

Size Distribution of Rare Earth Elements in Coal Ash

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ABSTRACT

Rare earth elements (REEs) are utilized in various applications that are vital to the automotive, petrochemical, medical, and information technology industries. As world demand for REEs increases, critical supply shortages may be expected, especially for the heavier REEs. Due to the retention of REEs during coal combustion, coal fly ash is increasingly considered a potential resource. Previous studies have demonstrated that coal fly ash is variably enriched in REEs relative to feed coal¹⁻³ and that enrichment increases with decreasing fly ash size fractions^{4,5}. In order to further explore the REE resource potential of coal ash, and determine the partitioning behavior of REEs as a function of grain size, we studied whole coal and four fly ash size-fractions collected from three U.S. commercial-scale coal-fired generating stations burning bituminous coal from the Appalachian Basin (samples Ap-1 and Ap-2) or subbituminous Powder River Basin coal (sample PRB-1). Whole fly ash was separated into <5 μm , 5 to 10 μm , 10 to 100 μm , and >100 μm particle size fractions, using mechanical shaking and trace-metal clean procedures. Our separation method allowed for the collection of two size fractions (<5 μm and 5 to 10 μm) not previously reported, and the mass of starting fly ash and resulting separates was recorded in order to better understand the mass balance of REEs in individual size fractions. In order to assure complete digestion of recalcitrant mineral phases containing REEs (e.g. monazite) we utilized a sinter method for all digestions, with analyses completed via ICP-MS. This method also allowed for the quantification of other trace metals of economic interest (e.g., Y, Mo, and Nb). Our results demonstrate enrichments of REEs in whole fly ash of 5.6 to 18.5 times that of feed coals. The bulk of fly ash falls into the 10 to 100 μm size fraction with less than 10% of the total fly ash collected in the > 100 μm fraction and less than 1 % in the < 10 μm fractions. Our > 100 μm fraction was depleted in REEs relative to whole coal ash and the smaller size fractions. We observed little or no increase in REE concentrations in the two smallest size fractions, suggesting that enrichment in REEs with decreasing size fraction observed by other workers is not expressed in size fractions < 10 μm . The concentration of trace metals (Y, Zr, Nb, Mo, Hf, Th) followed the same general trend with depletions in the coarse fraction and nearly constant enrichment among whole ash and the smaller size fractions.

INTRODUCTION

Rare earth elements are utilized in various industrial processes, are essential in the medical and defense industries, and are required for the production of green technologies and consumer electronics. Due to a combination of geologic, economic, and environmental considerations, the vast majority of REEs are supplied by China. However, as demand continues to increase there is renewed incentive to identify new and unconventional sources of REEs. Coal fly ash is considered a potential unconventional source of REEs due to the fact that REEs are retained during the combustion of coal¹ and because large quantities of coal fly ash are stockpiled worldwide^{2,3}.

Previous work on the REE content of coals and coal fly ash demonstrate that both are enriched in REEs relative to average continental crust, with a 5- to 20-fold increase in REE concentration in fly ash relative to feed coal¹⁻³. Some coals have higher initial REE concentrations than others due to the presence of ash beds or phosphate minerals, both of which are known to host REEs⁴. Preliminary work has been completed comparing the distribution of REEs in coal ash size separates^{4,5}. These studies suggest that there is an inverse relationship between coal ash size and the concentration of REEs for separates between 100 μm and 30 μm . However, these studies also suggest that the concentration of REEs in the feed coal exerts a stronger control on the REEs concentrations in the fly ash than does particle size.

This study addresses two important questions relating to the potential for coal fly ash to serve as a source of REEs. First, we test the hypothesis that REE concentrations increase with decreasing size fraction and include the analysis of smaller size fractions than previously studied. And second, we provide a mass balance for our size separates in order to better understand the distribution of REE in the whole fly ash, and its proportions.

METHODOLOGY

Three fly ash samples, AP-1, AP-2, and PRB-1, were collected from commercial-scale coal-fired power plants. AP-1 and AP-2 were collected from plants which burn coal mined from the Appalachian Coal Basin whereas PRB-1 was obtained from a plant utilizing Powder River Basin coal. Fly ash samples were collected via access ports to electrostatic precipitators, and were stored in steel cans at room temperature until separation and analysis.

Fly ash samples were separated into the following size fractions using a mechanical shaker outfitted with sieves of appropriate mesh sizes: <5 μm , 5 to 10 μm , 10 to 100 μm , 100 to 1,000 μm , and > 1 mm (hereafter referred to as <5 μm , 5 μm , 10 μm , 100 μm , and 1 mm, respectively). Approximately 500 to 1000 g fly ash were shaken for 120 minutes, collected and weighed, and then stored at 4°C. Trace clean techniques were applied to the mechanical separation process to avoid sample contamination, such as the use of acid-cleaned (0.1 N HNO₃) polycarbonate sieve

frames, nylon mesh, and enclosure of the sieves in clean polyethylene bags during shaking. After shaking, fly ash fractions were collected using nylon brushes and stored in acid-cleaned (0.1 N HNO₃) polypropylene jars. Sieve frames were acid-washed and nylon meshes and brushes were replaced prior to size separation of each fly ash sample.

We analyzed the <5 μm, 5 μm, 10 μm, 100 μm fractions for REEs and trace metal concentrations (the 1 mm fraction was not analyzed for this study). In order to assure complete digestion of REE-bearing refractory phases such as monazite and zircon, whole fly ash and fly ash separates were subjected to a sodium peroxide sinter digestion⁶. Digests were analyzed via ICP-MS at the U.S. Geological Survey Crustal Geophysics and Geochemistry Science Center Geochemical Labs in Denver, CO.

RESULTS

Large (10s of kg) fly ash samples, amalgamated from multiple ESP (electrostatic precipitator) hoppers at each power station, were collected to insure sufficient material would be obtained in the finest size fractions. Table 1 summarizes the size separation mass balance for each of the three North American coal ash samples we studied. For all samples, the vast majority of the bulk fly ash (90.1 to 98.6 %) was retained in the 10 μm fraction. The 100 μm size fraction contained from 0.7 to 9.1 % and the 5 μm and <5 μm samples represented less than 0.5 % of the starting mass combined. The REE concentrations for the whole fly ash samples are enriched relative to average U.S. coal⁷ and the North American Shale Composite⁸ in all cases (Fig 1). Whole fly ash from AP-1 was most enriched relative to whole coal on a chondrite-normalized basis. Enrichments for our samples were of the same magnitude as that previously reported for whole fly ash^{4,5}.

Sample	Mass (kg)	Percent Recovered					Total (%)
		<u>1 mm</u>	<u>100 μm</u>	<u>10 μm</u>	<u>5 μm</u>	<u>< 5 μm</u>	
AP-1	63.1	< 0.1	2.1	96.6	0.4	< 0.1	99.1
AP-2	39.3	0.1	9.1	90.1	0.1	< 0.1	99.5
PRB	39.6	< 0.1	0.7	98.6	< 0.1	0	99.3

Table 1. Size separation mass balance. Fraction sizes are listed by their lower bounds.

For ease of sample comparison and elimination of the Oddo-Harkins effect, in which even numbered elements are more abundant than odd numbers, REE concentrations for each of the fly ash samples studied are presented on a chondrite-normalized basis (Figs. 2-4). For all three of the fly ash samples we observe depletion in REEs in the coarse fraction relative to the concentration of REEs in the whole fly ash. This depletion is most pronounced in sample AP-2 and least pronounced in PRB-1. In addition to containing the largest depletion in REEs in the coarse fraction, AP-2 also has the largest coarse fraction at 9.1% of the starting mass. The concentration

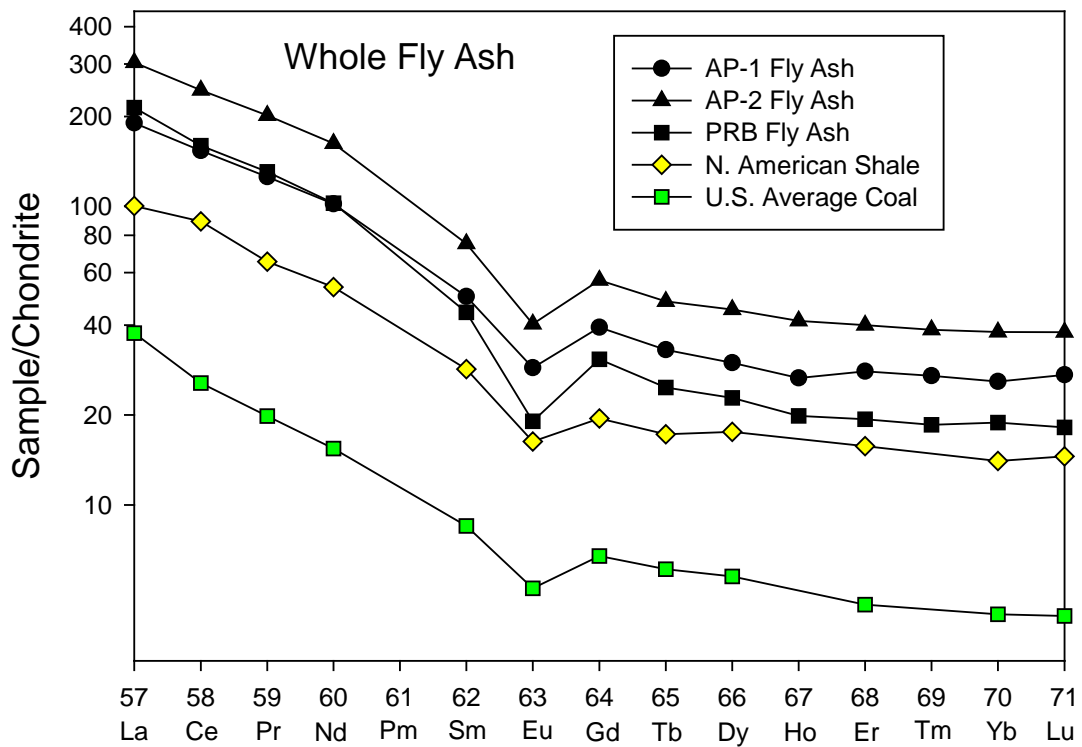


Figure 1. Chondrite-normalized rare earth elements in studied bulk fly ash, U.S. average coal, and North American shale. The U.S. Average coal is dominated by samples from the Appalachian Basin⁷.

of REEs in the smaller fractions was similar to that of the bulk fly ash, reflecting little or no enrichment in REEs relative to the bulk fly ash. This is in contrast to previous work that demonstrated increasing enrichment in REEs with decreasing sample size for the < 100 μm size fractions^{4,5}.

In addition to REEs, selected trace elements (Y, Zr, Nb, Mo, Hf, Th) were determined by ICP-MS following the same sinter sample digestion procedure (Figs 5-8). For these elements, we observed some variation of trace metal concentration between individual size fractions of the same fly ash sample but no systematic variation among the different fly ash samples. For AP-1 we observe enrichment in Mo in the whole fly ash and the 5 μm separate relative to the 100 μm , 10 μm , and <5 μm separates. For AP-2 we observe depletion in all trace elements relative to the whole fly ash and the smaller size separates with the largest depletion in Y. Trace elements in PRB-1 demonstrate little variation between size fractions with minor enrichments in Zr and Hf in the coarse fraction relative to the bulk fly ash. Whereas the trace element results are somewhat variable, in almost all cases, the coarsest fraction has among the lowest element concentrations, similar to results obtained for REE.

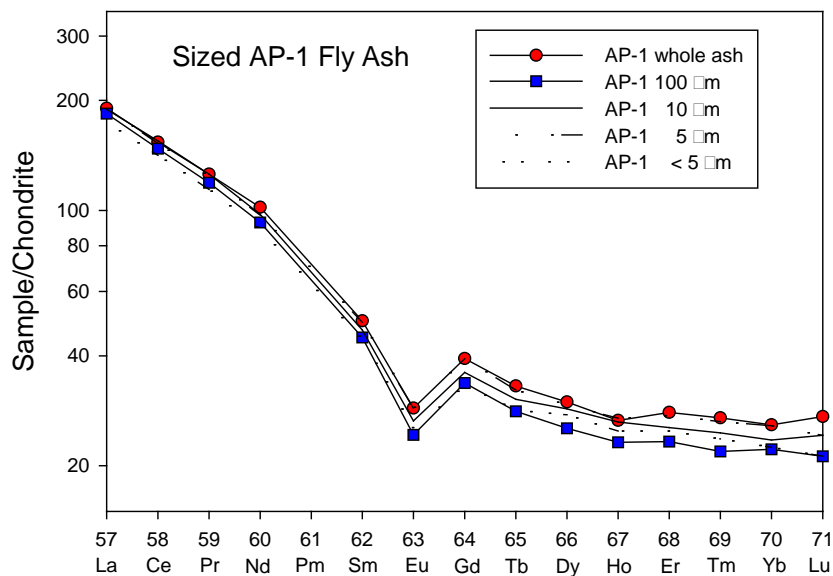


Figure 2. Rare earth element concentrations in whole ash and size separates of AP-1.

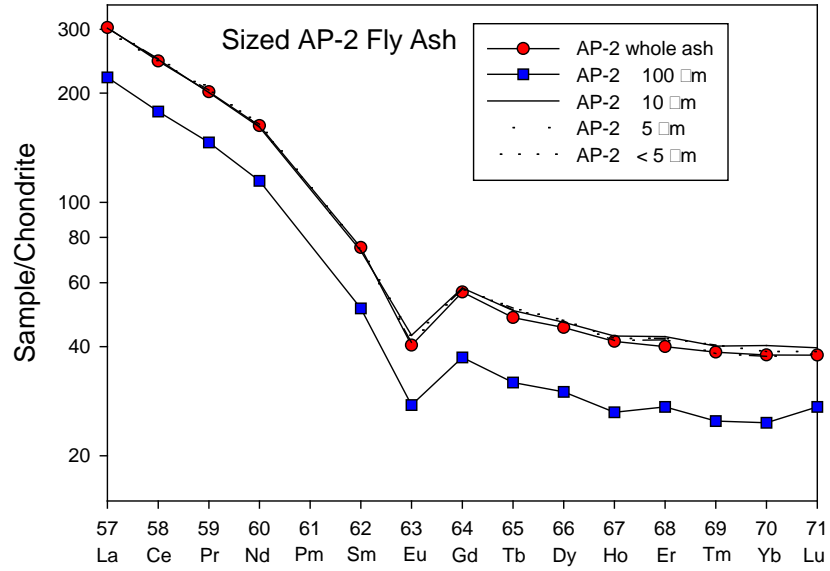


Figure 3. Rare earth element concentrations in whole ash and size separates of AP-2.

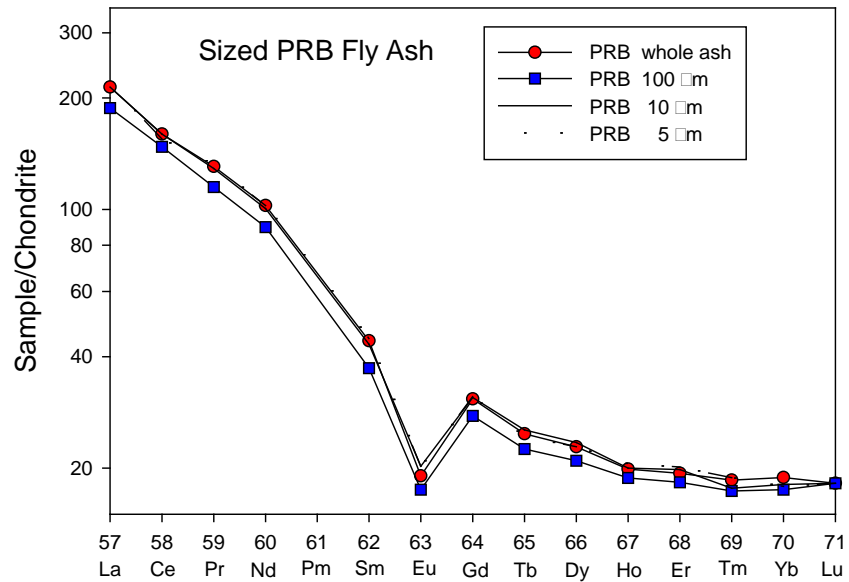


Figure 4. Rare earth element concentrations in whole ash and size separates of PRB-1.

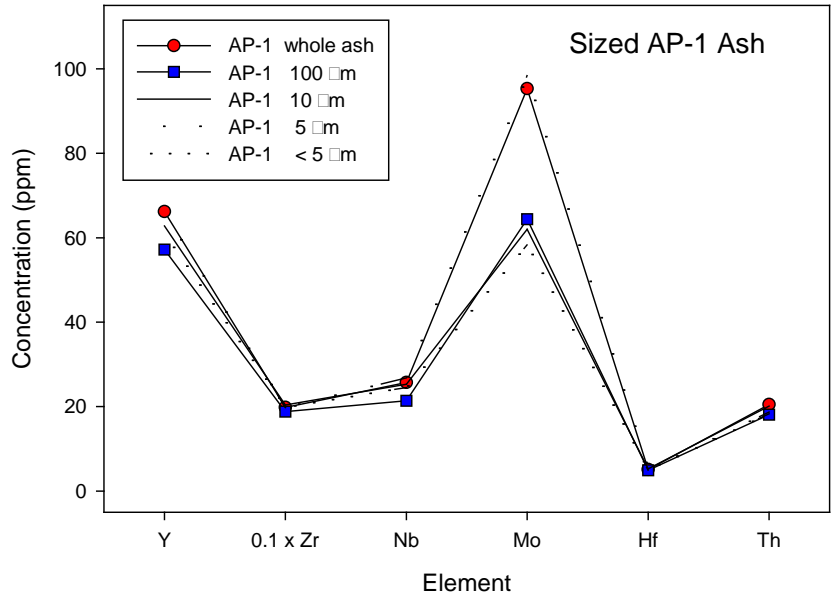


Figure 5. Trace element concentrations in whole ash and size separates of AP-1.

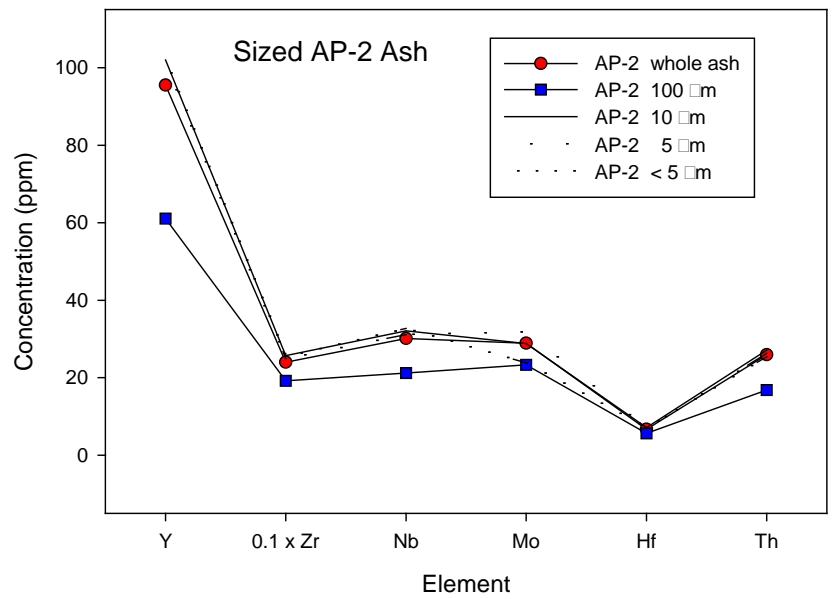


Figure 6. Trace element concentrations in whole ash and size separates of AP-2.

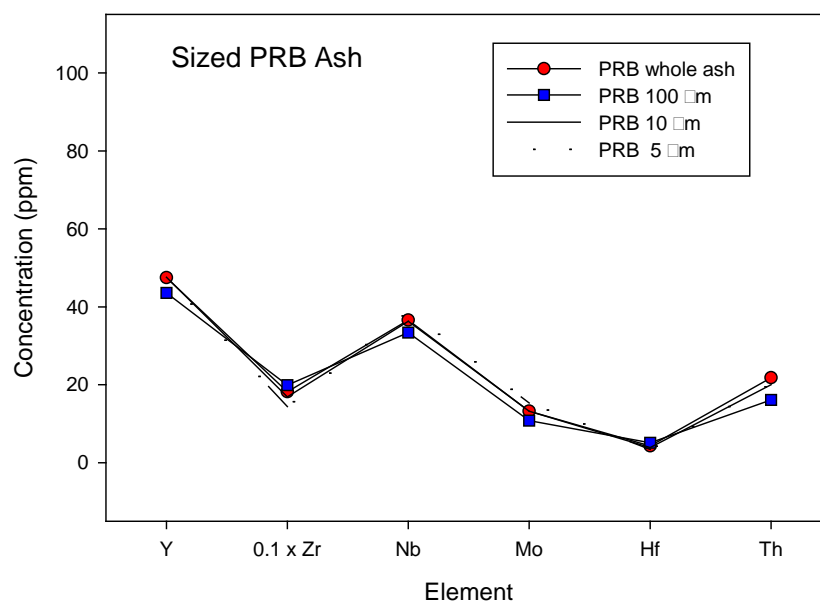


Figure 7. Trace element concentrations in whole ash and size separates of PRB-1.

CONCLUSIONS

The mass balance results from the fly ash size separations provide insight into the possibility of exploiting coal fly ash as a source of REEs. Our 100 μm was the easiest to remove and approaches 10 % of the total in sample AP-2. Conversely, the 5 μm and < 5 μm fractions were much more difficult to separate, due to the fine grain size, but represented an insignificant part of the total mass in each of the three fly ash samples. Based on our mass balance results and the increasing difficulty of separating increasingly fine separates, we propose that future work on REEs in size separates should focus on removing the coarser fractions.

For the bulk fly ash samples, the extent of enrichment of REEs relative to U.S. average coal⁷ was within the range of previously published values^{4,5}. For each of these samples, the concentration of REEs in the size separates less than 100 μm are within analytical error of the whole ash concentrations. Based on these results, and those previously published, we suggest that the concentration of REEs in these fly ash samples and separates are typical of enrichments widely encountered in commercial coal use.

Whereas previous work demonstrated enrichment in REEs with decreasing size fractions between 100 μm and 30 μm^{4,5}, in the present study, we collected single separates between 100 μm and 10 μm as well as two smaller size fractions, 5 μm and < 5 μm and did not observe the same trend. Comparing these studies is difficult because of the different size ranges, but taken

together it either suggests there is a limit to REE enrichment with decreasing grain size, or that in the present study, a finer increment of sampling is needed. Regardless, the present study confirms that REEs are depleted in the coarse fraction ($> 100 \mu\text{m}$) relative to the whole ash. Removal of the coarse fraction represents a relatively simple step that would result in a minor enrichment of REEs in the remaining fly ash. Conversely, separation of smaller size fractions is increasingly difficult and with decreasing benefit below $\sim 10 \mu\text{m}$ due to the limited fraction of material obtainable at this size.

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