Enrichment of Rare Earth Elements from Coal and Coal By-Products by Physical Separations

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Abstract

Rare earth elements (REE) are of strategic importance because they find numerous applications in various sectors of the global economy. The concern about the REE supply challenge has led to increasing interest and research in the recovery of REE from end-of-life products and secondary sources such as coal and coal by-products. The work reported here was focused on examining the technical feasibility of physical separation techniques for the enrichment of REE from coal and coal by-products. Particle size, magnetic and density separations were performed on coal, coal ash, clay and shale samples. It was found that the samples responded to particle size separation differently. For all ash samples, higher REE concentrations were found in the finer fractions. For the clay and shale samples, however, the REE concentrations decrease as the particle size reduces possibly because RE minerals were not effectively released by grinding. Magnetic separation showed that REE are enriched in non-magnetic fractions for all ash samples. All samples responded similarly to density separation. Among the three methods, density separation showed the highest enrichment of REE. A combination of these methods is recommended. Finally, correlations between elements were demonstrated, which leads to the classification of three groups containing mainly Al/Si, Fe and Ca, respectively. REE are strongly associated with the Al/Si group.

Keywords: Rare earth elements (REE), coal, fly ash, physical separation, magnetic separation, float-sink separation, density separation

1. Introduction

Rare earth elements (REE) are a group of seventeen chemical elements of the periodic table including the fifteen lanthanides plus yttrium and scandium. The latter two are included because they are usually found in the same ore deposits as the lanthanides and exhibit similar geochemical properties. Rare earth (RE) metals are of strategic importance because they find numerous applications in various sectors of the global economy such as clean energy production, health care, oil refining and electronics. They are the key ingredients for magnets for wind turbines and other devices, batteries for vehicles, phosphors for lighting, catalysts for petroleum refining and many others [1-2]. Due to their critical roles in modern economy, both the European Commission [3] and the U.S. Department of Energy [1] consider REE as critical raw materials. In the global market, however, China dominates the REE supply chain of mining, separation, refining and manufacturing, producing more than 85% of the REE raw materials and oxides [2,4]. The concern about the REE supply challenge has led to increasing interest and research in the recovery of REE from end-of-life products such as permanent REE magnets, nickel metal-hydride batteries and lamp phosphors [5] and from secondary sources such as coal and coal mining and combustion by-products [6,7].

It is well known that coal contains REE in addition to many other trace metal elements and that the majority of REE are associated with inorganic minerals in coal. The worldwide average total REY (lanthanides and yttrium) concentrations are 68.5 ppm and 404 ppm for coal and coal ash, respectively [7,8]. Recent studies showed that the beneficial recovery of REE from coal requires a minimum rare earth oxide (REO) concentration of 800–900 ppm in the coal ash [6, 9-11]. Based on this datum, Zhang et al. [6] further estimated the cut-off grade of REE in coal which is 115-130 ppm on the whole coal basis and 677-762 ppm on the ash basis. An analysis of

the U.S. Coal Quality Database showed that greater than 700 ppm (ash basis) REE are distributed in the U.S. coal basins [6]. A study by Rozelle et al. [12] suggested that U.S. coal by-products may be technically suitable as REE ores. Therefore, coal and coal by-products are promising alternative sources for REE recovery. Advantages of utilizing coal and coal by-products as feedstocks for REE production include: (1) large and reliable sources, (2) already mined materials (no need for new mining permits), (3) potential environmental and health benefits from no new mining, and (4) utilizing potential waste materials. The recovery of REE from coal and coal by-products is promising also because of current limitations with developing new conventional metalliferous mines, the decreasing reserves of RE metals in conventional deposits, and growing application of these valuable metals in modern technology [13]. Development of processes and technologies for the economic recovery of REE from coal and coal by-products would be game-changing and beneficial, particularly to countries like the U.S. that rely heavily on REE imports. Incorporation of the REE recovery process into the coal mining, processing and combustion processes, on the other hand, would also benefit the society by using coal by-products and thus reducing the environmental impacts of these by-products.

Physical separation methods have been widely applied in the traditional processes for the beneficiation of RE minerals from conventional RE ore deposits. These methods mainly include particle size separation, magnetic separation, density (or gravity, float-sink) separation, electrostatic separation and flotation. Limited applications of these methods in the recovery of REE from coal and coal by-products have been reported in recent studies [14-17]. Dai et al. [14] investigated the abundance and distribution of minerals and elements in high-alumina coal fly ash from a Chinese coal power plant. The fly ash was first separated into three fractions, namely magnetic, MCQ (mullite + corundum + quartz) and glass phases. It was found that REE were

enriched in the glass phase but depleted in the magnetic and MCQ phases and heavy REE (HREE) in the glass phase were more enriched than light REE (LREE). In the magnetic and MCQ phases, however, the LREE were more enriched than HREE despite the overall depletion. They further examined elemental distribution in size-fractionated fly ash and found that there was a significant increase in the REE concentrations with the decrease in particle size. They also noticed that the enrichment factors for LREE were greater than those of the HREE as the particle size decreases. Studies by Dai et al. [15], Hower et al. [16] and Blissett et al. [17] confirmed that the REE concentrations in coal ash increase as the particle size decreases. Hower et al. [16] also found that LREE/HREE showed a minimum in the 160×300 mesh fraction and a maximum in the finest fraction. Blissett et al. [17] proposed and analyzed a pilot-scale multi-stage REE enrichment scheme composed of froth flotation, magnetic separation and hydrocyclone separation. They found a slight enrichment of REY from 419 to 529 ppm and suggested that the technical feasibility of using such a process for enrichment and extraction of REE should be further evaluated.

Recent projects funded by the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) explored the technical feasibility of using a variety of physical separation techniques for REE enrichment from coal and coal by-products [18-21]. The University of Kentucky and Virginia Tech (UK&VT) team [18] tested six different separation techniques including table concentration, enhanced gravity concentration, wet high intensity magnetic separation, electrostatic separation, froth flotation and agglomeration on coal and coal by-product samples. They found that froth flotation was the only method that could be used for REE enrichment. Density-based separators were the least effective methods due to ultrafine grain size of RE minerals. Higher REE concentrations were found in the magnetic fractions of all

samples. However, this method was not effective due to the extremely low mass recovery. The University of Utah team [20] examined magnetic, flotation and float-sink separations on Western U.S. coal samples. They found that the wet high intensity magnetic separation method was effective for the removal of the pyritic content of the coal, but they concluded that this method could not be used for the efficient recovery of REE from coal for the same reason as the UK&VT team determined. They found that the froth flotation method was ineffective in concentrating REE from fine coal of smaller than 100 mesh (150 μm) due to the poor liberation of RE minerals which are smaller than 5 μm and uniformly dispersed in the coal matrix. They also found that density-based mineral concentration methods could be used for concentrating REE and the recoveries could be increased by decreasing particle sizes. The Pennsylvania State University team [21] evaluated float-sink, magnetic and electrostatic separation methods for the enrichment of REE from coal and coal by-products including roof rock, pit cleanings and coal refuse samples. They found that the roof rock samples showed a best response to gravity separation, while the pit cleaning sample and one of the refuse samples responded best to magnetic separation and electrostatic separation, respectively. From these findings obtained by different research groups, it can be concluded that different REE feedstocks respond to physical separation methods differently. Furthermore, there are some disagreements among these studies that need to be further addressed.

The work reported here is part of the REE from Coal and Coal By-Products R&D Program, an NETL initiative aiming to address the current global REE separations market and process economics and to demonstrate the techno-economic feasibility of U.S. domestic REE separation technologies [22]. This work was focused on examining the technical feasibility of physical

separation techniques including particle size, magnetic and density separations for the enrichment of REE from coal, coal ash, clay and shale.

2. Experimental

2.1 Materials

Hundreds of coal and coal by-product field samples have been collected and analyzed at NETL. Detailed information on these samples is available elsewhere [23]. Seven representative samples were selected from them and studied in this work. They include one clean coal sample (240) from a coal preparation plant, four coal ash samples (251, 339, 345 and 357) from coal power plants and two coal mining by-product samples (clay S1 and shale S2) from coal mining sites. A detailed description of the samples is provided in **Table 1**. All samples except fly ash samples 251 and 345 were ground prior to physical separations. Particle size and density separations were performed on all samples, while magnetic separation was performed on ash samples only because the coal and coal mining by-product samples are essentially non-magnetic. Lithium metatungstate (Geoliquid, Inc., Illinois, USA) was used as a separation medium in the float-sink separation experiments. It contains by volume 79.2% lithium metatungstate and 20.8% water and has a density of 2.95 g/ml, as provided by the supplier.

2.2 Physical Separations

Physical separation methods employed in this work for the enrichment of REE from coal and coal by-products include particle size, magnetic and density separations. A brief description of the methods follows.

Particle size separation of coal and coal by-products was performed using a Gilson Performer III 3-inch sieve shaker equipped with an electromagnetic vibrator. The shaker is capable of

separating particles down to 20 μm using a 635 mesh sieve. A combination of 5-7 Sieves of desired mesh sizes (100, 200, 270, 325, 400, 500 and 625 mesh or 150, 75, 53, 45, 38, 25 and 20 μm) were selected and installed, and known amounts of dry samples (typically 10-30 g) were loaded onto the top sieve. The sieving operation generally lasted 30-90 min depending on particle size and the amount of sample loaded. After separation, samples were collected and weighed.

Magnetic separation of coal and coal by-products was carried out using a simple setup as shown in **Figure 1**. An electromagnet was secured and attached to a metal stand and placed above an adjustable lab jack. Samples were loaded on a white paper placed on the lab jack. The magnetic field strength was manually adjusted by changing the distance between the lab jack surface and the magnet surface as indicated by “h” in the figure. The magnetic field strength applied to samples increases as the “h” value decreases. The “h” values used in this work were 2.0, 1.5, 1.0, 0.5 and 0.3 cm, and the corresponding magnetically-separated samples were denoted by mag-1 (2.0 cm), mag-2 (1.5 cm), mag-3 (1.0 cm), mag-4 (0.5 cm), mag-5 (0.3 cm) and non-mag.

Density separation of coal and coal by-products was done using the traditional float-sink method as follows. Lithium metatungstate was used as a separation medium. Known amounts of samples were placed in 50-ml plastic centrifuge tubes and then 40 ml lithium metatungstate was added to each tube. The tubes were shaken by hand to ensure thorough dispersion of sample particles in the heavy liquid. Samples were then centrifuged to achieve complete float-sink separation. Heavier solids on bottom of the tubes were carefully transferred to new 50-ml centrifuge tubes using disposable Pasteur pipettes. Deionized water was added to the remaining samples to adjust the liquid density to a next lower level. This procedure was repeated to obtain

several different density fractions. Density-fractioned samples were washed with deionized water and centrifuged at least three times to minimize lithium metatungstate residue in the samples. Finally, samples were dried at 120 °C overnight prior to weighing, elemental analysis and characterization.

2.3 Analytical Methods

2.3.1 Elemental Analysis

Major, minor, and trace element concentrations were measured in the dried solid samples in order to quantify the REE enrichment that occurred after each physical separation step. Samples were dried at 107°C under N₂ for 2 hours and then ashed at 550°C for 4 hours under air. Drying and ashing was typically completed in a LECO thermogravimetric analyzer (TGA). Occasionally, the sample size was too small for the TGA (< 0.5 g). Those samples were dried and ashed in a muffle furnace using the same conditions. Approximately 50 mg of ashed sample was mixed in a platinum crucible with 400 mg of lithium metaborate (LiBO₂) and fused at 1100°C for 5 minutes in a microwave fusion oven. The fused glass was then digested in 5% HNO₃ with low heat and stirring. The platinum crucibles were rinsed in triplicate with 5% HNO₃ and diluted to a final volume of 100 ml to ensure a complete digestion of the fused glass. For quality control and quality assurance, certified reference solids that most closely matched the starting material were processed along with each batch of samples. These standards included coal standard reference material NIST 1632a, and coal fly ash NIST 1633b, USGS Brush Creek Shale (SBC-1), Cody Shale (SCO-1) and rare earth ore (REE-1) from Natural Resources Canada. Element concentrations were measured by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) operated in kinetic energy discrimination mode. . The precision and accuracy of the ICP-MS

technique and the drawbacks and limitation of this method were discussed elsewhere [24]. Based on duplicate sample measurements precision can be generalized as less than 10% relative standard deviation for most major elements and metals and less than 5% for rare earth elements except Sc. Based on recovery of standard reference materials the accuracy is expected to be $\pm 20\%$. Carbon and sulfur concentrations were determined on the dried but unashed solid using a 2400 CHNS/O Series II Elemental Analyzer (Perkin Elmer).

2.3.2 XRD and SEM

Powder X-ray diffraction (XRD) analysis of the bulk mineral composition of the samples was carried out using a PANalytical X'Pert PRO diffractometer equipped with a Cu anode operated at 45 kV and 40 mA. Phase identification was verified by comparison to the International Centre for Diffraction Data (ICDD) inorganic compound data base. Scanning electron microscopy/energy dispersive x-ray analysis (SEM/EDS) of select samples was carried out using an FEI Company Quanta 600 field emission scanning electron microscope operated at 20kV at a working distance of 10 mm. The SEM was equipped with secondary and backscatter electron detectors and an Oxford Inca Energy 350 X-act energy dispersive x-ray analyzer (EDS) to investigate minor minerals not observed by XRD and to determine mineral associations and crystal size distribution. Samples were not coated so were analyzed in low vacuum mode to avoid charging. A backscattered electron detector was used so that elemental contrast could be used to more easily locate the minerals of interest.

3. Results and Discussion

3.1 Raw material characteristics

Physical and chemical characteristics of the raw materials were analyzed by TGA, ICP-MS, and other methods as described in section 2.3.1. Moisture contents, dry ash yields, major, minor and trace element contents of the samples are listed in **Table 2**. It should be noted that the as-received field samples with the exception of fly ash sample 345 and clay sample S1 have higher moisture contents than listed in **Table 2**. These samples were dried overnight at 120 °C for easy grinding and processing. The ash yields vary significantly depending on the type of samples. The coal combustion products contain 95-98 % dry ash except sample 251 which contains 85%. The dry ash yields of both clay and shale samples are almost the same at about 93%. The coal sample has much lower mineral content resulting in only 7.8% dry ash.

The dry-ash-basis REE concentration (hereafter referred to as the total concentration of lanthanides) vary significantly among samples. The coal sample has the highest ash-basis REE concentration of 1658 ppm. The REE concentrations of the coal ash samples vary from 312 to 623 ppm with sample 251 having the maximum. The shale and clay samples have REE concentrations of 296 and 414 ppm, respectively. The LREE (La, Ce, Pr, Nd, Sm, Eu and Gd) to HREE (Tb, Dy, Ho, Er, Tm, Yb and Lu) ratios are in the range of 8.1 -9.5 except for the clay sample S1 which has an LREE/HREE ratio of 15.9. The outlook coefficient C_{outl} defined by Eq (1) varies from 0.7-1.2 for all samples. This index is an indication of the quality of REY ores [9]. According to Dai et al. [25], REY sources with $0.7 \leq C_{outl} \leq 1.9$ are promising. Taking into consideration of both the C_{outl} value and the cut-off grade discussed earlier, coal 240 and fly ash 251 are the promising alternative sources for the REY recovery. The rest of the samples do not reach the cut-off grade and thus are considered to be unpromising.

$$C_{outl} = \frac{(Nd + Eu + Tb + Dy + Er + Y)/\sum REY}{(Ce + Ho + Tm + Yb + Lu)/\sum REY} \quad (1)$$

The starting materials were analyzed by XRD to determine the primary crystalline mineral compositions of the matrix. The results are listed in **Table 3** along with a qualitative estimate of the relative amount of each identified mineral [based on relative peak intensities](#). As expected, the compositions fall in three general categories; clay and shale containing quartz, kaolinite and muscovite/illite; ashes containing quartz, mullite, iron oxides and a large amount of amorphous silica-rich glassy material; and coal containing quartz, kaolinite, muscovite/illite and a large amount of amorphous carbon-rich material. Diffraction patterns for these materials are shown in **Figure 2** with the primary diffraction peaks of the major crystalline components labeled.

SEM/EDS was used to examine the particle morphologies and attempt to identify minor minerals of interest in a representative sample from each sample category. The samples examined were ash 251 (as received), shale S2 (ground) and the clean coal sample 240 (as received). Backscattered electron imaging was used to more easily locate REE-containing minerals as well as other heavy element-containing minerals. Secondary electron imaging was used to determine the mineral matrix morphology.

The ash sample 251 had a particle size distribution and morphology typical of a fly ash. It contained a wide range of particle sizes from around 150 μm to smaller than 1 μm and particle morphologies from jagged and irregular to smooth and spherical. The RE minerals monazite and xenotime were identified based on EDS. Monazite appears much more prevalent than xenotime. In addition, the RE minerals were commonly but not always embedded in the glassy ash matrix as can be observed by comparing backscattered versus secondary electron images of the same particle (**Figure 3A**).

The shale sample S2 had been ground and sieved prior to examination. The minus 100 mesh (-150 μm) fraction was examined so, as would be predicted, the particles were all smaller than

150 μm and ranged to smaller than 1 μm . Most particles consisted of agglomerates of smaller individual mineral particles. Monazite was the only RE mineral identified in this screening (**Figure 3B**). Pyrite was the most prevalent heavy mineral observed in this shale. Other minerals observed include zircon and barite.

The coal sample 240 consisted of large coal particles up to nearly 500 μm with smaller coal and mineral particles intermixed. Monazite was the only RE mineral identified in this sample (**Figure 3C**). Other heavy minerals observed include pyrite, gypsum and barite.

3.2 Particle size separation

REE concentrations of particle-size-fractioned samples are plotted in **Figure 4** along with the weight percentage of each particle size fraction. For the two fly ash samples (251 and 345), more than 97 wt% of the ash particles are smaller than 150 μm and more than 60 wt% are smaller than 45 μm , as shown in **Figure 4A&B**. The particle size distributions of both fly ash samples are very similar and show a distinct peak at 38-25 μm , although the 25-20 μm fraction was not separated for the fly ash 345. This characteristic peak is also observed for the other two ash samples (339 and 357) containing both fly ash and bottom ash (**Figure 4C&D**). This result suggests that regardless of their sources, fly ash samples have a very similar particle size distribution, which may further imply the same fly ash formation mechanism during coal combustion.

All samples except fly ash samples 251 and 345 were manually ground using a mortar and pestle prior to physical separations. The grinding procedure resulted in very similar particle size distribution for the resulting samples. For the two ash mixture samples (339 and 357), the majority of >45 μm fraction consisted of ground bottom ash particles and the <45 μm fraction

consisted primarily of the fly ashpart as indicated by the 38-25 μm peak (**Figure 4C&D**). The percentage of particle-size-fractioned ground bottom ash decreases as the particle size decreases. For the coal, clay and shale samples, as shown in **Figure 4E-G**, the weight percentage of particle-size-fractioned samples increases from the first to the second fraction and then decreases. This particle size distribution pattern indicates that the grinding process applied in this work may be unable to effectively release RE minerals from the matrix as the particle size of the RE mineral particles are typicallymuch smaller based on SEM observation.

Despite some variations, the REE concentrations in particle-size-fractioned fly ash samples generally increase as the particle size decreases (**Figure 4A&B**), showing moderate enrichment of REE in the smaller ash particles. This result is in good agreement with previous findings [14-17]. Although samples 339 and 357 are mixtures of fly ash and bottom ash and the REE concentration of each of these components was not independently determined, the analyses of thesamples suggest that the REE concentrations of fly ashmay be higher than those of bottom ash from the same coal combustion process (**Figure 4C&D**), though the measured REE concentrations are not statistically different. The REE concentration of particle-size-fractioned clean coal generally decrease as the particle size decreases except for the 45-38 μm fraction which has the highest REE concentration (**Figure 4G**). For the clay andshale samples, the REE concentration generally decreases as the particle size decreases, despite some small fluctuations (**Figure 4E&F**), which indicates that grinding preferentially created smaller particles from non-REE components andRE minerals were not effectively mobilized. If grinding did effectively release small REE-containing mineral particles from the hosting matrix, the REE concentration in the smallest particle size fraction would be expected to be higher than or at least the same as that in the feed depending on the effectiveness of grinding of non-REE components.

3.3 Magnetic separation

Magnetic separation was performed only on the coal ash samples as preliminary tests indicated that the coal, clay and shale samples are essentially non-magnetic. Fly ash 345 was tested first and separated into six fractions. The ICP-MS analysis showed that the REE concentrations of the mag-1, mag-2 and mag-3 fractions are significantly lower than those of the mag-4, mag-5 and non-mag fractions. Therefore, mag-1 and mag-2 fractions were not separated for the rest of coal ash samples, and only four fractions were obtained for them: mag-3 (containing mag-1 and mag-2), mag-4, mag-5 and non-mag. The REE concentrations and weight recoveries of magnetically-separated coal ash samples are plotted in **Figure 5** showing that the REE concentrations of magnetically-separated fractions increase as the magnetic susceptibility decreases from mag-1 to non-mag fractions and the non-mag fraction has the highest REE concentrations for all samples. The REE concentrations of mag-4 and mag-5 fractions are very similar except for fly ash 251, in which the mag-4 fraction contains a much lower REE concentration. Fly ash 251 is also different from others in terms of the mass distribution of magnetically-separated fractions. It contains more than 95wt% non-magnetic ash while the other three contain less than 50wt%. The iron contents of magnetically-separated ash samples are plotted in **Figure 6** showing, as expected, a decrease in iron concentration from mag-1 to non-mag fractions. All these results suggest that REE are enriched in the non-magnetic fraction and likely associated with non-iron minerals. This result agrees well with the previous finding reported by Dai et al. [14] on separation of fly ash samples but shows a disagreement with the work by Honaker et al. [18] where higher REE concentrations were found in the magnetic fractions of coal and coal mining by-products. One explanation is that Honaker et al. [18] used

pre-combustion materials. Monazite might have been liberated from these materials and separated using Wet High Intensity Magnetic Separation, leading to higher REE concentrations in the magnetic fractions. Another possibility is that the differing magnetic field intensities used in each study caused different magnetic properties of the resulting magnetic and non-magnetic fractions. Additional research is required to address this issue.

3.4 Density separation

The fact that different minerals have different densities forms the foundation for density-based separation. Typical minerals in coal and coal by-products reported in literature [15, 26, 27] and observed by SEM/EDS in this work are shown in **Table 4** along with their chemical formulas and density ranges [28]. The densities of three common RE minerals, monazite, bastnasite and xenotime, are in the range of 3.9-5.5 g/ml. It was thus anticipated that RE minerals would concentrate in the heaviest fraction (>2.95 g/ml) because their densities are greater than that of the heavy liquid used in the experiment.

Figure 7A-D shows REE concentrations and weight percentages of density-fractionated ash samples. The REE concentrations of fly ash samples 251 and 345 reach maximum values in the density ranges of 2.95-2.71 g/ml and 2.71-2.45 g/ml, respectively, while those of the other two ash mixtures reach maximum values at the same density range of 2.71-2.49 g/ml. As the density of ash particles decreases, for ash samples 251 and 357, the REE concentrations increase to maximum values and then decrease, while for ash samples 339 and 345, they similarly increase, reach maximums, and then decrease, but finally they increase slightly again. This result disagrees with the hypothesis that REE would be enriched in the heaviest fraction and suggests that RE minerals are associated with other lower density minerals and embedded in fly ash particles.

Previous studies have also indicated that REE are disbursed throughout the entire glassy fly ash particles [29]. As a result, RE minerals are diluted by lower-density components and the density of particles containing REE are reduced and thus density separation becomes less effective than would be predicted. To improve the effectiveness of this method, grinding is necessary to reduce particle size and release RE minerals from their ash particle matrix, which, however, would require a substantial increase in energy consumption. In addition, the ICP-MS analysis (**Table 5**) shows that the >2.71 g/ml fractions of all ash samples contain significant amounts of iron. These iron-containing minerals are mainly hematite and magnetite, as confirmed by the XRD analysis (**Table 3**). Consequently, the REE concentrations of these heavier fractions are diluted by the iron-containing minerals. Since these iron-containing minerals are magnetic, removal of these minerals by simple magnetic separation would further increase REE concentration. Finally, different mineral compositions of these ash samples, as indicated by different mass distributions of density-fractionated ash samples, suggest that these combustion products might have been derived from different coal sources.

Figure 7E&F shows the results for density separation of the clay and shale samples. The majority (98wt%) of the clay S1 is within the narrow density range of 2.56-2.62 g/ml (**Figure 7E**) indicating that this clay sample is mainly composed of quartz which has a density of 2.59-2.63 g/ml (**Table 4**). This result agrees with the ICP-MS analysis (**Table 5**) which shows that the 2.56-2.62 g/ml fraction of the clay S1 contains 33% of Si, higher than all other fractions. It is further confirmed by the XRD analysis (**Table 3**) that the major component of this clay sample is quartz. The XRD analysis also shows intermediate amounts of kaolinite and muscovite which have a density of 2.61-2.68 g/ml and 2.77-2.88 g/ml, respectively. However, the significant less amounts of >2.62 g/ml fractions suggest that these dense REE-bearing minerals are embedded in

the quartz matrix. The REE concentration of the clay S1 decreases as density decreases, with the highest of 1340 ppm found in the 2.71-2.95 g/ml fraction. Different to the clay S1, the shale S2 contains fractions with a broader density range from 2.95-2.49 g/ml (**Figure 7F**), which is an indication that this shale sample contains significant amounts of minerals other than quartz. This is also confirmed by the XRD analysis (**Table 3**) showing that in addition to the major component quartz, it also contains intermediate amounts of kaolinite and muscovite and minor amounts of gypsum (2.31 g/ml) and pyrite (5.01 g/ml). The highest REE concentration of the shale S2 was 412 ppm obtained from the 2.95-2.71 g/ml fraction. The REE concentrations of the >2.95 g/ml fraction is much less than that of the second heaviest fraction, which, as discussed above, is an indication that RE minerals were not effectively released from the rock matrix by the grinding method used in this study. In addition, the REE concentrations generally decrease as density decreases which indicates that there is potential for improvement in the density concentration of the RE minerals.

Figure 7G&H shows the results for density separation of the clean coal sample. The clean coal contains only 7.8 wt% dry ash (**Table 2**), and as expected, the density is much lower than coal ash, clay and shale samples. As the density drops from >1.45 g/ml to 1.34-1.30 g/ml, the ash yield reduces dramatically from 49% to 4% and the dry ash-basis REE concentration increases significantly from 1143 ppm to 2056 ppm. As the density drops further, the ash yield remains stable at 3-5% and the REE concentration reduces slightly with some fluctuations. The highest REE concentration (dry ash basis), 2056 ppm, was obtained from the 1.34-1.30 g/ml fraction which makes up 30% of the coal. **Figure 7H** also shows a strong correlation between the REE concentration and the ash yield. The dry ash-basis REE concentration generally decreases as the

ash yield increases, which can be explained by the dilution effect of non-RE minerals. The whole coal-basis REE concentration, however, increases as the ash yield increases.

3.5 Enrichment factors and LREE/HREE distribution

We have observed the enrichment of REE from coal and coal by-products by physical separations from the above discussion. To further quantitatively characterize REE enrichment by each separation method, we define an enrichment factor (EF) by dividing the total REE concentration in the physically-separated fraction by that in the feed, as given by Eq (2). The total REE concentration in the feed was obtained through mass balance calculation to minimize the influence caused by sample inhomogeneity.

$$EF_i = \frac{REE_i}{\sum_{i=1}^n (REE_i W_i)} \quad (2)$$

Where REE_i is the total REE concentration of the i^{th} fraction, W_i is the weight percentage of the i^{th} fraction, and n is the total number of fractions. The maximum EF values for each sample by each method are presented in **Table 6** along with the corresponding REE recoveries. The REE recovery (R) is defined by the ratio of the amount of total REE in a given fraction to the amount of total REE in the feed, as follows:

$$R_i(\%) = \frac{REE_i W_i}{\sum_{i=1}^n (REE_i W_i)} \times 100 \quad (3)$$

The results indicate that density separation has an overall better performance than particle size and magnetic separations. The maximum enrichment factors obtained for the particle size and magnetic separations are 1.19 and 1.16, respectively, both for the ash sample 339, while that of the density separation reaches 3.58 for the clay sample S1. Increased enrichment factors are anticipated through a combination of these physical separation methods. Additional research is ongoing to address this issue and results will be reported in future publications.

REE are often described as being a LREE or HREE. In this discussion, the LREE and HREE are defined as the groups of elements of lanthanide through gadolinium (La-Gd) and terbium through lutetium (Tb-Lu), respectively, based on the electron configuration of each REE. The LREE/HREE ratios of particle size, magnetic and density separated coal, coal ash, clay and shalesamples are presented in **Figure 8**. It was found that the LREE/HREE ratios of ash, clay and shalesamples generally decrease as the particle size decreases(**Figure 8A&C**) and the lowest LREE/HREE ratios are found in the finest fractions. This result disagrees with a previous study by Hower et al. [16] where the highest LREE/HREE ratio was found in the finest fraction. For fly ash 251 (**Figure 8A**), this ratio drops as the particle size increases from 75 μm to above 150 μm . This is because the larger particles contain mainly magneticfractions and the LREE/HREE ratios of magnetic fractions are much lower than those of the non-magnetic fractions, as shown in **Figure 8D&E**. The LREE/HREE ratio of the clean coal sample remains nearly constant over the entire particle size spectrum (**Figure 8B**). The LREE/HREE ratios for all density fractioned samples generally reduce to minimum values and then increase as the densities of the samples decrease, as shown in **Figure 8F-I**. This parameter is directly related to REE concentrations, andas illustrated in **Figure 9**, it varies with REE concentrationdepending on the separation method used. Particularly for the clean coal sample (**Figure 9G**), it increases significantly asthe ash-basis REE concentrationdecreases. However, on the whole coal basis, it drops significantly as the REE concentrationreduces. It can be concluded that the LREE and HREE do not contribute equally to the enrichment of REE by physical separations. The LREE contribute more than the HREE towards the enrichment. In addition, compared with the LREE, the HREE favor finest particles and magnetic fractions. One possible explanation of this observation is that althoughREE macroscopically tend to occur in the same minerals, the chemical composition of

individual RE mineral grain varies. This leads to unequal distributions of LREE and HREE across RE minerals and thus the unequal enrichment of LREE and HREE in physically-separated coal and coal by-product samples. Additional research is necessary to address these issues.

3.6 Elemental correlations

In addition to REE, major ($>0.1\%$), minor (100ppm-0.1%) and trace ($<100\text{ppm}$) elements were also analyzed for all 146 original and physically-separated samples. The data provide useful information on not only the concentration levels of these elements but also the correlations between them. The Pearson product-moment correlation coefficient [26] is applied here to characterize the correlations between elements. Results are plotted in **Figure 10**. According to their correlations, elements can be classified under three groups. The first group includes Al, Si, Ti, K, Na, V, REE, Nb, Ga, Th and U. As Al and Si dominate this group, the major minerals may include quartz, kaolinite, muscovite, illite, mullite, as observed by XRD (**Table 3**), and some other aluminosilicates. REE are strongly associated with this group. The second group includes Fe, Mn, Ni and Co. The elements of this group have negative correlations with the elements in the first group, indicating that they belong to different minerals. The major minerals in this group may include pyrite, hematite, magnetite (**Table 3**) and other magnetic minerals. REE have weak positive or negative correlations with elements in this group. This result agrees well with the observation from magnetic separation that REE are enriched in non-magnetic fractions containing less amounts of iron. The major element, Ca, has a negative correlation with Al and a weak positive correlation with Fe, and therefore it forms the third group. This group may also include Ge, Mg, Mo and Zn, which have relatively strong positive correlations with Ca. The major minerals of this group may include gypsum and calcite, as showed by the XRD analysis

(**Table 3**). REE also have negative correlations with this group. The above classification of elements agrees well with a previous study on mineralogy and geochemistry of coals by Moore and Esmaeili except that they classified Ni as an additional group resulting in a total of four groups [26]. Furthermore, the well-known strong correlation between REE and This also observed. In addition, REE also have relatively strong correlations with U, Hf, Sb, Cd, Nb, Zr, Ga, Ag, Cu, Cr, V and Be, as shown in **Figure 10**.

4. Conclusions

Physical separations including particle size, magnetic and density separations were performed on seven coal and coal by-product samples to investigate the enrichment of REE in these samples by these physical separation methods. The samples studied include one clean coal, two fly ash samples, two fly ash and bottom ash mixtures, one clay sample and one shale samples. It was found that the samples responded to particle size separation differently. For all ash samples, higher REE concentrations were found in the finer fractions. For the clay and shale samples, however, the REE concentrations decrease as the particle size decreases. One possible explanation is that RE minerals were not effectively released from the matrix by grinding because RE minerals are usually much smaller than the final particle size obtained in this work. Magnetic separation showed that REE are enriched in non-magnetic fractions for all ash samples. All samples responded similarly to density separation. The densities of RE minerals are higher than that of the heavy liquid used in this work. They were thus expected to be concentrated in the highest density fractions. However, the highest REE concentrations were not found in the highest density fractions. This is another indication that RE minerals are trapped in other minerals and not effectively released. Improved enrichment of REE would require

substantial grinding to mobilize RE minerals from coal and coal by-products. Among the three methods, density separation showed the highest enrichment of REE, which was obtained with the clay sample S1. The REE were enriched by a factor of 3.58 to 1341 ppm. The combination of these methods would be beneficial to improve REE separation. However, different combinations would be needed for the different material types. Research is ongoing at NETL to improve this methodology. Finally, correlations between elements were demonstrated, which leads to the classification of these elements into three groups. The strong positive correlation between REE and Al indicates that REE in coal and coal by-products are likely associated with the Al/Si group.

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Alternative Resources

Physical
Separations

REE Enrichment

Figure 1. A photograph of the magnetic separation unit. The letter “h” indicates the distance between the magnet and the sample loading surface.

Figure 2. XRD analysis of ash (A), coal, clay and shale samples (B)

Figure 3. SEM/EDS images of ash 251 (A), shale S2 (B) and coal 240 (C). The bright areas indicated by the white arrows are monazite minerals.

Figure 4. REE concentrations and weight percentages of particle-size-fractionated coal, ash, clay and shale samples. FA : fly ash; BA: bottom ash.

Figure 5. REE concentrations and weight percentages of magnetically-separated coal ash samples. FA: fly ash, BA: bottom ash.

Figure 6. Iron concentrations of magnetically-separated coal ash samples.

Figure 7. REE concentrations and weight percentages of density-fractionated ash (A-D), clay (E), shale (F) and coal (G&H) samples. FA: fly ash, BA: bottom ash.

Figure 8. LREE/HREE ratios of physically-separated clay, ash and coal samples. FA: fly ash, BA: bottom ash.

Figure 9. Correlations between LREE/HREE ratios and REE concentrations of ash, clay, shale and coal samples. FA: fly ash, BA: bottom ash.

Pearson Product-Moment Correlation Coefficients

Figure 10. Pearson product-moment correlation coefficients between elements.

Table 1.A description of coal and coal by-product samples studied in this work

Sample ID	Description
240	Clean coal sample collected from a coal preparation plant in Kentucky, USA. The coal was originally from the central Appalachian basin coal region.
251	Fly ash collected from an ash disposal site at a power plant in Kentucky, USA. Ponded fly ash. Landfill fly ash. Feed coal was originally from the central Appalachian basin coal region.
339	Ash pond sample containing mostly fly ash with lesser amount of bottom ash. Collected from a pulverized coal power plant in Ohio, USA. Coal seams unidentified.
345	Dry fly ash collected from a pulverized coal power plant in Ohio, USA. Coal seams unidentified.
357	Dry ash pond sample containing mostly bottom ash with lesser amount of fly ash. Collected from a pulverized coal power plant in Ohio, USA. Coal seams unidentified.
S1	Clay sample collected from a clay pile in a coal mining site in Clearfield County, Pennsylvania, USA.
S2	Shale sample collected from the Redstone floor in a coal mining site in Monongalia County, West Virginia, USA.

Table 2 Characteristics of coal, coal ash, clay and shale samples

Sample ID	240	251	345	339	357	S1	S2
Moisture (%)	1.36	0.36	0.28	0.22	0.04	1.43	0.79
Ash Yield (% dry basis)	7.80	84.95	97.15	95.85	98.34	92.60	93.09
Be	59	16	142	9	BDL	BDL	BDL
Na	3485	2364	4003	3785	2817	1122	884
Mg	3535	5422	4509	4723	4777	2503	4206
Al	203790	112112	157321	113596	147470	157595	102878
Si	284430	274087	285408	270463	228665	245488	320062
P	1218	BDL	BDL	1057	BDL	611	BDL
K	13944	17428	18540	16586	12786	22075	20295
Ca	15107	9902	36613	21767	22966	1199	16328
Sc	123	83	108	86	89	74	83
Ti	13304	8325	7943	7043	5662	10368	5863
V	424	246	328	385	258	182	108
Cr	212	156	204	192	138	150	107
Mn	172	154	399	384	420	19	135
Fe	29421	31559	158558	144108	186456	14404	31034
Co	65	54	51	47	36	5	24
Ni	131	101	172	146	121	35	70
Cu	221	177	92	97	74	BDL	86
Zn	146	86	211	298	145	17	167
Ga	167	112	67	67	46	62	45
Ge	45	18	63	47	25	3	BDL
As	37	60	106	59	12	22	51
Se	12	BDL	BDL	BDL	BDL	BDL	10
Y	336	132	95	66	70	44	62
Zr	1175	272	302	262	210	324	188
Nb	75	29	29	25	20	29	19
Mo	15	4	48	43	13	BDL	4
Ag	5	2	2	2	BDL	2	BDL
Cd	29	7	6	8	6	8	4
Sn	15	8	14	5	9	25	7
Sb	16	6	10	6	3	1	3
Ba	1202	1400	418	551	534	486	511
La	319	115	87	57	69	93	47
Ce	662	246	184	124	142	178	112
Pr	79	29	22	14	18	20	14
Nd	300	113	85	58	72	71	59
Sm	62	24	18	11	15	13	14
Eu	7	4	4	3	3	3	3
Gd	62	25	20	12	15	11	15
Tb	10	4	3	2	2	2	2
Dy	63	26	17	13	14	9	14
Ho	12	5	3	2	3	2	3
Er	36	14	10	7	8	5	7
Tm	5	2	1	1	1	1	1
Yb	34	13	8	7	7	5	5
Lu	5	2	1	1	1	1	1
Hf	29	10	8	7	6	9	7
Tl	2	2	BDL	4	BDL	1	BDL
Pb	137	92	34	114	19	43	26
Th	105	42	23	19	20	24	23
U	43	17	13	27	18	6	7
REE	1658	623	463	312	371	414	296
REY	1994	754	558	378	441	457	358
REE/Th	15.8	14.8	19.8	16.4	18.3	17.5	12.9
LREE/HREE	9.0	8.5	9.5	8.7	9.3	15.9	8.1
C _{out}	1.0	1.1	1.1	1.1	1.1	0.7	1.2

BDL: below detection limit. Unit: ppm. REE: summation of lanthanides. REY: lanthanides + yttrium.

Table 3XRD analysis results. Approximate magnitudes of phases estimated.

Sample ID	Description	Quartz	Amorphous /glass	Hematite	Mullite	Magnetite		
251	Ash	Major	Major	Trace	Intermediate			
339	Ash	Major	Major	Intermediate	Intermediate	Intermediate		
345	Ash	Major	Major	Intermediate	Intermediate	Intermediate		
357	Ash	Major	Major	Intermediate	Intermediate	Intermediate		
Sample ID	Description	Quartz	Kaolinite	Muscovite /Illite	Pyrite	Gypsum	Calcite	Carbon/ amorphous
240	Coal	Major	Minor	Trace				Major
S1	Shale	Major	Intermediate	Intermediate				
S2	Shale	Major	Intermediate	Intermediate	Minor	Minor	Trace	

Table 4 Chemical formula and density of typical minerals found in coal and coal by-products [27]

Mineral	Chemical Formula	Density (g/ml)
Albite	$\text{Na}_{1.0-0.9}\text{Ca}_{0.0-0.1}\text{Al}_{1.0-1.1}\text{Si}_{3.0-2.9}\text{O}_8$	2.6-2.65
Bastnasite	$(\text{Ce}, \text{La})(\text{CO}_3)\text{F}$, $(\text{La}, \text{Ce})(\text{CO}_3)\text{F}$, $\text{Nd}(\text{CO}_3)\text{F}$, $\text{Y}(\text{CO}_3)\text{F}$	3.9-5.2
Biotite	$\text{K}(\text{Mg}, \text{Fe}^{2+})_3(\text{Al}, \text{Fe}^{3+})\text{Si}_3\text{O}_{10}(\text{OH}, \text{F})_2$	2.7-3.3
Calcite	CaCO_3	2.71
Gibbsite	$\text{Al}(\text{OH})_3$	2.40
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	2.31
Hematite	$\alpha\text{-Fe}_2\text{O}_3$	5.26
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	2.61-2.68
Magnetite	$\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$	5.18
Monazite	$(\text{Ce}, \text{La}, \text{Nd}, \text{Th})\text{PO}_4$	4.98-5.43
Mullite	$\text{Al}_6\text{Si}_2\text{O}_{13}$	3.11-3.26
Muscovite	$\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH}, \text{F})_2$	2.77-2.88
Orthoclase	KAlSi_3O_8	2.55-2.63
Pyrite	FeS_2	5.01
Quartz	SiO_2	2.59-2.63
Spinel	MgAl_2O_4	3.6-4.1
Tridymite	SiO_2	2.25-2.28
Xenotime	YPO_4	4.4-5.1

Table 5 Concentrations (ppm) of major elements of density-fractionated coal and coal by-products

Sample ID	Density Range (g/ml)	Na	Mg	Al	Si	K	Ca	Ti	Fe
251	>2.95	793	4,320	70,263	117,176	5,751	6,879	13,892	367,258
251	2.95-2.71	1,445	6,998	106,862	180,064	9,637	16,221	18,300	173,752
251	2.71-2.49	2,322	5,283	133,489	306,287	14,130	14,002	10,181	42,643
251	2.49-2.31	2,506	4,450	146,806	328,478	16,358	7,873	8,048	22,873
251	<2.31	1,844	3,534	121,069	244,681	14,427	4,331	6,092	12,687
339	>2.95	1,460	2,478	52,485	106,057	5,913	12,192	4,799	443,225
339	2.95-2.71	3,084	4,362	95,068	179,067	11,873	26,970	7,807	188,624
339	2.71-2.49	5,213	5,545	146,385	272,359	19,647	16,689	8,276	84,207
339	2.49-2.31	5,026	4,434	127,184	316,500	20,415	9,888	6,480	50,324
339	2.31-2.14	4,056	3,921	120,612	329,969	18,766	7,536	6,083	41,289
339	2.14-2.00	3,923	4,425	147,805	318,826	19,728	7,845	6,693	46,122
339	<2.00	4,212	4,760	159,929	314,916	21,362	6,706	6,761	40,377
345	>2.95	1,041	2,052	47,654	80,210	4,918	19,683	2,797	396,075
345	2.95-2.71	1,984	3,349	82,770	137,969	7,125	37,018	3,782	102,426
345	2.71-2.45	4,194	4,330	180,460	245,392	13,846	17,763	6,710	63,762
345	2.45-2.26	4,168	3,989	168,505	318,476	15,489	11,885	5,838	44,435
345	2.26-2.01	3,557	3,806	170,641	282,667	13,327	9,089	5,437	34,794
345	<2.01	3,757	4,578	204,515	312,378	16,318	9,511	5,917	37,998
357	>2.95	2,194	3,660	84,020	171,651	9,854	18,504	4,762	317,585
357	2.95-2.71	2,990	4,487	102,096	232,270	13,826	21,455	5,888	173,206
357	2.71-2.49	3,813	5,106	131,019	302,965	18,634	21,257	6,707	117,670
357	2.49-2.31	3,413	4,440	110,862	285,740	17,612	15,082	6,070	79,332
357	2.31-2.14	3,634	4,526	125,335	298,826	19,141	11,733	6,147	68,858
357	2.14-2.00	2,916	4,096	118,453	272,400	17,116	7,195	5,779	54,816
357	<2.00	1,501	1,933	58,701	127,557	7,854	2,698	2,651	20,236
S1	2.95-2.71	1,753	2,396	101,739	236,051	18,808	4,072	23,052	101,648
S1	2.71-2.62	1,133	2,461	115,424	297,720	19,992	1,772	13,291	52,028
S1	2.62-2.56	997	2,246	122,032	325,769	17,755	1,050	10,124	11,713
S1	<2.56	1,033	2,333	145,211	282,875	18,361	1,199	9,139	11,293
S2	>2.95	826	2,202	63,832	180,613	11,950	8,299	3,478	185,555
S2	2.95-2.71	1,310	3,363	83,151	226,154	18,340	15,597	11,503	110,155
S2	2.71-2.60	2,164	3,484	85,887	301,452	19,636	10,578	5,147	24,597
S2	2.60-2.55	1,575	4,136	105,460	363,889	20,735	9,167	5,031	16,857
S2	2.55-2.49	1,482	4,750	118,444	361,942	22,527	7,773	4,696	14,932
S2	<2.49	2,108	4,489	97,531	260,315	21,509	6,040	4,522	30,444
240	>1.45	3,238	3,601	176,857	352,827	17,842	1,955	7,444	43,544
240	1.45-1.39	2,468	2,878	179,126	327,749	14,681	2,363	10,309	26,959
240	1.39-1.34	2,560	3,081	176,739	279,251	14,575	4,128	11,590	26,519
240	1.34-1.30	3,363	3,765	202,723	314,286	15,446	11,337	18,291	32,001
240	1.30-1.26	2,078	2,402	114,536	173,053	7,027	11,107	10,711	22,008
240	1.26-1.21	2,844	3,129	160,198	253,857	9,456	14,295	14,966	27,615
240	1.21-1.17	2,334	2,453	141,006	218,047	7,775	9,933	12,382	21,307
240	<1.17	2,713	3,268	175,387	290,699	13,536	8,919	13,602	33,017

Table 6 Maximum REE enrichment factors and recoveries for physical separations of coal and coal by-products

Sample ID	Particle Size Separation		Magnetic Separation		Density Separation	
	EF_{max}	R (%)	EF_{max}	R (%)	EF_{max}	R (%)
240	1.12	8.24	n/a	n/a	1.21	40.68
251	1.05	36.85	1.01	96.19	2.14	3.49
339	1.19	20.15	1.16	40.79	1.18	24.70
345	1.04	13.14	1.13	49.79	1.27	37.15
357	1.05	20.61	1.15	55.18	1.25	30.29
S1	1.18	5.53	n/a	n/a	3.58	0.88
S2	1.05	34.49	n/a	n/a	1.71	13.74