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Trends in the Rare Earth Element Content of U.S.-Based Coal Combustion Fly Ashes

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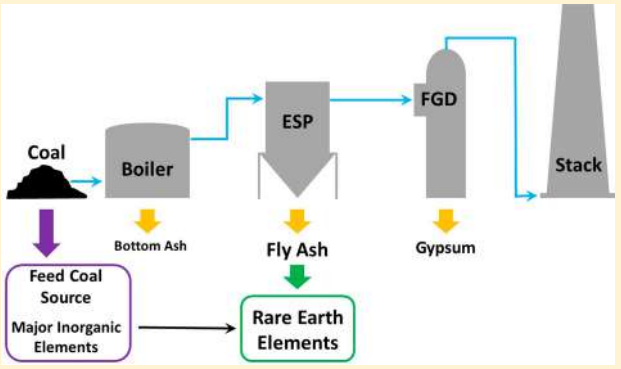
Supporting Information

ABSTRACT: Rare earth elements (REEs) are critical and strategic materials in the defense, energy, electronics, and automotive industries. The reclamation of REEs from coal combustion fly ash has been proposed as a way to supplement REE mining. However, the typical REE contents in coal fly ash, particularly in the United States, have not been comprehensively documented or compared among the major types of coal feedstocks that determine fly ash composition. The objective of this study was to characterize a broad selection of U.S. fly ashes of varied geological origin in order to rank their potential for REE recovery. The total and nitric acid-extractable REE content for more than 100 ash samples were correlated with characteristics such as the major element content and coal basin to elucidate trends in REE enrichment. Average total REE content (defined as the sum of the lanthanides, yttrium, and scandium) for ashes derived from Appalachian sources was 591 mg kg^{-1} and significantly greater than in ashes from Illinois and Powder River basin coals (403 and 337 mg kg^{-1}, respectively). The fraction of critical REEs (Nd, Eu, Tb, Dy, Y, and Er) in the fly ashes was 34−38% of the total and considerably higher than in conventional ores (typically less than 15%). Powder River Basin ashes had the highest extractable REE content, with 70% of the total REE recovered by heated nitric acid digestion. This is likely due to the higher calcium content of Powder River Basin ashes, which enhances their solubility in nitric acid. Sc, Nd, and Dy were the major contributors to the total REE value in fly ash, based on their contents and recent market prices. Overall, this study shows that coal fly ash production could provide a substantial domestic supply of REEs, but the feasibility of recovery depends on the development of extraction technologies that could be tailored to the major mineral content and origins of the feed coal for the ash.



INTRODUCTION

Coal combustion residues are a major economic and environmental burden in the United States due to their abundance and potential to leach toxic metals at disposal sites. However, coal ash has also been effectively reused for commercial purposes. A proposed application is to mine coal ash for rare earth elements (REEs), which are critical to the automotive, energy, electronics, and defense industries. REEs consist of the lanthanide series, yttrium, and scandium. ("Total REEs" refer to all 16 elements, herein, unless otherwise noted. Promethium is not included as it does not occur naturally.) REEs are relatively abundant elements with total REE average crustal content between 160 and 205 mg kg^{-1}.[1−4] However, REEs are not found in nature as pure metals and must be isolated from the host minerals, which do not often occur in easily exploitable deposits.[5−7] REEs also do not occur individually as mineral constituents due to their chemical similarity.[8] There are approximately 200 distinct rare earth minerals, but of these only bastnaesite, monazite, xenotime, and ion-adsorbed clays are mined for commercial REE production.[9] Currently, more than 86% of REE production, nearly half of known reserves, and the majority of REE processing and separation occur in China.[10] With this monopoly and recent instabilities in the REE global supply market, the United States government has outlined the need for alternative sources,[11] especially for critical elements such as Nd, Eu, Tb, Dy, Y, and Er.[12]

The U.S. generates more than one-third of its electricity from coal.[13] As a result, approximately 115 million metric tons (t) of coal combustion products (CCPs) are generated annually, and this sum includes 45 million t of fly ash. Only 45% of CCPs are reused for applications such as concrete and other construction materials.[14] The remainder is held in landfills or wet impoundments where the leaching of toxic trace elements (e.g., As, Se, Cr) is a concern for groundwater and surface water quality.[15−17] Ash impoundments are also susceptible to

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catastrophic failures, resulting in large ash spill events such as the Tennessee Valley Authority Kingston Fossil Plant in 2008 and the Duke Energy Dan River Steam Station in 2014.[16−18] The magnitude of these spills and the heavy economic and environmental costs associated with disposal have renewed efforts to find beneficial reuse opportunities that extend the value chain for coal ash.

The recovery of REEs from fly ash has several notable advantages over traditional REE ores. First, it is a readily available waste product with strong environmental incentives and an established market for beneficial reuse. Second, fly ash does not require extensive excavation, which is capital intensive and can be environmentally destructive. REE mines can generate large volumes of waste rock with high contents of uranium and thorium, a challenge with respect to radioactive wastes.[10,19,20] Finally, fly ash is a fine powder, which makes it ideal for chemical processing and eliminates several costly ore processing steps (although it does preclude most physical beneficiation of the ash).[21] There is already precedent for metal recovery from fly ash, including gallium, germanium, and aluminum.[22,23]

While there are potential advantages, the economic feasibility of REE recovery from coal ash is uncertain. This is due to a lack of information on the REE contents of the different types of coal ash produced across the U.S. and how ash characteristics are related to extractability of the REEs. The REE content of coal ash depends heavily on the geological origin of the feed coal.[24−26] Therefore, prioritization of ash sources for REE extraction requires an understanding of geochemical characteristics that are indicative of high REE content in fly ashes. Previous studies have shown that many coal deposits around the world contained high REE levels, and the respective ashes were also enriched in REEs.[19] For example, Seredin found REE contents of up to 1290 mg kg^{-1} in the Pavlovka coal deposit (Russian Far East), with up to 1% REE in the resulting ash.[19,27] Two studies of the Kentucky Fire Clay coal bed revealed REE contents between 1965 and 4198 mg kg^{-1} (ash basis) in coal samples and 1200 to 1670 mg kg^{-1} in fly ash from a power plant burning this coal source.[24,25] The Fire Clay Coal may not be typical, however, as the REE enrichment was largely due to a volcanic ash fall during the formation of the coal seam.[25] Recent surveys published by the U.S. Department of Energy indicated total REE contents (not including Sc) of 41 to 1286 mg kg^{-1} in U.S. coals.[28] While REEs have been reported in laboratory-produced ashes, the REE contents of fly ashes produced at power plants are not widely documented, particularly for utilities in the U.S.

This research aimed to expand previous findings through the analysis of REEs in fly ashes and other CCPs obtained from a broad survey of U.S. power plants. In addition to the total REE content (as determined by whole rock acid digestion), nitric acid-extractable REE content was measured as a means to gauge the accessibility of REEs in fly ash subjected to industrially-relevant leaching processes. Trends in total and extractable REE content of fly ashes were examined in relation to variations in coal origin, major element content, and collector row at each power plant. These data were used to identify possible strategies to leach REEs from the ash during recovery operations and understand the potential valuation of the fly ash with respect to the REE reserves.

MATERIALS AND METHODS

Coal Combustion Product Samples. CCP samples were collected in the time frame between 1994 and 2015 from 22 U.S. coal-fired power plants located in Kentucky (13 plants); Missouri (3); Texas (3); and individual plants located in South Carolina, Georgia, and New Mexico (Table S1). Fly ash samples were also obtained in 2015 from two power plants in South Africa. Fly ash samples were taken from multiple electrostatic precipitator (ESP) or baghouse rows for most of the power plants to track the fractionation of REEs in fly ash particles as they passed through the collection system. For many plants, ash samples were collected from multiple operational boilers. In addition, several plants were revisited for sampling over the years. The collection represented over 100 fly ash samples generated from feed coals from the Appalachian Basin (8 power plants), Illinois Basin (6), Powder River Basin coals (7), a 70/30 Illinois-Powder River blend (1), and one sample each from San Juan Basin and Gulf Coast coal sources. More than 20 samples of bottom ash, mechanical fly ash, silo ash, and ash from landfills and disposal ponds were obtained from a selection of the same power plants and were also analyzed for total REE and acid-extractable REE content.

Materials. Optima-grade acids and quartz-distilled water were used for HF acid digestion. Screw-cap Teflon vials (Savillex) and zirconium crucibles were used for two different types of total element digestions while 50 mL polypropylene digestion tubes (Environmental Express) were used for HNO_3 extractions. After the acid extraction procedures, all samples were stored in 50 mL polypropylene tubes and diluted using Milli-Q water (>18 MΩ-cm, EMD Millipore) and trace-grade hydrochloric acid (HCl) prior to analysis.

Chemical Analysis Methods. For total REE quantification, CCP samples (34 ± 1 mg) were digested overnight at 90−100 °C in a 1:1 mixture of concentrated HF and concentrated HNO_3 (2 mL each). The acidified samples were then dried down completely and redigested overnight at 90−100 °C in a mixture of 15 M HNO_3 (1 mL), H_2O_2 (1 mL; Optima-grade, 30−32%), and quartz-distilled water (5 mL). Following redigestion, the samples were diluted to 50 mL, and metal concentrations were determined via inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700x). Accuracy of the HF-HNO_3 extraction method was assessed using the National Institute of Standards and Technology (NIST) standard reference material (SRM) for fly ash, SRM 1633c.

Sodium peroxide (Na_2O_2) alkaline sintering (as described by the U.S. Geological Survey[29−31]) was employed as a second method for total REE quantification in CCP samples. Ash samples (0.1 g) were placed into zirconium crucibles, mixed with Na_2O_2 (0.6 g), and heated to 450 °C for 30 min. After cooling, the crucibles and their contents were submerged overnight in 20 mL of Milli-Q water. The next day, the crucibles were removed using forceps and carefully rinsed into the solution using 20 mL of 25% v/v HNO_3. Additional Milli-Q water was added to dilute the samples to 50 mL for storage and ICP-MS analysis.

Acid-extractable REE content was estimated using heated HNO_3 digestion. Ash samples (0.1−0.5 g) were digested in 10 mL of concentrated HNO_3 (~15 M) for 4 h at 85−90 °C. After digestion, samples were diluted for storage and ICP-MS analysis. Major element compositions in each sample (reported as percent oxides: SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O,

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P_2O_5, TiO_2, and SO_3) were determined by X-ray fluorescence (XRF).[24,32]

During ICP-MS analyses, the primary REE interferences were oxides of lighter elements (including other REE). The formation of these oxides in the plasma was monitored using the 156/140 mass ratio (CeO/Ce) as a proxy and kept below 2% for all ICP-MS runs. Common polyatomic interferences of other elements (e.g., As, Fe) were minimized by introducing helium to the collision cell. Doubly charged interferences (for Se) were counteracted using hydrogen as a reaction gas in the collision cell. Reportable lower limits of quantification for REE were in the single-digit parts-per-trillion range (we defined this as 10 times the instrument detection limit). For all analyses, measured REE values for the samples were generally an order of magnitude or more higher than the limit of quantification.

Statistical Analyses. Data analyses were performed using the statistical software R.[33] Nonparametric statistical tests were used because the data (as a whole and for each basin) were not normally distributed as determined by the Shapiro-Wilk test in R. An initial Kruskal–Wallis test was used to determine if grouping the samples by coal basin yields significant differences between groups (defined as $p < 0.05$) with respect to total REE content, the percentage as the critical REEs (Nd, Eu, Tb, Dy, Y, and Er), and the HNO_3-extractable REE (content and % of total) . If significant differences were found, Dunn's test was used for post hoc multiple comparisons to determine which basins differed and how. The Wilcoxon rank-sum test (Mann–Whitney U test) was used to test for significant differences between individual pairs of coal basins (defined as $p < 0.05$).

RESULTS

In the HF:HNO_3 digestion of the fly ash SRM, the recovery (n = 9 digestions) of individual REEs was between 89.2% and 102.4% (94.9% on average) for those REEs with reference and information mass fraction values (Sc, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, and Lu) (Figure S1). The alkaline sintering method had similarly high recoveries for REEs in the fly ash SRM (average recovery between 85.8% and 101.3% of SRM values for individual REE, 126.2% for Sc). However, for a subset of fly ash samples tested for this study, the sodium peroxide sinter method recovered only a fraction of the REE value determined by the HF digestion (Table S2). Therefore, all total REE values reported herein refer to the HF:HNO_3 digestions.

Total REE contents for all of the CCP samples in this study ranged from 200 to 1220 mg kg^{-1} with a median value of 481 mg kg^{-1} (Figure 1). Just over 40% of the samples exceeded 500 mg kg^{-1}. For most power plants in which multiple fly ash samples were taken, little difference was observed in the total REE content of fly ash collected on the same date from different ESP or baghouse rows of the same boiler unit (Figures S2 and S3). This relatively constant REE content with respect to ESP/baghouse row is consistent with findings from a previous study.[24] In contrast, the contents of other trace elements such as arsenic, selenium, lead, and gallium (which are known to be more volatile than REEs in coal combustion flue gas[24]) increased with ESP collector row (Figure S4).

With these observations, the total REE contents for samples from multiple rows were averaged to produce a single value to represent the fly ash generated by that boiler unit at the time of sampling. The data shown in Figure 1 correspond to these average values with the respective standard deviations (Note: several units were revisited over multiple periods.). These averaged content values were herein used for the statistical evaluations.

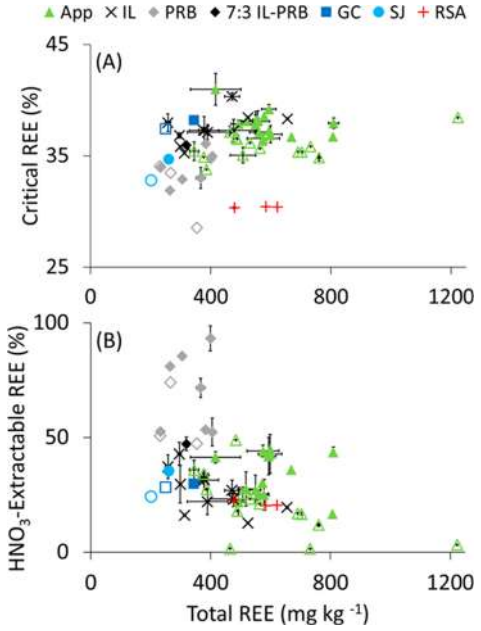

Figure 1. Percentage of the total REEs (including the lanthanides, yttrium, and scandium) in coal ash samples as (A) critical REEs (Nd, Eu, Tb, Dy, Y, and Er) and (B) the nitric acid-extractable REEs. Samples have been labeled according to the origin of the feed coal: Appalachian (App), Illinois Basin (IL), Power River Basin (PRB), Gulf Coast (GC), San Juan (SJ), and the Highveld/Witbank coalfields of South Africa (RSA). Closed symbols represent fly ash; open symbols are other types of CCPs (stoker ash, economizer ash, mechanical fly ash, bottom ash, silo ash, pond ash, landfill ash, and FGD waste). Error bars are the mean ± standard deviation (n = 2–12) of samples collected from multiple ESP and baghouse rows of the same plant, boiler, and sampling date.

The fraction of critical REEs (Nd, Eu, Tb, Dy, Y, and Er) in U.S. CCPs ranged from 28.5% to 41.0% with a median of 36.5% (Figure 1A). In the three fly ash samples from South Africa, 30.4% of the REE total was comprised of the critical elements. These percentages are consistent with previously reported values in fly ashes from Poland (35.6–36.1%) and the U.K. (33.4–35.8%).[34] The critical REE content of Chinese coal ashes was generally lower (16.8–41.2%), while the critical REE content of Russian (31.5–63.2%) and Mongolian (48.6%) coal ashes greatly exceeded the samples in this study due to their very high yttrium content (up to 3540 mg kg^{-1} in Russian coal ashes).[19]

The heated nitric acid extraction efficiency relative to total REE content was highly variable, ranging from 1.6% to 93.2% with a median value of 29.6% (Figure 1B). In absolute terms, the HNO_3-extractable REE mass content ranged from 7.4 mg kg^{-1} to 372 mg kg^{-1} with a median of 126.9 mg kg^{-1}.

As shown in Figure 1, the total REE content, critical REE (%), and extractable REE (%) for all of the CCP samples appeared to cluster according to the origin of the feed coal used to produce the ash samples. Fly ash samples represented the largest proportion of the CCP samples. Therefore, we examined the fly ash data further by feed coal origin (Figure 2, Table S3).

The total REE content of fly ash samples differed significantly by coal basin (Tables S4 and S5). Fly ashes from Appalachian basin coals had significantly higher total REE

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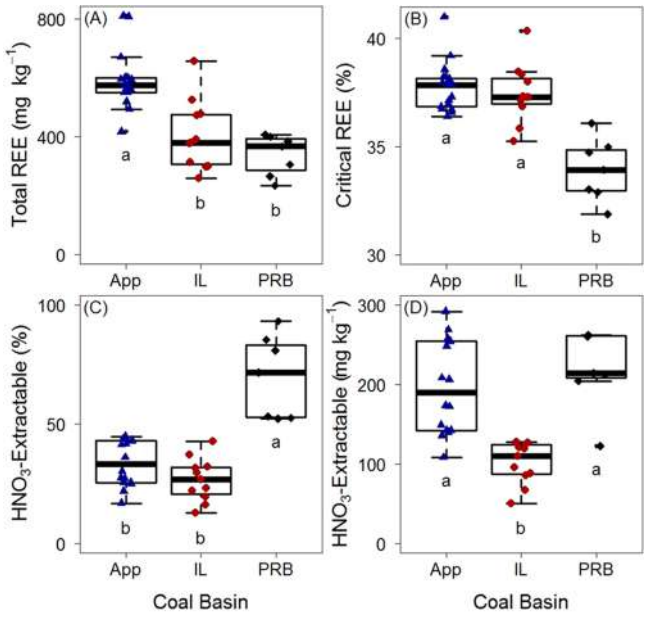

Figure 2. Fly ash REE parameters differed by the origin of the feed coal: Appalachian Basin (App), Illinois Basin (IL), and Powder River Basin (PRB). (A) Total REEs (lanthanides, Y, and Sc); (B) critical REEs (Nd, Eu, Tb, Dy, Y, and Er); (C) and (D) nitric acid-extractable REE content. Each data point represents the average of samples from multiple ash collector rows of the same power plant, boiler, and sampling date. Letters (e.g., "a" and "b") denote statistically significant differences between groups (see Table S4 for summary statistics).

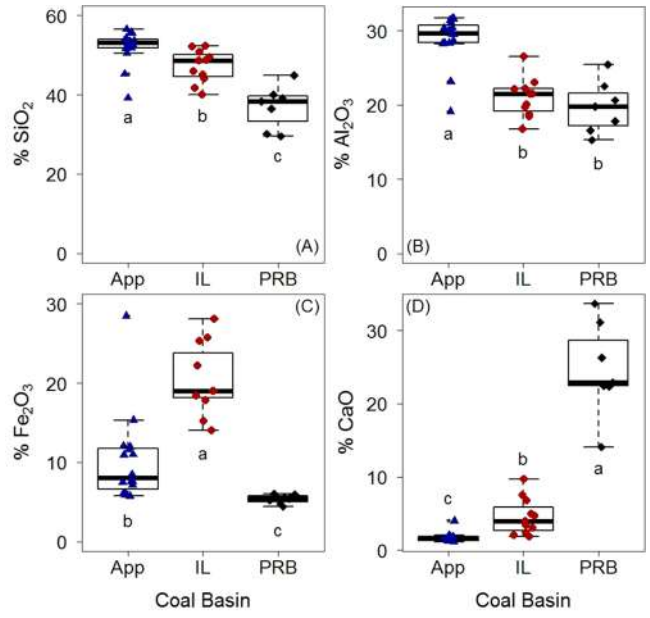

Figure 3. Major element composition (reported as % oxides) of fly ash samples grouped according to the origin of the feed coal: Appalachian (App), Illinois Basin (IL), and Powder River (PRB). Each data point represents the average of samples from multiple ash collector rows of the same power plant, boiler, and sampling date. Letters (e.g., "a" and "b") denote statistically significant differences between groups (Table S4).

content (591 ± 98 mg kg^{-1}) than those of Illinois Basin (403 ± 119 mg kg^{-1}) and Powder River coals (337 ± 69 mg kg^{-1}). The median difference (Hodges-Lehmann estimator) in total REE between Appalachian and Powder River ashes was 228.7 mg kg^{-1}; the median difference was 197.3 for Appalachian and Illinois Basin ashes. Total REE contents of Illinois Basin and Powder River coal ashes were not significantly different from each other (p = 0.37, Table S4). Differences between each coal basin group for the nonparametric analysis are listed in Table S4.

The critical REE content (as a percentage of total REE) differed significantly between coal basins (Kruskal–Wallis test, χ^2 = 15.8, p = 3.8 × 10^{-4}). Powder River basin ashes had significantly lower critical REE percentages than ashes from Appalachian coals (median difference of 3.82%) or Illinois Basin coals (median difference of 3.39%). Appalachian and Illinois Basin ashes did not differ significantly in critical REE content (median difference of 0.11%, p = 0.78). The nitric acid-extractable REE percentage also differed significantly by coal basin (Kruskal–Wallis test, χ^2 = 18, p = 1.2 × 10^{-4}), with the extractable REE fraction in Powder River basin coal fly ashes significantly greater than those of Illinois Basin and Appalachian coals (Figure 2C, Table S4). The median differences in extractable REE percent between Powder River Basin ashes and ashes from Appalachian and Illinois Basin sources were 36.3% and 42.1%, respectively. The median difference between Appalachian and Illinois ash percent extractability was only 7%.

As can be seen in Figure 3, the major elements comprising the fly ash samples differed significantly by coal basins (Table S5). Appalachian coal fly ashes had significantly higher SiO_2 and Al_2O_3 content relative to both Illinois Basin and Powder River coal ashes (Table S4). Illinois Basin coal ashes had significantly higher Fe_2O_3 content than Appalachian or Powder River ashes (median differences of 10.9% and 13.6%, respectively). Powder River ashes were characterized by relatively high CaO content (21% and 20% median difference with Appalachian and Illinois Basin ashes, respectively). These major element signatures of the Appalachian coal fly ash (high Si and Al, low Ca), Illinois Basin coal fly ash (high Fe, low Ca), and Powder River coal fly ash (low Si and Al, high Ca) are consistent with expectations for these coal sources.[35]

DISCUSSION

Total REE Content and Trends in Fly Ash. Our examination of the total REE contents in the samples of this study suggested trends according to origins of the feed coal. The Appalachian and Powder River ashes formed two distinct clusters (Figure 1), while Illinois Basin ashes straddled the two groups. Approximately 70–80% of the U.S. coal production occurs in mines located in these three basins.[36] The markedly higher REE content of fly ashes derived from Appalachian coals suggests that ashes from Appalachian sources should be prioritized in any REE recovery operation. Importantly, the elevated REE contents in Appalachian coal ashes were present across a variety of coals burned by six different utility power plants between 1994 and 2014. This implies that generic coals burned in the U.S. (not just specific coal seams such as the Fire Clay Coal) can produce fly ashes with greater than 500 mg kg^{-1} total REE (or approximately >600 mg kg^{-1} as total rare earth oxides). While these values do not meet the cutoff grade of >1000 mg kg^{-1} (expressed as rare earth oxide) suggested by Seredin and Dai (2012), they still represent significant added value to other metal recovery operations (e.g., aluminum recovery with simultaneous REE extraction).[19]

Total REE content also correlated strongly with the fraction of aluminum oxides comprising the fly ash (r^2 = 0.71) (Figure 4A). This trend suggests that the same geological factors

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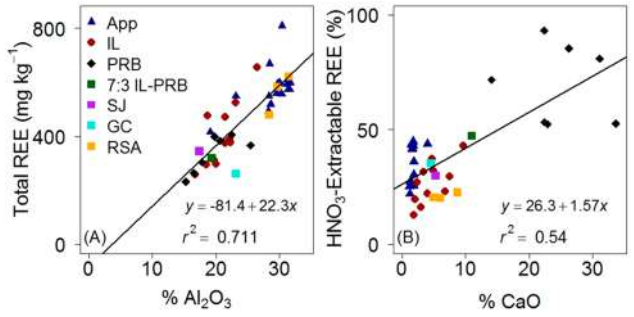

Figure 4. Total and extractable REE content of coal fly ashes depended on the fractions of major elements comprising the ash. (A) Higher Al_2O_3 content (as observed in Appalachian basin fly ashes) correlated with higher total REE levels. (B) High CaO content indicated greater extractability via HNO_3. The coal sources were Appalachian (App), Illinois Basin (IL), Powder River Basin (PRB), a blend, San Juan basin, Gulf Coast, and the Highveld/Witbank coal fields in South Africa (RSA).

responsible for determining aluminum oxide content in coal ashes may have an influence on REE enrichment. However, it is not clear whether these processes are related or simply the result of the source coal geology.

When normalized to the REE content of the upper continental crust (UCC),[37,38] the individual REEs showed differing enrichment trends between coal basins (Figure S5). The enrichments of Appalachian basin coal ashes tended to be greater in medium and heavy REE, especially Gd, relative to the light REEs. Illinois Basin and South African ashes were also enriched in Gd, but light, medium, and heavy REEs otherwise had similar enrichment factors. Powder River Basin ashes had relatively even enrichment across REEs relative to the UCC. A notable exception is an observed enrichment of Eu; however, we cannot rule out the possibility that this data reflects $^{137}Ba^{16}O$ interference during ICP-MS analyses.

Fly ash represents a complex mixture of the unburned coal material along with glassy aluminosilicate particles that condensed in and were captured from the flue gas stream. Little is known regarding which components of the fly ash matrix may be enriched with REEs, if at all. The lack of difference in REE contents as a function of ESP/baghouse row implies that the REEs were not partitioning onto the fly ash particles from the gas phase. This process is known to occur with volatile elements such as arsenic, selenium, lead, and gallium, which tend to adsorb to particle surfaces at cooler temperatures, resulting in higher contents in fly ash collected at later rows (shown in Figure S4).[24] Instead the REEs are likely distributed throughout the glassy particles, as demonstrated in a previous study that examined the distribution of cerium within cross sections of two fly ash samples.[39] Future investigations into the mineralogy and speciation of REEs in fly ash could provide insight into the correlations between REE and other elemental contents as well as methods for extraction.

Critical Rare Earth Fraction. The 16 REEs are typically grouped together because of their colocation in geological media. However, the abundances of the individual REEs relative to each other do not coincide with their utility. The supply challenges are primarily for the critical REEs, whereas excessive REEs (e.g., Ce, Ho, Tm, Yb, and Lu) are produced in surplus.[19]

The data in this study demonstrated that the critical REEs were greatest for the Appalachian and Illinois basin samples relative to the Powder River Basin samples. Regardless of the differences in critical REE contents of the various coal basins, the balance of critical and excessive REE in the coal ashes studied was superior to those of bastnaesite ores currently being mined, including the world's largest REE deposit at the Bayan Obo formation in China, which has less than 10% critical REE.[19] Although the absolute REE contents in fly ash were approximately two orders-of-magnitude less than those of conventional ore, the higher fraction of critical REE in fly ash may represent a major advantage. Continued REE production from the same deposits may not alleviate the shortage of critical REEs and could result in the overproduction of excessive REEs (particularly cerium).[9] Our findings show that the coal fly ashes currently being produced in the U.S. would provide more than three times the critical REE mass per kg of total REE extracted than conventional ores. This makes fly ash an attractive source for REEs if the cost per kg of REE extracted can match that of REE mining (the cost of which will increase as REE mineral deposits are exhausted).

REE Reserves and Valuation of Fly Ash. The total REE "reserve" available in the fly ash depends not only on the content of REEs in the ash but also on the quantity of available fly ash. In 2014, 46% of fly ash produced in the U.S. was reused for beneficial purposes such as construction and road materials, while the remainder was generally discarded (Table S6).[40] Assuming that fly ash coal sources mirror the relative coal production by coal basin (22.3% in Northern/Central Appalachia, 11.7% Illinois, and 36.1% Powder River for 2013),[41] then the amount of unused fly ash produced annually is approximately 5.5, 2.9, and 8.9 million t for the Appalachian, Illinois, and Powder River Basin coals, respectively (Table S6). After converting the measured contents of each REE to rare earth oxide (REO) units (Table S7), we estimate that the annual total tonnage of rare earths (reported as REO) in unused fly ash is 4000 t for the Northern and Central Appalachian Basin, 1280 t for the Illinois Basin, and 3630 t for the Powder River Basin, for a total of approximately 8910 t as REO (Table S8). This total fly ash "reserve" of REOs produced annually at U.S. coal-fired power plants is the same order of magnitude for annual REO production at the Mountain Pass Mine (3473 t REO in 2013; 4769 t in 2014).[42] (Note that this mine ceased operations in 2015 due to bankruptcy filings by the parent corporation).

The total annual value of the rare earths derived from the fly ash reserve was estimated at $4.3 billion, based on 2013 prices for select REOs (Table S8). The valuation would be smaller if only a portion of the unused fly ash was usable for REE recovery (a more likely scenario). However, legacy ash in ash ponds and other impoundments could be a resource that was not part of this valuation.

The REO value per metric ton of ash was $329 for Appalachian-derived ashes, $238 for Illinois Basin ashes, and $203 for Powder River ashes (Table S9). These per-ton REO values provide a basis for evaluating the use of fly ash as an alternative REE resource. The costs of recovery, which would include transportation as well as separation technologies, should be scaled in relation to this valuation. Moreover, only a subset of fly ashes would be feedstock candidates, as shown by the variations of REE contents and extractability in this study. Therefore, these valuations will require adjustments according to the recovery technologies that are currently under development. Other opportunities for added value, such as the recovery of other metals and reuse opportunities for wastes

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after extraction, will likely need to be incorporated in the REE recovery process.

This analysis also shows that the potential value of the REEs in fly ash is driven by specific elements. The significant value of scandium ($3700−5000 per kg in 2011−2013), as well as high prices of critical REEs such as neodymium, dysprosium, europium, and terbium, contributes to more than 80% of the overall REE value in fly ash (Tables S8 and S9). This underscores the importance of the higher critical REE fraction in fly ash, which is one notable advantage over conventional ores. Efforts to optimize and commercialize REE recovery processes may benefit by focusing on these elements.

The other major contributor to the total value of REE in fly ash is the sheer volume of the fly ash waste stream. While the REO value per metric ton of fly ash is only a few hundred dollars, the amount of fly ash generated and not reused is substantial: approximately 27 million t per year. Moreover, in the U.S. coal ash is disposed of in approximately 1000 landfills and surface impoundments, which have been accumulating coal combustion residuals for years and sometimes for decades.[43] Waste management rules recently issued by federal and local authorities could provide additional incentives for REE recovery, particularly for ash impoundments that need to be excavated.

Nitric Acid Extractable Rare Earth Content. The REE resource potential for fly ash strongly hinges on the ease of extraction from the ash. The HNO_3-extractable REE content in the coal ashes varied considerably in our sample set and was not necessarily related to the total REE content. For example, the sample with the highest total REE content (1220 mg kg^{-1}) was a stoker ash from a Kentucky power plant burning an Appalachian Basin coal (Figure 1). However, only 3% of the total REEs in this sample were extracted via heated nitric acid.

In contrast, the fly ash samples derived from Powder River basin coals were among some of the lowest in total REEs for all of the fly ash samples (Figure 2A). However, these samples were notable for their superior recovery by nitric acid extraction (Figure 2C). These results coincided with their significantly higher calcium content (Figure 4B). This trend could be due to the major element composition of Power River Basin-based coals and their respective ashes, which are generally high in Ca content. Nevertheless, for other fly ashes such as those burned from Illinois Basin coals, the acid-extractable REE fraction appeared to correlate with the %CaO value; this relationship was not apparent for Appalachian fly ashes. Calcium-bearing particles (such as calcium oxides) were likely to be more soluble in nitric acid than the other major oxides comprising fly ash, such as silicon and aluminum oxides. It is not clear, however, if the REEs were present in the Ca-bearing phases of the fly ash particles. Previous research has indicated that REE are dispersed throughout the glassy matrix of the fly ash particles.[39] Therefore, high calcium content likely caused a greater fraction of each ash particle to dissolve during the nitric acid extraction process, perhaps exposing more surface area that could release REEs from the fly ash matrix. If the REEs were diffusely distributed within coal ash particles, one could reasonably expect an increase in specific surface area for the particles to lead to gains in REE recovery. Historically, one of the primary difficulties in extracting metals from fly ash has been incomplete dissolution. New REE recovery technologies will need to address this challenge, perhaps by focusing on methods to decompose the overall fly ash matrix rather than dissolve the individual REE-bearing minerals entrained within the aluminosilicate glasses.

The concentration of REEs in the HNO_3 leachate before dilution was typically between 3 and 7 mg L^{-1} (approximately 10 mg L^{-1} for Powder River ashes). It should be noted that the ratio of acid (10 mL) to sample mass (~0.1 g) was chosen to optimize analysis, not extraction efficiency. Future development of leaching methods will need to minimize costs of reagents for the extraction processes. The fly ashes with high Ca contents might have an advantage in this respect in that sufficiently high extraction efficiencies could be achieved with smaller volumes of acid.

Overall, the results showed that ashes with high calcium content (e.g., class C fly ashes) such as those derived from Powder River Basin coals may be promising for REE extraction despite their lower overall REE levels. Notably, the extractable mass concentrations of REE for Powder River fly ashes were not significantly different from the extractable REE mass for Appalachian ashes (Figure 2D, Table S4). This suggests that higher extraction efficiency may be able to compensate for lower REE content in some ashes. Illinois Basin ashes had significantly less extractable REE mass than either Appalachian or Powder River Basin ashes (Table S4), indicating that ashes from this coal source may be the least promising of the three major basins.

Due to the nonspecific nature of the nitric acid digestion, many elements were leached from the fly ash in addition to the REEs and often in higher concentrations. Major impurities in the leachate include those elements comprising the fly ash particles themselves: Na, K, Al, K, Ca, and Fe (Si was not measured but is also expected in high concentrations). Trace elements of interest present in concentrations comparable to or exceeding the total REE included Sr, Ba, V, Cr, Mn, and As. Co, Ni, Cu, Ga, and Mo concentrations did not exceed total REE but were similar in concentration to Ce. Some of these impurities, such as Ga, are valuable in their own right. Nitric acid digestion was highly effective at mobilizing As and Se from the fly ash, recovering more than 80% of the total values in most samples. These preliminary results suggest that recovery of REE from coal fly ash would reduce the toxic metal content of the solid wastes, perhaps lowering the risks of solids disposal or reuse. However, these metals in leachates as well as large acid volumes are significant challenges that need to be addressed in the development of recovery technologies.

Implications for Fly Ash as an Alternative REE Resource. This research represents one of the first extended studies reporting REE contents and their extractable fraction for a broad variety of coal ashes generated at power plants across the United States. These results demonstrated widely variable total REE contents that appeared to depend on the origin of the feedstock coal which produced the ash. Power plants do not always burn coal from one source and can change suppliers over time or burn mixtures. Nevertheless, characteristics of the fly ash product (e.g., major element content) are often quantified by ash producers and recyclers as a way to determine suitability for the resale market. In this case, the percent major oxides reported by XRF data could provide indications of REE content, extractability, and other insights for power plants burning multiple coal sources.

The results of this study also highlight the importance of extraction efficiency in REE recovery in addition to the total REE content. To take advantage of the higher REE content identified in Appalachian Basin ashes, it will be necessary to

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develop scalable, high-efficiency recovery processes. These processes might need to be tailored specifically to the type of fly ash. Outside of the Powder River samples, nitric acid digestion was not an efficient means of leaching REE from fly ash. The maximum percent recovery by nitric acid for all of the ashes except for the Power River Basin ashes was only 44.1%, and many recoveries were significantly lower, even though heat (85−90 °C) and concentrated (~15 M) HNO_3 were used. In contrast, the Na_2O_2 sinter pretreatment and leach with 25% v/v (~4 M) HNO_3 yielded much greater leaching efficiency (generally >80% of HF values) than HNO_3 alone (Table S5). The dramatic increase in REE extractability from Na_2O_2 sintering (as compared to HNO_3 digestion alone) suggests that pretreatment with an alkaline agent (such as lime roasting, a common metallurgical process) would be an effective way to liberate REEs without resorting to HF digestion, which may be too hazardous for large-scale industrial use.

In summary, the ease of extractability may matter more than the total REE content, which has been the major focus thus far in the research literature. More attention is needed for improved methods of extraction and recovery. In this respect, the economic feasibility and environmental sustainability of coal fly ash as an alternative REE resource will hinge upon future developments in scalable recovery technologies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b00085.

Additional information on the sources of CCP samples for this study, results of statistical analyses of the data, data for the reserve and valuation estimates, and additional plots of the REE data (PDF)

Spreadsheets of all total and individual REE data for each sample in this study (XLSX)

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Notes

The authors declare no competing financial interest.

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