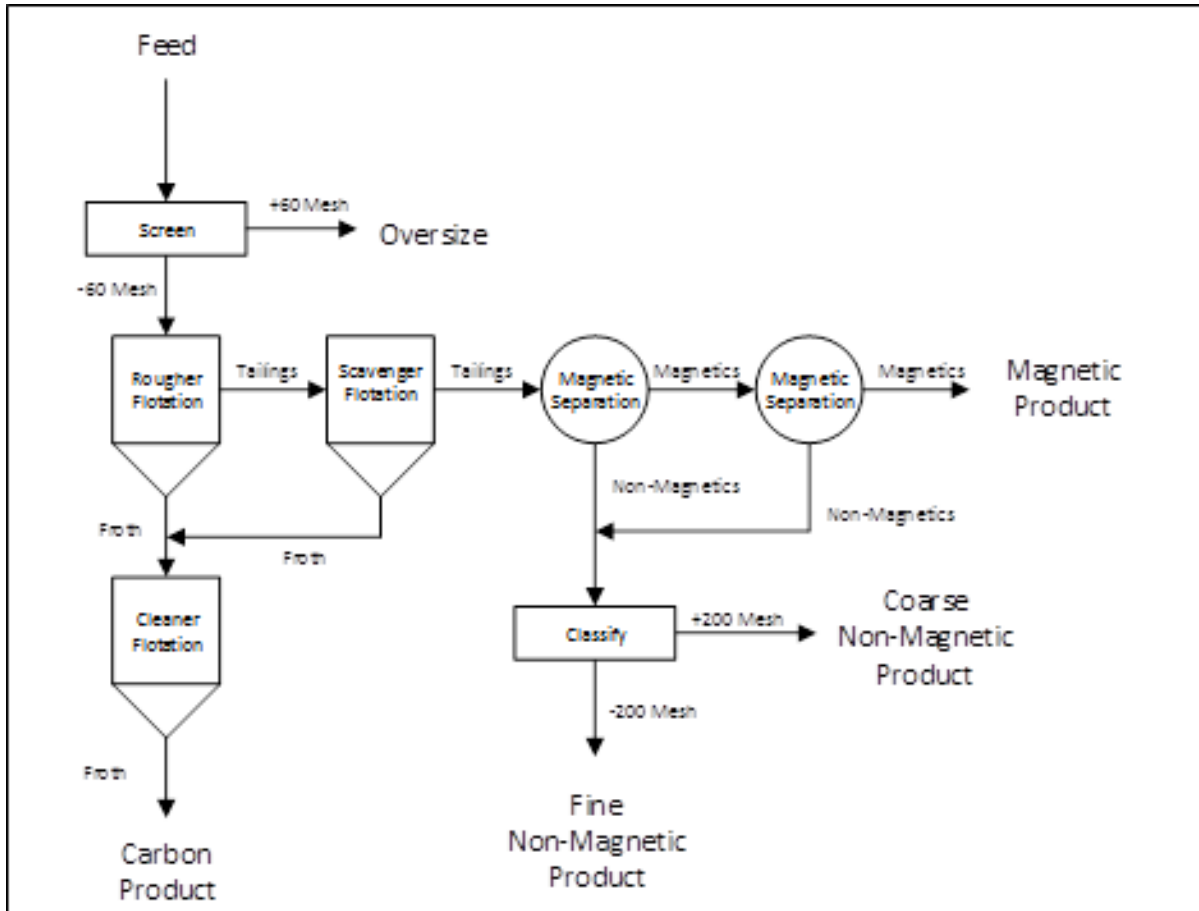
6. Batch Leaching Tests and Nitric Acid Extractions

All of the samples listed in Table A1 were batch leached in 4.2-4.9 weight percent (wt%) nitric acid aqueous solutions and the four bulk ashes were also leached in deionized (DI) water. The purpose of the leaching tests was not to recover all of the REYSc in the samples, but to determine how much of each element could readily dissolve in DI water and relatively mild acidic solutions, which could have commercial applications in the economic recovery of the elements. As a comparison with the batch leaching results, the coarse (+200 mesh) non-

magnetic plants I and W samples were heated in nitric acid and water to extract REYSc using a modification of section 9.2 of the ASTM D6357-04 procedure (ASTM, 2010).

Duplicate leachates were produced from some of the samples. The differences between the liquid-to-solid ratios of some of the nitric acid leachates and their duplicates were especially large and would affect any comparisons between the raw analytical results. To eliminate these effects, comparisons were made between the amount of each REYSc leached per gram of ash in micrograms per gram (µg/g), which is determined by multiplying the analytical results of the leachate in milligrams per liter (mg/L) by its liquid-to-solid ratio (details are given below). Absolute (positive values only) percent differences in the REYSc elements were then calculated for the samples and their duplicates with the following equation:

$$\text{Percent Difference} = \left| \frac{\text{Sample value} - \text{Duplicate value}}{(\text{Sample value} + \text{Duplicate value})/2} \right| \times 100$$

Less than values (non-detects) were not included in this calculation.

For comparisons between the leached/extracted µg/g values of different ash fractions, the following percent change equation was used:

$$\text{Percent Change} = \left[\frac{\text{First sample value} - \text{Second sample value}}{\text{Second sample value}} \right] \times 100$$

A positive percentage would indicate an increase from the second to the first value and a negative percentage would indicate a decrease. Less than values (non-detects) were also not included in this calculation.

6.1 Deionized (DI) Water Leachates

Deionized (DI) water batch leaching tests were performed on the D, I, KSU and W bulk samples to determine if they contain water-soluble REYSc phases in high enough concentrations to be readily recovered. Although water in the ash pond may have already leached out all or nearly all of any water-soluble REYSc phases in the plant D composite ash,

DI water leaching was done in case some water-soluble phases were retained in the ash because of an absence of thorough flushing from the pond water.

The U.S. Environmental Protection Agency (USEPA) requires that a minimum of 100 grams (g) of solid sample be leached for the regulatory Toxicity Characteristic Leaching Procedure (TCLP) (Method 1311, Section 7.1, *SW-846 Manual: Tests Methods for Evaluating Solid Wastes: Physical/Chemical Methods,* http://www.ehso.com/cssepa/SW846testmethods.htm). To ensure that the solid samples are representative, DI water leachates should also use a minimum of 100 g. Only the bulk ashes from the four plants were in suitably large enough quantities for the DI batch leaching tests.

The DI water procedure consisted of leaching 100 g of each ash in a glass jar with about 400 g of >18 milliohm (mΩ) DI water (Table A7). A duplicate leachate was produced from the plant W fly ash. The liquid-to-solid ratio of the leachates was low enough (4:1) to concentrate any water-soluble REYSc, yet high enough to produce mixtures that would flow and mix during agitation. The mixtures were agitated for 48 hours on an end-over-end tumbler, which is used in the TCLP.

After 48 hours, the pH values of the leachates were measured before and after 0.45 micron (μm) filtering (Nalgene disposable units). The pH meter was a Thermo-Orion 410+. The meter was calibrated with pH 7.00 (expires March 2018, Lot UX1) and pH 10.01 (expires April 2018, Lot UW1) Orion Thermo buffers. The filtered leachates were preserved at pH < 2 with Fisher nitric acid (Lot #094851; assay 69.4%) and refrigerated until analysis. The solid residues were air dried and kept for possible electron microscopy analyses. DI water-nitric acid blank C was prepared at the same time as the DI plant D leachate and blank K was produced with the I, KSU, and W leachates (Table A7). The detection limit of the elements is generally 0.001 mg/L. A second laboratory checked some of the results and had detection limits as low as 0.00002 mg/L for Ho.

6.2 Nitric Acid Leaching and Heated Extractions

For the nitric acid leaching tests, 100 g were not available for most of the samples in Table A1. For all of the nitric acid leachates and extractions, the sample sizes followed the ASTM D6357-04 procedure (ASTM, 2010). The leaching process involved weighing out

0.2000 to 0.5000 g of the as-received ashes and ash fractions (Table A8). After the solid samples were placed in vials, 20-22 g of DI water (> 18 mΩ) were added to each vial followed by 1.0 milliliter (mL) (1.4 g) of 69-70% J.T. Baker (Lot No. 104749, expiration date: February 20, 2020) or 69.4% Fisher (Lot No. 094851, no expiration date) nitric acid (Table A8). The mixtures were then tumbled for 48 hours on the same device used with the DI leachates, followed by filtering at 0.45 μm (Nalgene disposable units). The filtered leachates were refrigerated until analysis. The solid residues were air dried and kept for possible electron microscopy analyses. To confirm the analytical results, selected leachates were sent to a second laboratory.

As a comparison with the batch leaching results, the +200 mesh non-magnetic I and W samples were heated in nitric acid and water to extract REYSc using a modification of section 9.2 of the ASTM D6357-04 procedure (ASTM, 2010) (Table A8). The procedure uses 0.2000 to 0.5000 g of sample. Instead of adding 40 mL of hydrofluoric acid and aqua regia, 40 mL of 69-70% J.T. Baker nitric acid were added to each sample. The samples were heated until they were dry, but not baked. After drying, 20 g of DI water and 1.0-1.6 g of 69-70% J.T. Baker nitric acid were added to the samples (Table A8). They were reheated without boiling for one hour. The total mass of the sample and its water and nitric acid were then measured and the liquid-to-solid ratio was adjusted to allow for the evaporation of some of the liquid during the one hour reheating (Table A8). The extractions were then filtered at 0.45 μm and refrigerated until analysis. The solid residues from the extractions were air dried and kept for possible electron microscopy analyses. The filtrates of the leachates and extractions were clear and colorless, except for the heated extraction of the plant I non-magnetic +200 mesh fraction, which was clear and orange.

7. Results and Discussion

7.1 XRD

Qualitative XRD results for the ashes are listed in Table A2 and the diffractograms are shown in Appendix B. Overall, the samples are typical Class F fly ashes with the prominent phases being quartz (SiO_2), mullite (Al_4SiO_8), glass and other amorphous materials. Smaller amounts of hematite (Fe_2O_3), magnetite (Fe_3O_4), calcite ($CaCO_3$), cristobalite (SiO_2), microcline ($KAlSi_3O_8$) and sodium-rich plagioclase ($NaAlSi_3O_8 – CaAl_2Si_2O_8$) feldspars, and gypsum

($CaSO_4 \cdot 2H_2O$) may also be present. No known REEYSc minerals were detected in the samples.

The amorphous materials generally appear as an elevation or "hump" in the background of the diffractograms at approximately 20-30° 2θ (Appendix B). Both quartz and feldspars occur in coal and associated rocks and may pass through the combustion process and accumulate in ashes. Cristobalite is high-temperature SiO_2 that is present in some of the KSU samples. The traces of calcite in some of the plant D pond samples probably resulted from the weathering of amorphous materials in the presence of water and carbon dioxide. The weathered amorphous materials could provide the calcium in the calcite and the carbonate could originate from air, water, and/or the ash. Mullite may form from the dehydration of kaolinite clay ($Al_2Si_2O_5[OH]_4$) during combustion. Kaolinite is common in eastern bituminous coals and associated rocks. Hematite and magnetite often result from the combustion of pyrite (FeS_2) in coal. Hematite would form under more oxidizing conditions. Gypsum is common in scrubber sludge, but it may also result from moisture reacting with anhydrite ($CaSO_4$) in fly ashes. Anhydrite may form during combustion when calcite in the coal decarbonizes to form lime (CaO), which then reacts with SO_3 gases.

XRD results indicate that the plant W magnetic fraction contains trace amounts of micas and clay, which are very unusual (Table A2; Appendix B). The major mica and clay peaks were easily detected, but the minerals were not in high enough concentrations for the micas to be positively identified. The clay is probably kaolinite. The micas could be biotite ($K[Mg,Fe]_3[AlSi_3O_{10}][OH]_2$), phlogopite ($KMg_3[AlSi_3O_{10}][OH]_2$) or muscovite ($KAl_2[AlSi_3O_{10}][OH]_2$), which are typically found in igneous and metamorphic rocks. The exact origin(s) of the micas and clay in the plant W magnetic fraction is unknown. They are not expected to survive combustion in the coal and micas are usually not coal combustion products.

7.2 DI Water Leachates

Table A9 compares the concentrations in mg/L or parts per million (ppm) of some potentially toxic elements in the DI leachates with the US federal limits in mg/L for the toxicity characteristic of hazardousness for liquid wastes (40 *Code of Federal Regulations* [CFR] 261.24). Excluding any exemptions for certain types of wastes, if a TCLP leachate exceeds any one of these limits, then the waste is considered to have the toxicity characteristic of

hazardousness under US federal law. Although the federal limits only apply to TCLP leachates, the comparisons do provide some insights on the level of concentrations that might be expected if groundwater or rainwater were to come into contact with the ashes at a relatively low liquid-to-solid ratio of 4:1.

Except for arsenic, the results for the duplicated plant W sample are reasonably consistent (Table A9). As shown in italics and shaded in Table A9, the barium concentrations for blanks C and K are unusually high. A second laboratory confirmed the presence of barium in blank K and a selected number of samples. Both sets of values are listed in Table A9 with the value from the second laboratory following the first. In Table A9, the barium concentrations of the samples are those that were reported by the two laboratories and do **not** include subtraction of the blank values. In contrast to the blanks, the KSU sample contained very little barium. Because both the KSU sample and the blanks used the same water and preservation acid, the barium in the blanks most likely originated from the disposable filters or the bottles. Each sample and blank used a new filter and bottle, and both items were discarded after use.

Table A10 shows the pH results and the concentrations in mg/L of REYSc that were detected in the DI water leachates. Sc, Y, Ce, Nd, Sm, Eu, Gd, Dy, Tm, Yb and Lu were not detected in any of the DI leachates and their acid blanks. Trace amounts of Ho were detected in the blanks. Because the cause of the Ho trace concentrations is unknown, the values for the blanks were not subtracted from the DI leachate concentrations in Table A10. The low part-per-billion concentrations in the DI leachates are consistent with the general conclusion that REE elements are sparsely soluble in near-neutral pH water. REEs easily precipitate in the presence of hydroxide, carbonate, fluoride, phosphate and various organic ligands (Herrmann et al. 2016, 214).

The REE values for the leachates in Table A10 were multiplied by the liquid-to-solid ratios in Table A7 to obtain the micrograms of La, Pr, Tb, Ho, and Er leached per gram of sample (µg/g) as shown in Table A11. For Ho in sample D, <0.02 mg/L was used. The percent differences in Table A11 should be within 5% of each other, but 10% is generally considered acceptable. Of course, lower concentrations are expected to have higher percent differences

even though the mg/L differences may be trivial. For example, duplicate analyses of 0.010 and 0.020 mg/L are relatively trivial when compared with duplicates of 100.0 and 200.0 mg/L.

The micrograms of leached REEs per gram of sample (Table A11) were then divided by their concentrations in the solid ashes (Tables A3-A6) to obtain the percentage of each element leached from the ash (Table A12). The plant D composite ash contained no detectable Ho (Table A3). Because the concentrations of the REEs in the ashes greatly vary (Tables A3-A6), the 'less than' values in Table A12 vary.

The results for Ho in the DI water leachates of the I and W bulk ashes ranged from 5.2 to 8.1%, which seem high and questionable. Otherwise, DI water leached less than 1% of the detectable REYSc elements from the bulk ashes (Table A12). The leached percentages of the non-detected elements in the leachates (Sc, Y, Ce, Nd, Sm, Eu, Gd, Dy, Tm, Yb, and Lu) are <0.4%.

7.3 Nitric Acid Leaching and Heated Extractions

Tables A13-A16 list the mg/L concentrations of the REYSc in the nitric acid leachates/extractions and their blanks.   As with the DI leachates, the leachate/extraction results in Tables A13-A16 were multiplied by their liquid-to-solid ratios (Table A8) to obtain the micrograms of each REYSc element extracted/leached per gram of sample (µg/g) (Tables A17-A20).   The data in Tables A17-A20 were then divided by their respective REYSc concentrations in the solid ashes (Tables A3-A6) to determine the percent leached/extracted of each REYSc element for the ashes and their fractions (Tables A21-A24).

With the exception of Ho, Tm, Yb, and Lu in some of the plant D ashes (Table A3), REYSc elements were measured and detected in the analyses of the solid samples (Tables A3-A6). However, some elements were not leached/extracted in detectable concentrations (Tables A13-A16). Ho and Tm were not detected in any of the KSU leachates and many of the other leachates and extractions (Tables A13-16). The leachate of the KSU coarse (+200 mesh) non-magnetic fraction also contained no detectable Pr, Eu, Tb, and Lu. Tb was also not detected in the leachate of the KSU carbon fraction.

The percentages of Lu leached/extracted from the plant I non-magnetic +200 (coarse) and plant W non-magnetic -200 (fine) and +200 (coarse) fractions unrealistically exceed 100%

(Tables A22 and A24). Comparing the Lu values for the solid plant W samples in Table A6, the concentrations of the coarse and fine fractions are probably too low, which would result in the percentages of recovered Lu exceeding 100% (Table A24). When compared with the other plant I analyses in Table A4, the Lu concentration of 0.01 μg/g for the plant I non-magnetic coarse sample was probably underestimated, which resulted in a recoveries far above 100% (Table A22).

Although the solid KSU bulk ash and its fractions often contain higher concentrations of individual REYSc elements than the ashes from the other facilities (Tables A3-A6), the percentages of REYSc nitric acid leached from the KSU samples were usually significantly lower (Tables A21-A24). The percentages of total REYSc leached from the KSU samples were less than 5% (Table A23). The percentages of total REYSc nitric acid leached from the two plant D bulk samples ranged from 17.4 to 19.6% (Table A21). The leached percentages for the other plant D ashes were 10.6-22.4% (Table A21). For the plant I samples, the percentages of total REYSc leached/extracted ranged from 8.5 to 26.4% (Table A22). As mentioned earlier, the Lu percentages for the leachate and extraction of the plant I coarse (+200 mesh) non-magnetic sample unrealistically exceed 100% (Table A22), which probably resulted from the unusually low Lu concentration of 0.01 μg/g in the solid sample (Table A4). The plant W nitric acid leachates and extraction had some of the consistently higher percentages of total recovered REYSc, which ranged from 17.4 to 29.5% (Table A24).

For the nitric acid leachates of the plant D, KSU, and W ashes, a majority of the highest REYSc percent recoveries occurred with the fine (-200) fractions (Table A21, A23-A24). Except for Lu, which includes questionable results, and possibly Tm with its non-detects, the carbon fraction leached the highest percentages of REYSc among the plant I nitric acid leachates and extraction (Table A22). It is possible that relict acid-soluble REYSc phases from the unburned coal were present in the carbon fraction.

7.4 Comparisons of Duplicates

To evaluate the consistency of the ambient room-temperature leaching procedure, the homogeneity of the samples and the analyses, duplicate nitric acid leachates were produced of

the bulk plant D composite pond ash, the plant D Unit 1 row 1 ESP fly ash, the plant D coarse (+200) non-magnetic fraction, the magnetic plant I fraction, the bulk KSU sample, and the coarse non-magnetic plant W fraction (Tables A13-A16).

The majority of the percent differences of the duplicate results in Tables A17-A20 are within 10.0% of each other, which is acceptable. The percent differences of Sc, La, Gd, Er, and Yb were within 10.0% for all six pairs of duplicates. Lu exceeded 10.0% in five of the six pairs of duplicates (Tables A17-A20). Only the Lu measurements on the plant I magnetic fraction showed reasonable consistency (Table A18). Four of the six pairs of duplicates had Pr differences greater than 10.0%. Eu and Sm exceeded 10.0% in three pairs. One or two pairs of duplicates exceeded 10.0% for Y, Ce, Nd, and Dy (Tables A17-A20). Three of the five pairs with detectable Tb exceeded 10.0%. Ho was detected in two pairs of the duplicate samples and exceeded 10% in one of them and Tm exceeded 10% in one of the three duplicate sets that had detectable concentrations of this element (Tables A17-A20).

7.5 Comparison between Nitric Acid Hot Extractions and Ambient-Temperature Leachates

For the coarse (+200) plant I sample, REYSc recoveries were consistently higher in the more concentrated, hot nitric acid extraction when compared with the room-temperature, more dilute nitric acid 48 hour leaching procedure (Table A18). It is not surprising that hot nitric acid extractions over a few hours would be more effective in dissolving REYSc phases than more dilute solutions over 48 hours at ambient temperatures.

For unknown reason(s), the situation was very different between the hot extraction and two ambient leachates of the coarse plant W fraction (Table A20). Setting aside the problematic Lu results (Table A24) and the non-detects for Ho and Tm (Table A20), the REYSc concentrations for the coarse plant W extraction were usually not much higher than the averages of the leachate duplicates, and sometimes they were even less than one or both of the leachate results (Table A20).

8. REYSc Comparisons of Fine (-200 mesh) and Coarse (+200 mesh) Non-Magnetic Solid Samples and their Nitric Acid Leachates

Magnetite is the only strongly magnetic phase that was detected in the ash samples (Table A2; Appendix B). XRD results also indicate that magnetite was effectively removed from the fine (-200) and coarse (+200) non-magnetic fractions of the four ashes (Table A2; Appendix B).

Comparisons between the fine and coarse non-magnetic fractions and their leachates/extractions may provide insights into how processing of the coal, combustion, and ash handling affects the distribution and leaching properties of REYSc elements with particle size. Different particle size fractions are expected to have differences in surface areas and other physical, mineralogical, and chemical properties that could affect the concentrations of REYSc elements in the solid samples and their leachates/extractions. In general, the finer-grained fractions should have higher surface area particles and higher concentrations of total and nitric acid leachable/extractable REYSc.

8.1 Comparisons of REYSc Results in the Solid Samples

Ho was not detected in the fine and coarse non-magnetic fractions of the plant D composite pond sample (Table A3). Both fractions contained one µg/g of Lu (Table A3). For the other elements, only Y was in higher concentrations in the coarse fraction.

With the exception of the questionable Lu results, analyses on the solid fine non-magnetic plant I fraction had 36.4 – 80.0% more REYSc elements than the coarse fraction (Table A4). Like the plant I samples, the concentrations of REYSc in the solid fine plant W fraction were consistently higher than the coarse fraction. Excluding the questionable Lu results, the percent increase in the fine versus coarse plant W fractions ranged from 50.6% for Tb to 115% for Y (Table A6).

The plants D, I, and W results suggest that during combustion REYSc-bearing particles preferentially accumulated on high surface-area materials in the fine fractions. It is also possible that if some of the larger materials in the coarse fractions were not entirely dissolved during the digestion procedure and that significant amounts of REYSc-bearing phases could have been encased in these insoluble materials.

The distributions of REYSc in the solid KSU fine and coarse fractions were very different than the samples from the other three facilities (Table A5). With the exception of La

and Ce, each REYSc element was no more than 10% higher in the fine than the coarse fraction and in several cases the concentrations were actually higher in the coarse fraction (Table A5). XRD results indicate that the KSU fine and coarse fractions contained the same minerals in similar proportions (Table A2; Appendix B). However, unlike the D, I, and W ashes where the fine non-magnetic materials were far more abundant than the corresponding coarse non-magnetic fraction (Table A1), the percentage of coarse materials in the KSU ash was slightly higher than the fine fraction (29.6 vs. 21.9%; Table A1). Despite generally lower surface areas, a larger number of coarse particles in the KSU ash could accumulate more REYSc during ash formation and possibly exceed the concentrations of REYSc elements in the fine non-magnetic fraction.

8.2 Comparisons of REYSc Leaching Results

In general, the REYSc concentrations in the nitric acid leachates of the fine and coarse non-magnetic fractions had much greater differences with each other than the corresponding differences between the REYSc elements in the fine and coarse fractions of the solid ashes (compare Tables A3-A6 with A17-A20). Excluding the controversial Lu results, the detectable leached REYSc concentrations in the fine fractions were 68.9 to 603% higher than the corresponding values in the leachates of the coarse fractions (Tables A14-A17). The higher REYSc concentrations in the fine fractions are probably due to higher surface areas, as well as the presence of substantial acid-soluble REYSc-bearing phases.

9. Comparison of Magnetic and Fine Non-Magnetic Samples and their Nitric Acid Leachates

9.1 Comparisons of REYSc Results in the Solid Samples

Comparisons between the concentrations of REYSc elements in the solid fine non-magnetic (-200 mesh) and magnetic fractions of the ashes may provide some insight into whether or not each of the REYSc elements tends to associate with magnetite (Fe_3O_4) and other magnetic materials. For their eastern US fly ashes, Hulett et al. (1981, pp. vi, 46) found that Ce and La tended to associate with the magnetic fractions, but that other REEs generally concentrated in glass, which should be non-magnetic if it's reasonably pure and free of embedded magnetite particles. Tables A3-A6 give the percent changes in the REYSc concentrations between the solid magnetic and fine non-magnetic fractions. Besides being

influenced by the tendency of the elements to associate with magnetic materials or not, the distribution of REYSc elements between the two fractions would also be affected by the following factors:

- The purity of the fractions. Although XRD results indicate that magnetite is noticeably absent from the fine non-magnetic fractions, the magnetic fractions contain considerable quartz, mullite, amorphous materials, and other non-magnetic impurities (Table A2; Appendix B).

- Surface area. As with the comparisons between the fine- and coarse-fractions, during combustion REYSc elements in the fine non-magnetic and magnetic fractions may preferentially accumulate on smaller particles with higher surface areas. Surface area measurements are not available for the size fractions. The particle sizes and surface areas of the magnetic fraction were measured for the -60 mesh fractions (Figure A1), but otherwise they could be quite variable.

- The number of particles. Even if the surface areas of the individual fine non-magnetic and magnetic particles were the same, the fraction with the larger number of particles would have more surfaces for REYSc to accumulate during combustion. For all four ashes, the amount of magnetic materials is less than the amount of the corresponding fine non-magnetic fraction, especially in the samples from plants D, I, and W (Table A1).

In contrast to the conclusions in Hulett et al. (1981, pp. vi, 46), the concentrations of Ce and La are actually higher in the fine non-magnetic fractions of the D, I, and W ashes when compared with their magnetic fractions (Tables A3-A4, A6). This suggests that other factors are present in the three groups of ashes that are not present in the Hulett et al. (1981) samples, which may include: different magnetic phases, large amounts of non-magnetic impurities in the magnetic fraction, and/or differences in surface area and the number of particles between the two fractions. In contrast, all of the measured REYSc elements were more concentrated in the magnetic fraction in the KSU ash (Table A5). The magnetic fraction of the KSU ash contains considerable mullite and other non-magnetic impurities (Table A2; Appendix B) and its mass percentage was also more similar to its fine fraction (14.8% vs. 21.9%) than the other three ashes (Table A1).

Excluding the problematic results with Lu in the I and W ashes, the magnetic fractions of all four ashes were more enriched in Y, Pr, and Yb then their corresponding fine fractions (Tables A3-A6). The fine non-magnetic I and W fractions were especially enriched in Ho when compared with the magnetic fractions.

9.2 Comparisons of REYSc Leaching/Extraction Results

In addition to particle surface area, the number of particles in the fraction and the mineralogical associations of the REYSc elements, the distributions of REYSc elements between the nitric acid leachates of the fine non-magnetic and magnetic fractions would depend on the solubility of the REYSc host phases in the acid (Table A25). Tables A17-A20 list the percent changes in the concentrations of the REYSc elements in the nitric acid leachates of the fine non-magnetic versus the magnetic fractions of the four groups of ashes. Unlike the solid fractions, the REYSc elements are consistently higher in the nitric acid leachate of the plant D fine fraction when compared with the magnetic fraction leachate (Tables A3 and A17). When compared with the plant D magnetic fraction acid leachate, the concentrations of Sc, Ce, Nd, Er, and Tm are especially higher in the fine fraction leachate (Table A17). For the KSU nitric acid leachates, Y, La, Ce, Nd, and Pr have a strong preference for the fine fraction leachate. The W plant fine fraction leachate is exceptionally higher in Sc, Tb, and Ho (Tables A19-A20).

The differences in the concentrations of the REYSc elements in the plant I fine and magnetic fraction nitric acid leachates are far less extreme when compared with the leachates from the other three plants. Gd, Yb, and Lu even have higher concentrations in the magnetic fraction leachates.

10. Mineralogy

A review of the mineralogy database at webmineral.com indicates that over 280 minerals are known to contain significant Sc, Y, and/or REEs. However, only a few of them have actually been found in coal or rocks associated with coal (Table A25). Bästnasite (baestnasite or bastnasite, $[Ce,La,Y][CO_3]F$) probably also occurs in some REE-bearing coals, although a review of the literature was unable to confirm its presence.

Even fewer minerals have actually been identified in coal ashes. None of the minerals listed in Table A25 were detected by powder XRD in the samples (Table A2; Appendix B). Zircon is known to survive combustion and accumulate in coal ash. If their decomposition or melting temperatures are high enough or if combustion is suitably brief, other anhydrous silicate, phosphate and oxide minerals (such as brannerite, monazite, polycrase, and xenotime) could survive combustion and accumulate in ashes. Hydroxide, hydrated silicates, and carbonate minerals (allanite, biotite, crandallite, florencite, goyazite, illite, kaolinite, rhabdophane, and also bästnasite) would tend to decompose at high temperatures and release water and carbon dioxide. The thermal stability of apatite depends on the amount of hydroxide and halogens. Fluorapatite is stable up to 1200ºC under atmospheric pressure and hydroxylapatite loses hydroxyls at 850ºC in dry air (Tõnsuaadu et al. 2012, p. 650). REYSc released from the decomposition of their host phases would then accumulate in glass or other high-temperature phases.

The information in Table A25 on the solubility of minerals and other materials in nitric acid is limited and questionable. Available information from www.mindat.org indicates that bästnasite is "insoluble" in nitric acid. However, a bästnasite mineral with more carbonate than fluoride should at least decompose in nitric acid.

Silicate minerals are generally insoluble in nitric acid. Hulett et al. (1981, p. vi) found that most REEs tended to concentrate in fly ash glass. Silicate glasses in coal ashes also should be sparsely soluble in nitric acid, although silicate glasses richer in aluminum and calcium could be slightly more soluble.

The oxidizing properties of nitric acid could break down organic materials in the carbon fractions and release REYSc elements that are either in the organic structures or in acid-soluble microminerals trapped in the organic compounds. In the inorganic fractions, among the minerals listed in Table A25, brannerite and possibly polycrase are most likely to survive combustion and yet dissolve in nitric acid.

11. Conclusions

The distributions and concentrations of rare earth elements, Y, and Sc (REYSc) were investigated in coal ashes from four eastern US facilities, identified as plants D, I, KSU and W (Table A1). The plants I and W samples were fly ashes, the KSU sample was a stoker ash, and the plant D samples included a composite of 20 ash pond samples and five fly ashes. The bulk ashes from the four plants were also water separated into carbon-rich, magnetic, non-magnetic fine (-200 mesh) and non-magnetic coarse (+200 mesh) fractions. Due to frequent sample size limitations, the +60 mesh (very coarse) fractions were not investigated.

The studies included measurements of REYSc and other parameters on solid samples, nitric acid leachates of the samples, as well as deionized (DI) water leachates and hot nitric acid extractions of selected ashes. Powder X-ray diffraction (XRD) determined the mineralogy of the samples (Table A2; Appendix B). The following are main conclusions of this study:

- No known REEYSc minerals were detected in the samples by XRD (Tables A2 and A25; Appendix B). The XRD results indicate that the samples are typical class F fly ashes with the prominent phases being amorphous materials (especially glass), quartz (SiO_2), and mullite (Al_4SiO_8). Smaller amounts of hematite (Fe_2O_3), magnetite (Fe_3O_4), calcite ($CaCO_3$), cristobalite (SiO_2), microcline ($KAlSi_3O_8$) and sodium-rich plagioclase ($NaAlSi_3O_8 - CaAl_2Si_2O_8$) feldspars, and gypsum ($CaSO_4 \cdot 2H_2O$) may also be present. The plant W magnetic fraction also contains trace amounts of unidentified micas and clay (probably kaolinite), which are very unusual (Table A2; Appendix B). The exact origin(s) of the micas and clay in the plant W magnetic fraction is unknown. They are not expected to survive combustion in the coal and micas are usually not coal combustion products. Although magnetite was effectively removed from the non-magnetic fine (-200 mesh) and coarse (+200 mesh) fractions, XRD analyses indicated that the magnetic fractions contained considerable quartz and mullite impurities.Only the bulk ashes from the four facilities were in large enough quantities (100 grams) for leaching with deionized (DI) water. Small concentrations of arsenic, barium, chromium and selenium were detected in some of the DI water leachates (Table A9). The blanks were also high in barium. The barium probably resulted from the new filters or bottles rather than the DI water or the nitric acid preservative.

- Except for Ho in the I and W bulk ashes, which questionably range from 5.2 to 8.1%, DI water leached less than 1% of the detectable REYSc elements from the four bulk ashes (Table A12).

- Although the solid KSU bulk ash and its fractions often contained higher concentrations of individual REYSc elements than the ashes from the other facilities (Tables A3-A6), the total percentages of REYSc nitric acid leached from the KSU samples were less than 5% (Table A23). The percentages of total REYSc nitric acid leached from the plant D ashes were 10.6-22.4% (Table A21). Ignoring the unrealistic Lu results, the percentages of total REYSc leached/extracted with nitric acid for plant I ranged from 8.5 to 26.4% (Table A22). The plant W nitric acid leachates and extraction also had some unrealistic Lu results. However, overall the plant W nitric acid leachates and extraction had some of the higher percentages of total recovered REYSc, which ranged from 17.4 to 29.5% (Table A24).

- For the nitric acid leachates of the plant D, KSU, and W ashes, a majority of the highest REYSc percent recoveries occurred with the fine (-200) fraction (Tables A21, A23-A24). Except for Lu, which includes questionable results, and possibly Tm with its non-detects, the carbon fraction leached the highest percentages of REYSc among the plant I nitric acid leachates and extraction (Table A22).

- In most cases, the REYSc results for duplicated nitric acid leachates were acceptable and within 10.0% of each other (Tables A17-A20).

- REYSc recoveries were consistently higher in the more concentrated, hot nitric acid extraction of the coarse (+200) plant I sample when compared with the results of the ambient temperature, more dilute nitric acid 48 hour leaching procedure (Table A18). For unknown reason(s), the situation was very different between the hot extraction and two ambient leachates of the coarse plant W fraction (Table A20). Setting aside the problematic Lu results (Table A24) and the non-detects for Ho and Tm (Table A20), the

REYSc concentrations for the coarse plant W extraction were usually not much higher than the averages of the leachate duplicates, and sometimes they were even less than one or both of the leachate results (Table A20).

- In most cases, REYSc elements were more concentrated in the fine non-magnetic D, I, and W ash fractions than the corresponding coarse fractions. These results suggest that during combustion REYSc-bearing particles preferentially accumulated on high surface-area materials in the fine fractions.

- The distributions of REYSc in the solid KSU fine and coarse fractions were very different than the samples from the other three facilities (Table A5). With the exception of La and Ce, each REYSc element was no more than 10% higher in the fine than the coarse fraction and in several cases the concentrations were actually higher in the coarse fraction (Table A5). Unlike the D, I and W ashes where the fine non-magnetic materials were far more abundant than the corresponding coarse non-magnetic fraction (Table A1), the percentage of coarse materials in the KSU ash was slightly higher than the fine fraction (29.6 vs. 21.9%; Table A1). Despite generally lower surface areas, a larger number of coarse particles in the KSU ash could accumulate more REYSc during ash formation and possibly exceed the concentrations of REYSc elements in the fine non-magnetic fraction.

- In general, the REYSc concentrations in the nitric acid leachates of the fine and coarse non-magnetic fractions had much greater differences with each other than the corresponding differences between the REYSc elements in the fine and coarse fractions of the solid ashes (compare Tables A3-A6 with A17-A20). Excluding the controversial Lu results, the detectable leached REYSc concentrations in the fine fractions were 68.9 to 603% higher than the corresponding values in the leachates of the coarse fractions (Tables A14-A17). The higher REYSc concentrations in the fine fractions are probably due to higher surface areas, as well as the presence of substantial acid-soluble REYSc-bearing phases.

- For their eastern US fly ashes, Hulett et al. (1981, pp. vi, 46) found that Ce and La tended to associate with the magnetic fractions, but that other REEs generally concentrated in glass, which should be non-magnetic if it's reasonably pure and free of embedded magnetite particles. These relationships were not consistently seen between the fine and magnetic fractions of the four ashes and their nitric acid leachates. Other factors must be present in the ashes that are not present in the Hulett et al. (1981) samples, such as: different magnetic phases, large amounts of non-magnetic impurities in the magnetic fraction, and/or differences in surface area and the number of particles between the two fractions.

- Relatively few REYSc-bearing minerals found been found in coals (Table A25) and even fewer in their ashes. Zircon is known to survive combustion and accumulate in coal ash. If their decomposition or melting temperatures are high enough or if combustion is suitably brief, other anhydrous silicate, phosphate and oxide minerals (such as brannerite, monazite, polycrase, and xenotime) could survive combustion and accumulate in ashes. Hydroxide, hydrated silicates and carbonate minerals (allanite, biotite, crandallite, florencite, goyazite, illite, kaolinite, rhabdophane, and also bästnasite) would tend to decompose at high temperatures and release water and carbon dioxide. The thermal stability of apatite depends on the amount of hydroxide and halogens.

- Information on the solubility of REYSc-bearing minerals in nitric acid is limited and questionable. Silicate minerals and silicate glass are generally insoluble in nitric acid. A bästnasite mineral with more carbonate than fluoride should at least decompose in nitric acid. The oxidizing properties of nitric acid could break down organic materials in the carbon fractions and release REYSc elements. In the inorganic fractions, among the minerals listed in Table A25, brannerite and possibly polycrase are most likely to survive combustion and yet dissolve in nitric acid.

References

American Society for Testing and Materials, 2010. Standard test methods for determination of trace elements in coal, coke, and combustion residues for coal utilization processes by inductively coupled plasma atomic emission spectrometry, inductively coupled plasma mass spectrometry, and graphite furnace atomic absorption spectrometry method D6357-04, *Annual Book of ASTM Standards* 5.06: *Petroleum Products, Lubricants, and Fossil Fuels: Gaseous Fuels; Coal and Coke*, ASTM International: West Conshohocken, PA, USA, 673-680.

Birk, D., White, J.C., 1991. Rare earth elements in bituminous coals and underclays of the Sydney Basin, Nova Scotia: Element sites, distribution, mineralogy. International Journal of Coal Geology 19, 219-251.

40 *Code of Federal Regulations* (CFR) 261.24. Washington, DC: US Government Printing Office, Superintendent of Documents.

Dai, S., Seredin, V.V. Ward, C.R., Hower, J.C., Xing, Y., Zhang, W., Song, W., Wang, P., 2015. Enrichment of U-Se-Mo-Re-V in coals preserved within marine carbonate successions: Geochemical and mineralogical data from the Late Permian Guiding Coalfield, Guizhou, China. Mineralium Deposita 50, 159-186.

Dai, S., Graham, I.T., Ward, C.R., 2016. A review of anomalous rare earth elements and yttrium in coal. International Journal of Coal Geology 159, 82-95.

Franus, W., Wiatros-Motyka, M.M., Wdowin, M., 2015. Coal fly ash as a Resource for rare earth elements. Environmental Science and Pollution Research 22, 9464-9474.

Herrmann, H., Nolde, J., Berger, S., Heise, S., 2016. Aquatic toxicity of lanthanum – A review and an attempt to derive water and sediment quality criteria. Ecotoxicology and Environmental Safety 124, 213-238.

Hower, J.C., Ruppert, L.F., Eble, C.F., 1999. Lanthanide, Yttrium, and Zirconium anomalies in the Fire Clay coal bed, Eastern Kentucky. International Journal of Coal Geology 39, 141-153.

Hulett, L.D., Weinberger, A.J., Ferguson, N.M., Northcutt, K.J., Lyon, W.S., 1981. *Trace Element and Phase Relations in Fly Ash*, EA-1822, Research Project 1061, Final Report, Electric Power Research Institute: Palo Alto, CA, USA, 63pp.

Jeong, G.Y., 2006. Mineralogy and geochemistry of Metalliferous Black Slates in the Okcheon Metamorphic Belt, Korea: A metamorphic analogue of black shales in the South China Block. Mineralium Deposita 41, 469-481.

Jiang, Y., Zhao, L., Zhou, G., Wang, X., Zhao, L., Wei, J., Song, H., 2015. Petrology, mineralogy, and geochemical compositions of Early Jurassic Coals in the Yining Coalfield, Xinjiang, China. International Journal of Coal Geology 152, 47-67.

Liu, J., Yang, Z., Yan, X., Ji, D., Yang, Y., Hu, L., 2015. Modes of occurrence of highly-elevated trace elements in superhigh-organic sulfur coals. Fuel 156(9187), 190-197.

PANalytical B.V. 2005. *X'Pert PRO User's Guide*, 5th edition, PANalytical BV: Almelo, The Netherlands.

SW-846 Manual: Tests Methods for Evaluating Solid Wastes: Physical/Chemical Methods, Toxicity Characteristic Leaching Procedure (TCLP), Method 1311, U.S. Environmental Protection Agency, http://www.ehso.com/cssepa/SW846testmethods.htm

Tõnsuaadu, K., Gross, K.A., Plūduma, L., Veiderma, M., 2012. A review on the thermal stability of calcium apatites. Journal of Thermal Analysis and Calorimetry 110, 647-659.

Vassilev, S.V., Eskenazy, G.M., Tarassov, M.P. Dimov, V.I., 1995. Mineralogy and geochemistry of a vitrain lens with unique trace element content from the Vulche Pole Coal Deposit, Bulgaria. Geologica Balanica 25(3-4), 111-124.

Vassilev, S.V., Vassileva, C.G., 2005. Methods for characterization of composition of fly ashes from coal-fired power stations: A critical overview. Energy & Fuels 19, 1084-1098.

Wang, X., 2009. Geochemistry of Late Triassic coals in the Changhe Mine, Sichuan Basin, Southwestern China: Evidence for authigenic lanthanide enrichment. International Journal of Coal Geology 80(3-4), 167-174.

U.S. Environmental Protection Agency. *SW-846 Manual: Tests Methods for Evaluating Solid Wastes: Physical/Chemical Methods.* http://www.ehso.com/cssepa/SW846testmethods.htm

Zhang, J., Ren, D. Zhu, Y., Chou, C.-L., Zeng, R., Zheng, B., 2004. Mineral matter and potentially hazardous trace elements in coals from Qianxi Fault Depression Area in Southwestern Guizhou, China. International Journal of Coal Geology 57(1), 49-61.

Zou, J., Liu, D., Tian, H., Li, T., Liu, F., Tan, L., 2014. Anomaly and geochemistry of rare earth elements and yttrium in the Late Permian Coal from the Moxinpo Mine, Chongqing, Southwestern China. International Journal of Coal Science & Technology 1(1), 23-30.