Short discussion

Signatures of Rare Earth Element distributions in fly ash derived from the combustion of Central Appalachian, Illinois, and Powder River basin coals

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Abstract

The distribution of Rare Earth elements (REE) in coal-derived fly ashes can have distinctive patterns when fly ashes are produced from different coals within or between basins, such as the Pennsylvanian Class F fly ashes from the Illinois and Central Appalachian basins. Both the Fire Clay coal and a blend of a number of eastern Kentucky coals show strong Gd peaks and an H-type distribution in the Upper Continental Crust-corrected plots. The Fire Clay coal-derived ash has a higher heavy REE concentration than the blended coal-derived ash. The Illinois Basin-derived fly as has an overall lower REE concentration than the latter ashes. Class C fly ash derived from Powder River Basin coals has, with the exception of an Eu peak, a flatter distribution of REE and an overall L-type or indistinct H- versus L-type distribution. The signatures of the REE in fly ashes may be useful in predicting their behavior in the extraction of the REE; simple extrapolations from the basic concentrations and the predicted extraction percentages for ashes from different basins are not necessarily indicative of the actual distribution of the extracted REE.

Keywords: lanthanides; heavy rare earth elements; fly ash beneficiation; rare earth processing

1. Introduction

Rare earth elements (REE) are vital in the production of electronics, magnets, catalysts, optics, ceramics, and other products necessary for the functioning of modern society.[1-7] Albeit a moving target, based on a combination of their utilization needs versus their overall abundance, certain REE can be more critical (versus "excessive"). Coal combustion products, including, but not restricted to fly ash, are among the resources considered to be potential sources of lanthanides, Sc, and Y.[8-12] With over 29 Mt of fly ash (out of more than 78 Mt of coal combustion products) produced in the US in 2019,[13] plus the landfilled and ponded ashes from previous years, the resource potential is large. While there is potential to beneficiate fly ash to a relatively uniform material for the acid extraction of REE,[14-31] beneficiation alone does not resolve issues related to the basic elemental concentrations of the original ash, much less the natural variation in the relative concentrations of the elements.

In this investigation, selected case studies of fly ashes derived from Central Appalachian and Powder River Basin coal sources are examined from the standpoint of the distribution of the REE within the ashes. Illinois Basin coal sources were covered by Hower et al.[32] and will be briefly noted here. The discussion of the other basins expands upon the work of Taggart et al.[33] (first full paragraph on p. 5923 and Fig. S5 in the Supplementary Information). Specifically, with a focus on the shift in the Central Appalachian coal supply in one plant and a broader view of the entire suite of major oxides and minor elements in the sources from both basins, a greater understanding of the REE distributions can be achieved.

2. Methods

2.1 Nomenclature surrounding Rare Earth Element distributions

In this study, the lanthanide elements are referenced as REE and the addition of Y and Sc to the REE is designated as REY and REYSc, respectively. REE nomenclature can vary between users; for this study, light rare earth elements (LREE) include La through Sm and the heavy rare earth elements (HREE) include Eu to Lu.[34-37] The Upper Continental Crust (UCC) corrections, a means of normalizing the REE distributions, after McLennan and Taylor[38] are:

- L-type ($La_N/Lu_N > 1$; $_N$ indicates a value corrected against a standard distribution, such, in this study, as the Upper Continental Crust),
- M-type ($La_N/Sm_N < 1$, $Gd_N/Lu_N > 1$), and
- H-type ($La_N/Lu_N < 1$) enrichment patterns.

The following ratios, all based on the UCC corrections, decouple Ce, Eu, and Gd from the other REE in the distribution patterns[37, 39-41]:

$$Eu_N/Eu_N^* = Eu_N/(0.67Sm_N + 0.33Tb_N) \quad (1)$$

$$Ce_N/Ce_N^* = Ce_N/(0.5La_N + 0.5Pr_N) \quad (2)$$

$$Gd_N/Gd_N^* = Gd_N/(0.33Sm_N + 0.67Tb_N) \quad (3).$$

2.2. Sample and Data Collection

Every five years from 1992 to 2012, the University of Kentucky Center for Applied Energy Research (CAER) sampled the feed coal (in most cases, the pulverized feed coal), pulverizer rejects, fly ash, bottom ash, and flue-gas desulfurization products at all of the utility-based power plants in Kentucky. Up to 22 utility-based coal-fired power plants with 61 units were in operation in the state, although not all were operating at the same time. More limited collections were made in the off years for various research projects. For all post-2000 collections, fly ash was obtained from multiple rows (including cyclone (mechanical), baghouse/fabric filter (FF), and electrostatic precipitator (ESP) systems) and from multiple ash-collection hoppers in each row; an effort was made to sample the same hoppers every time. The 2007 and 2012 results are discussed by Hower et al.[42-43] and the partitioning of select elements between the pulverized feed coal and the fly ash is discussed in Hower et al.[44] Rather than identify power plants in publications, a letter code system was developed in 1992 at the start of the collection efforts.

The samples investigated here represent select units burning Appalachian, Illinois Basin, and Powder River Basin (PRB) coals, with an emphasis on Kentucky power plants. Power plants from Georgia, Texas, and Missouri were added in order to broaden the coverage of PRB-derived fly ashes. The complete data set for the Appalachian and PRB samples is in the Supplementary Information and the Illinois Basin data is in the Supplementary Information associated with Hower et al.[32]

The proximate, heating value, and sulfur forms analyses of the feed coals and the ultimate analysis and major oxides and select minor elements, both done by X-ray fluorescence, determinations were performed at the CAER following the ASTM standards for the various techniques. The details of the HF-digestion REE analysis are presented in detail in Taggart et al.[33] The analyses were conducted by via inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700x) at Duke University.

3. Results and discussion

The concentration of REE varies between coal seams[45-48] and between coal-bearing basins. At a finer scale, as demonstrated by the latter authors, REE varies between locations across the extent of a coal deposit and, potentially, even more between lithotypes of the same coal. Owing to the relative impact of the multiple modes of emplacement and redistribution of REE, the relative concentrations of the REE may vary at all of the noted scales. There is no reason to expect that a discrete depositional event would have impacted any more than one coal. For example, the deposition of the REE-rich volcanic ash within the Central Appalachian Fire Clay coal did not influence any other Central Appalachian coal and, indeed, like any wind-blown deposit, the thickness and nature of the ash fall varies across the extent of the Fire Clay coal and the influence of the ash-fall event is not seen throughout the entire coal at any of the sites studied.[36, 45-46]

3.1 Illinois Basin-coal-derived fly ashes

Hower et al.[32] discussed fly ashes from the combustion of high-S, high volatile C through high volatile A bituminous Illinois Basin coals. They emphasized the variation among the fly ashes from the power plants in their study, demonstrating that variations in the coal source certainly account for the variations between the plants and the collection times and that coals from different parts of the basin or even different proportions of the same coals could lead to different patterns. Despite the differences in the relative concentrations, all the patterns showed a general similarity, including high Gd concentrations and the overall H-type distributions. Relatively high Gd concentrations have been seen in several fly ashes, for example, the Fire Clay coal-derived fly ash discussed in section 3.2 and fly ashes beneficiated for chemical extraction.[27,

[47] The latter two studies demonstrated that the magnetic fraction of the fly ash is particularly enriched in Gd. In that context, high Gd concentrations in fly ashes from medium- to high-S coals, with relatively high contributions of pyrite in the mix of minerals, are logical since magnetite and other Fe-rich spinels are formed in the breakdown of pyrite at the 1400-1500°C boiler temperatures.

3.2 Different Central Appalachian coals combusted at the same plant

Plant I, a two-unit southeastern Kentucky power plant, was sampled many times over the course of the University of Kentucky CAER's studies. In normal operations, a blend of southeastern Kentucky and northern Tennessee low- to medium-S, high volatile A bituminous coals is burned in both units. Sakulpitakphon et al.[49-50] arranged a single-seam, single-mine run of the Manchester coal, Mardon and Hower[36] arranged a similar run of the Dean coal (a Fire Clay correlative), and Hood et al.[51] sampled the fly ash from an exclusive run of the Fire Clay coal. Using the UCC-corrected values for the fly ashes, the latter 2014 sampling from unit 1 is compared with the 2007 sampling of blended-coal-derived fly ashes (Figure 1; after Hower et al.[32]). The average total REE is 430 ppm for the blended coal-derived fly ashes and 622 ppm for the Fire Clay-derived ashes. Mardon and Hower[36] reported an approximately 1000-1400-ppm range for Fire Clay-derived fly ashes from unit 1 at the same power plant.[footnote 1] In contrast to the fly ash from the combustion of the blended coals, the fly ash from the combustion of the Fire Clay coal has a negative Eu_N anomaly and a sharp positive Gd_N peak.

The contrast between the two runs is further emphasized in the plots of the Gd_N/Gd_N^* vs. Eu_N/Eu_N^* (Figure 2), Ce_N/Ce_N^* vs. Eu_N/Eu_N^* (Figure 3), and Nd_N/Sm_N vs. Gd_N/Sm_N (Figure 4; all

[1] By the time of the 2014 sampling,[51] the configuration of unit 2 had changed and it was no longer possible to sample fly ash from that unit.

data in Supplementary files); in both cases the two sets of fly ash are shown to be distinctly different, confirming the distributions seen on Figure 1. The Gd_N/Gd_N* vs. Eu_N/Eu_N* and Ce_N/Ce_N* vs. Eu_N/Eu_N* plots were used previously in geologic evaluation of coals.[42] The Gd_N/Gd_N* seen in this study compares favorably with the distribution seen in the latter study, the Ce_N/Ce_N* range is limited to the low end of their range, while the Eu_N/Eu_N* values correspond to the high end of their distribution, although it is noted that Hower et al.[46] were examining specific coal and rock lithologies, not the entire coal bed and not fly ash derived from the coal. While the Gd_N/Gd_N*, Ce_N/Ce_N*, and Eu_N/Eu_N* are not strictly unique to a certain coal source, they do convey information about the coals.

The Nd_N/Sm_N vs. Gd_N/Sm_N convention has been used in an evaluation of the partitioning of REE in the beneficiation[27] and subsequent chemical processing of fly ashes.[52] Because, at least in the pilot study, the Sm concentration was relatively unchanged between the feed ash, the HNO_3-extracted ash, and the spent ash, Sm was used to normalize the concentrations of Nd and Gd, two of the REE exhibiting greater variations. The plotted points (Figure 4) represent the baseline for a contrast of a feed ash (these samples) against the REE concentrate extracted from the ash and the spent ash following the chemical REE extraction (note, the latter material is not a "waste" or "refuse" since every product stream has the potential to be the feedstock for further processing or a direct input stream for utilization).

Both sets of fly ashes exhibit H-type REE distributions, although the Fire Clay-derived fly ash has a relatively higher concentration of heavy REE vs. light REE than the fly ash from the blended coals. Aside from the Eu_N and Gd_N anomalies, the REE distribution patterns from La through Sm and Tb through Lu are basically parallel.

3.3 Powder River Basin subbituminous coal sources

Particularly in the time before flue-gas desulfurization was required for power plants (the Cross-State Air Pollution Rule (CSAPR))[53], power plants in several midwestern states, but also including Kentucky and Texas, began to burn low-S PRB coals in order to meet the SO_2-emission standards. So, despite the abundant coal resources in those states, subbituminous PRB coal are utilized and the resultant fly ashes continue to be accumulated in these regions.

Dai et al.[37] noted that the analysis signal for ^{153}Eu via inductively coupled plasma mass spectrometry overlaps with the signals for barium oxide polyatomic species

($^{137}Ba^{16}O$, $^{136}Ba^{17}O$, $^{135}Ba^{18}O$, and $^{134}Ba^{18}OH$). If samples with Ba/Eu>1000 (mass basis), slightly more than 3X the world average for Ba/Eu,[54] are flagged as unreliable for the interpretation of Eu anomalies ,[37, 55] most of the PRB-derived fly ashes in this study would be problematical. All but two PRB-derived samples in this study have Ba/Eu<1000 and one of the two is >3X the world average (Supplementary Information, Ba and Ba/Eu data in columns CW and CZ, respectively). The distribution of Eu_N vs. Ba/Eu for the PRB-derived samples show disparate trends (Figure 5). Plant G, with a common coal source for all the fly ashes, shows an increase in Eu_N with an increase in Ba/Eu. By themselves, the other five plants show an increase in Eu_N with a decrease in Ba/Eu. The variation is understandable since each of the other points represents with an individual plant or a different acquisition time for the same plant; sources vary between plants, with the coals potentially coming from different mines within the PRB, and, even with the same mines supplying the coal, through time the variation is expected.

Figure 6 shows the UCC-corrected REE concentrations for several power plants burning Powder River Basin subbituminous coals. The average REE for the fly ashes plotted on Figure 6 is 281 ppm. The most striking aspect of the UCC plot is the sharp Eu peak for all of the ashes except the Plant G/ mechanical (cyclone) ash. Except for the Eu peak, this is a much more even distribution than the Central Appalachian (Figure 1) distributions. As noted above, though, owing to the high Ba/Eu in most of the ashes, all but the data for the Plant G/ mechanical ash is suspect, so the REE distributions are flatter than the data would suggest. The ashes have L-type to indistinct H-type vs. L-type distributions. The plot of Nd_N/Sm_N vs. Gd_N/Sm_N (Figure 7) shows a relatively tight distribution for Plant G compared to the other fly ash sources. Owing to the complications imposed by the Ba interferences in the Eu determination, the Gd_N/Gd_N^* vs. Eu_N/Eu_N^* and Ce_N/Ce_N^* vs. Eu_N/Eu_N^* plots are not considered for the PRB-derived fly ashes.

3.4 Discussion

While it is well established that various types of fly ash, both ashes from coals within and between basins, can have different REE concentrations, there has been less discussion about the differences in the REE distributions between fly ashes. The REE-distribution signatures seen in the examples discussed here have some distinct aspects, whether it is the relative concentration of heavy versus light REE; the concentrations of individual elements, such as Eu or Gd; or the ratios of the elements. Just as much as the relative extraction if REE from the fly ashes, as noted in the Introduction, all the latter aspects contribute to the relative values of an ash. For example, the Fire Clay coal-derived fly ashes have a higher percentage of critical REE than the PRB coal-derived ashes (Supplementary Information; after definitions by Seredin and Dai[56]) while the PRB ashes are more easily extracted.[20, 22] Just considering the critical REE concentrations of the

Central Appalachian- (*not* including the Fire Clay coal-derived ashes), Illinois Basin-, and PRB-coal derived fly ashes along with the approximate HNO_3-extractable REE for each fly ash type,[33] the PRB and Central Appalachian fly ashes are both in the 75- to 80-ppm range while the Illinois Basin fly ashes were in the 50- to 55-ppm range. The caveat is that the number of sources for each basin were limited, therefore, this is only an approximation of the recovery of critical REE. Such balances between the percent of economically extractable REE versus the value of the recovered REE need to be addressed in the evaluation of REE-processing tests.

The relative mineralogy of the coals and the resultant ashes, while not directly addressed here, is an underlying factor in the variation between the ashes. While many of the REE-bearing minerals and, perhaps, amorphous phases in fly ash appear to be finely (few-nm to sub-nm) or heterogeneously dispersed in glass,[47, 51, 57-62] a few minerals have been noted. Aside from the common occurrences of minerals such as monazite, high resolution transmission electron microscopy (HRTEM) studies by Hower et al.[58] noted variations of the proportions of Ce, Nd, Pr, and Sm in a fly ash glassy phase from a Fire Clay coal-derived fly ash. A Ce-rich phosphate was found in a high-REE stoker ash.[57] Lanthanum-, Ce-, and Nd-bearing monazite; Y-bearing zircon; and La- and Ce-bearing davidite (with trace Nd and Y) (Figure 8) were found in a stoker ash from a possible Fire Clay coal source.[58] Resolution of REE-bearing minerals in the PRB fly ashes has proven to be more elusive. Figure 9 (after the study by Hood et al.[51]) shows a Ca-Mg-Al-Si sphere (Figure 9A) with no apparent REE (Figure 9B) and a solid sphere with Nd Lα and Lβ peaks and the Pr Lβ peak (Pr Lα would be in the Ba – Nd Lα region). If Ce is present, it is obscured in the Ba Lβ (the higher keV Ba peak) and the Nd Lα peaks.

Ultimately, the energy dispersive spectroscopy (EDS) resolution of heavier even-number REE is difficult; for example, in an HRTEM study [footnote 2] of the REE-bearing phosphate rhabdophane in an eastern Kentucky coal, Gd could be determined with certainty but the Dy concentration did not meet the standard of the peak being three-times the background and neither Er nor Yb were detectable above the background.[63] It is possible, given the limitations of the ultra-fine mineral sizes and the vanishing resolution of lower-concentration REE elements, the descriptions of the distribution of REE within fly ash will remain in the realm of the bulk chemistry of the samples.

4. Summary

For Central Appalachian coal-derived fly ashes, comparison of the fly ash from a blend of coals versus the Fire Clay coal, a coal known to be a REE resource, shows that the fly ashes have parallel REE-distribution patterns from La through Sm and Tb through Lu. The Fire Clay-derived fly ash shows a negative Eu anomaly and a strong Gd peak compared to the blended coal ash. Both are H-type ashes, with the Fire Clay fly ash have a greater proportion of heavy REE compared to the blended coal ash. In contrast, the previously investigated Illinois Basin coal-derived fly ashes,[32] in general, have a lower concentration of the lanthanides (about 350 ppm vs. over 400 ppm for the Central Appalachian blend-derived fly ashes and over 600 ppm for the Fire Clay coal-derived fly ash studied here and 1000-1400 ppm for the Fire Clay coal-derived fly ashes studied by Mardon and Hower[36]). The Illinois Basin coal-derived fly ashes have relatively high Gd concentrations and an overall H-type distribution.

[2] FEI Talos F200X operating at 200 keV, operated by University of Kentucky Electron Microscopy Center.

With the exception of a strong Eu peak, which, as noted, is likely to be an anomaly related to the high-Ba content of the PRB ashes, the Class C PRB coal-derived fly ashes studied here show a substantially more muted REE distribution than the Class F Central Appalachian and Illinois Basin coal-derived fly ashes. The REE pattern shows L-type to indistinct H-type vs. L-type distributions. The Gd_N/Gd_N^* vs. Eu_N/Eu_N^*, Ce_N/Ce_N^* vs. Eu_N/Eu_N^*, and Nd_N/Sm_N vs. Gd_N/Sm_N plots show a clustering of the points for Kentucky Plant G. This is not a surprise since a common coal source was used to produce all of those ashes. In contrast, while the other fly ashes all were the product of the combustion of PRB coals, the broader elemental distributions were the consequence of coal deliveries from different mines or, at least, different times than the coal deliveries to Plant G.

Overall, the signatures of the REE distributions are immutably the consequence of the different and varying modes of emplacement of REE into coals.[45-46, 56] Coals from the same basin might have similar patterns, but differences, however subtle, in the patterns are the rule. An extraordinary event, such as the volcanic ash deposit (tonstein) in the Fire Clay coal, might not be repeated in volume, distribution, or at all in any other coal in the basin. There is no reason to expect that another coal bed at the same location would be equally enriched, and, without the proper level of exploration, there is no justification to extrapolate results, good or bad, from one location to another within the same coal bed. As with most other elements, the concentrations of REE in the fly ash are the product of the input coals with the modification of the combustion and ash-collection systems. During the combustion process, the lanthanides present within coal will partition exclusively to the fly ash and bottom ash at a coal-burning power plant.[64-65] Nevertheless, the extraordinary complexity of a modern coal-fired power plant, often employing coal preparation, fuel additives, and various sorbents, can complicate interpretation of rare earth distributions found in the fly ash.

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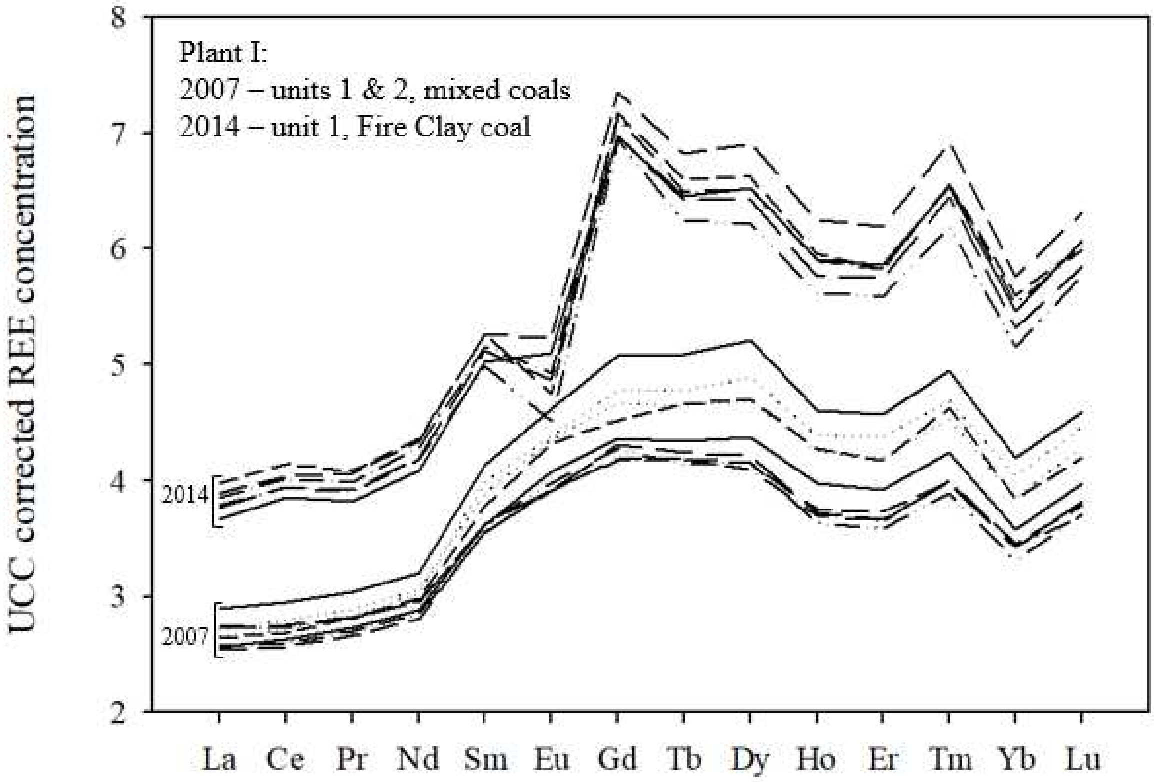
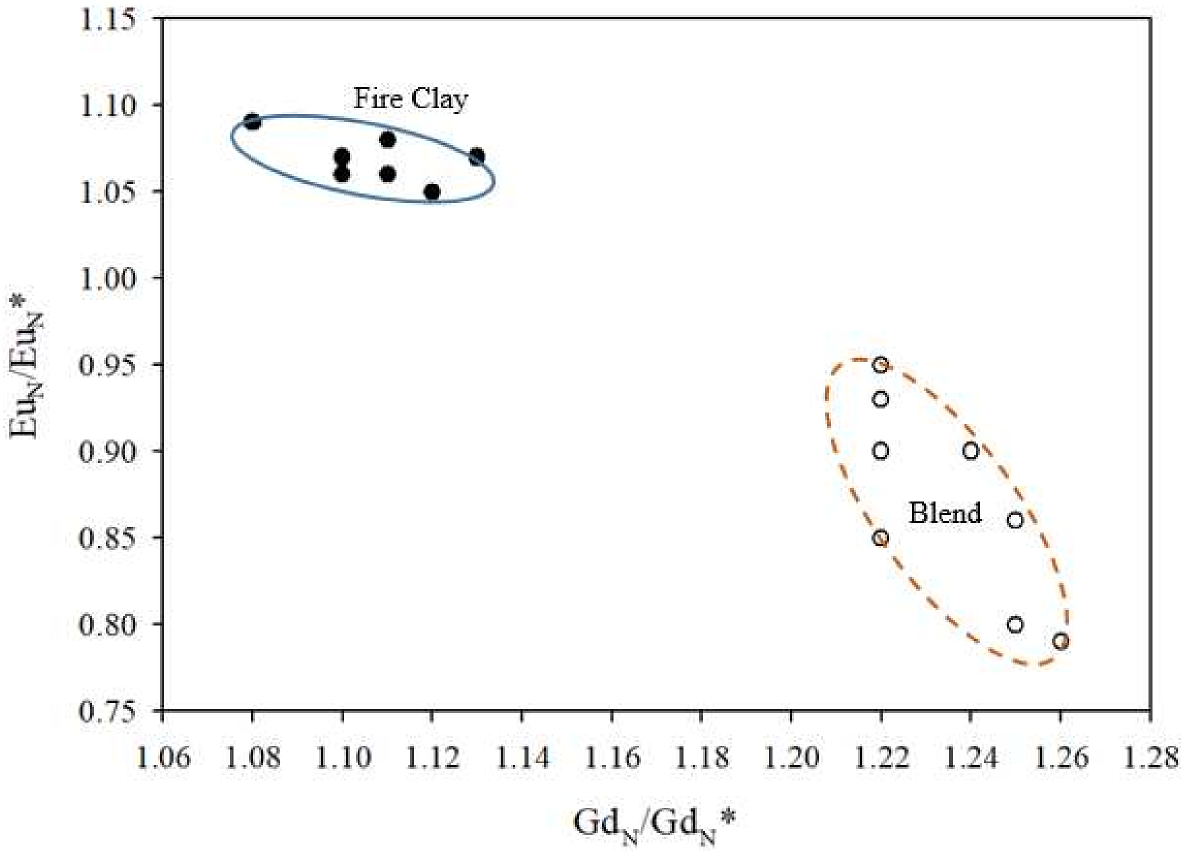
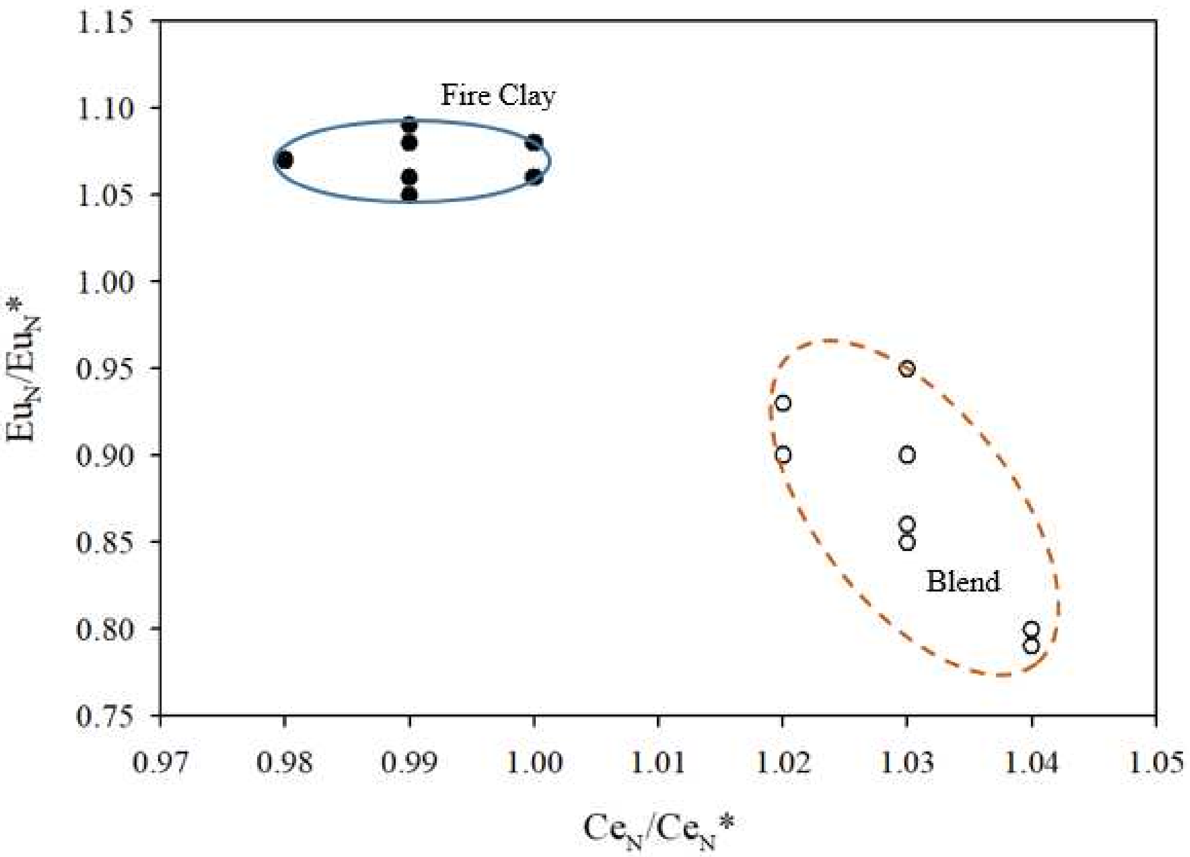
Figure captions:



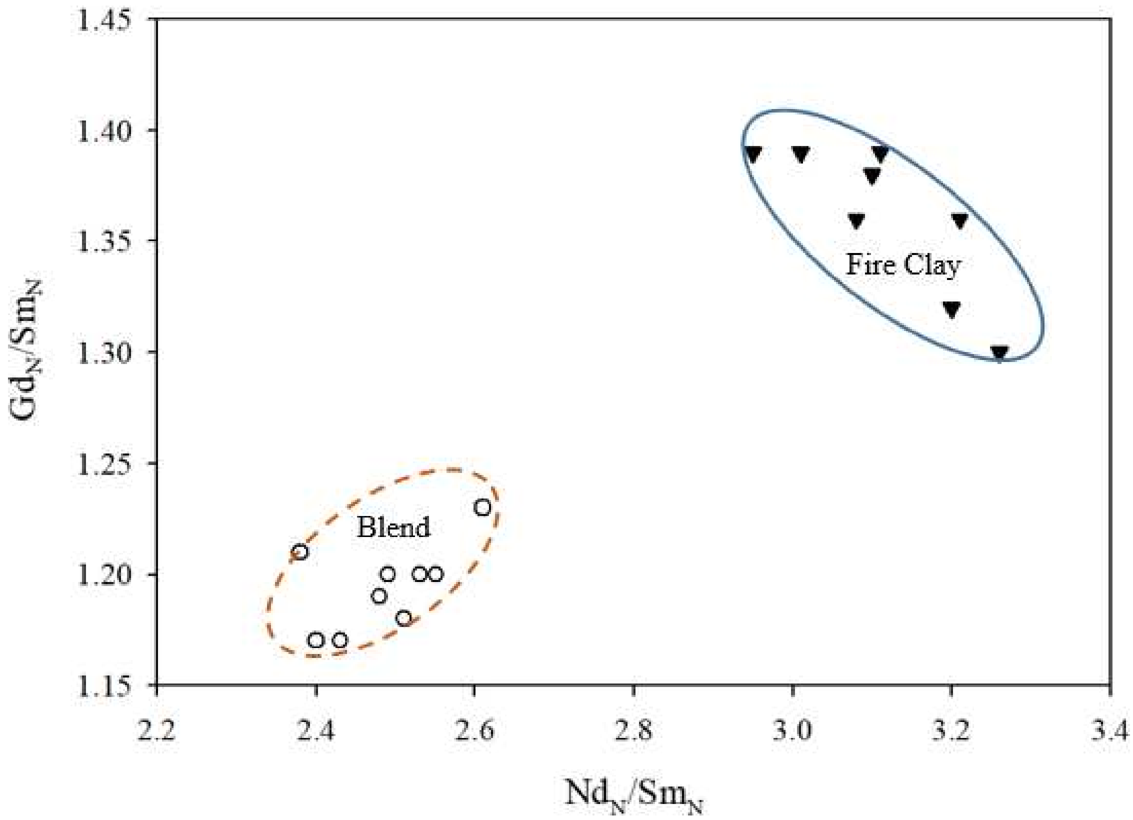
1. Upper continental crust-corrected rare earth concentrations (after McLennan and Taylor[38]) for the fly ashes from the combustion of an Eastern Kentucky coal blend collected in 2007 and the Fire Clay coal collected in 2014. The collections were from units 1 and 2 (2007) and unit 1 (2014) of Kentucky Plant I.



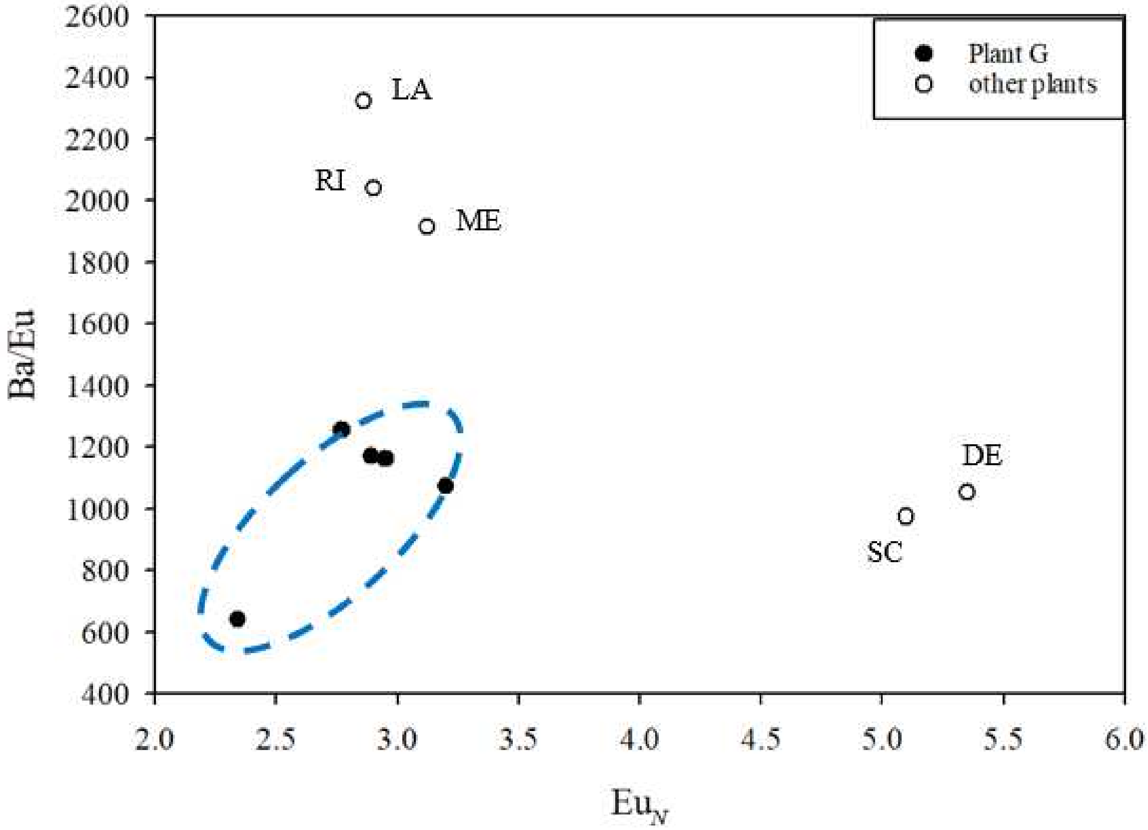
2. Gd_N/Gd_N* vs. Eu_N/Eu_N* for the fly ashes from the combustion of an Eastern Kentucky coal blend collected in 2007 and the Fire Clay coal collected in 2014.



3. Ce_N/Ce_N* vs. Eu_N/Eu_N* for the fly ashes from the combustion of an Eastern Kentucky coal blend collected in 2007 and the Fire Clay coal collected in 2014.



4. Nd_N/Sm_N* vs. Gd_N/Sm_N* for the fly ashes from the combustion of an Eastern Kentucky coal blend collected in 2007 and the Fire Clay coal collected in 2014.



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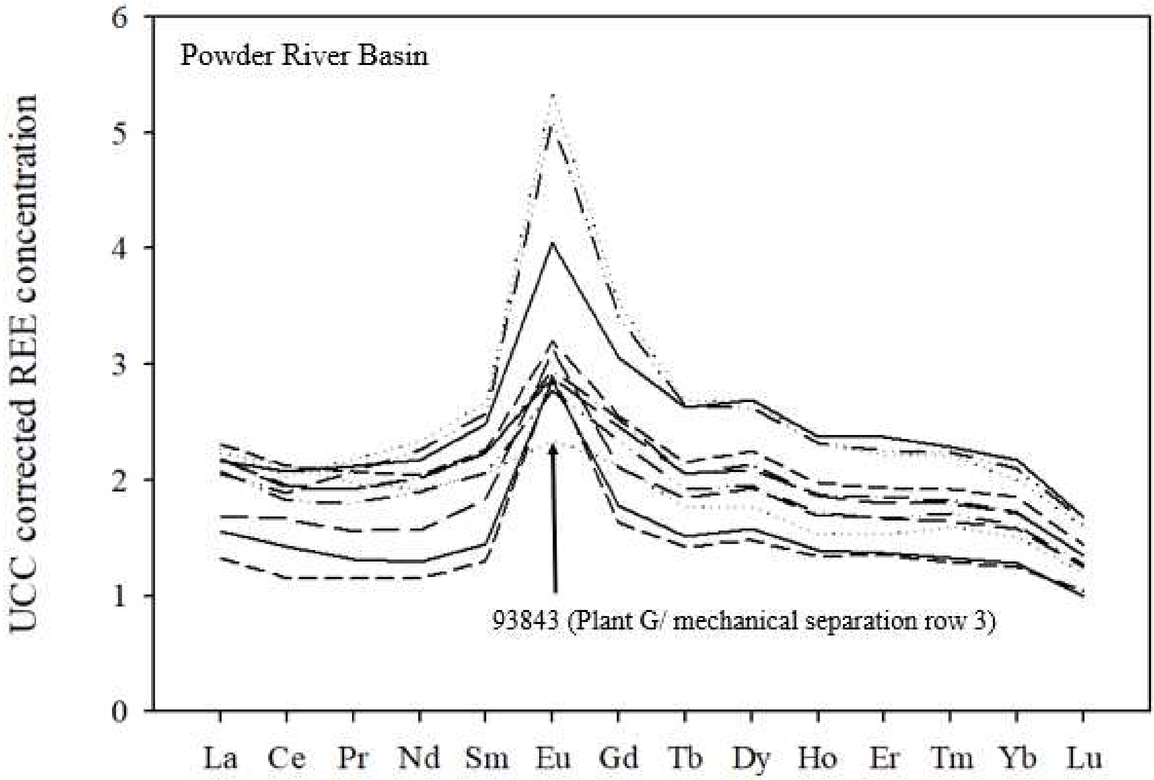
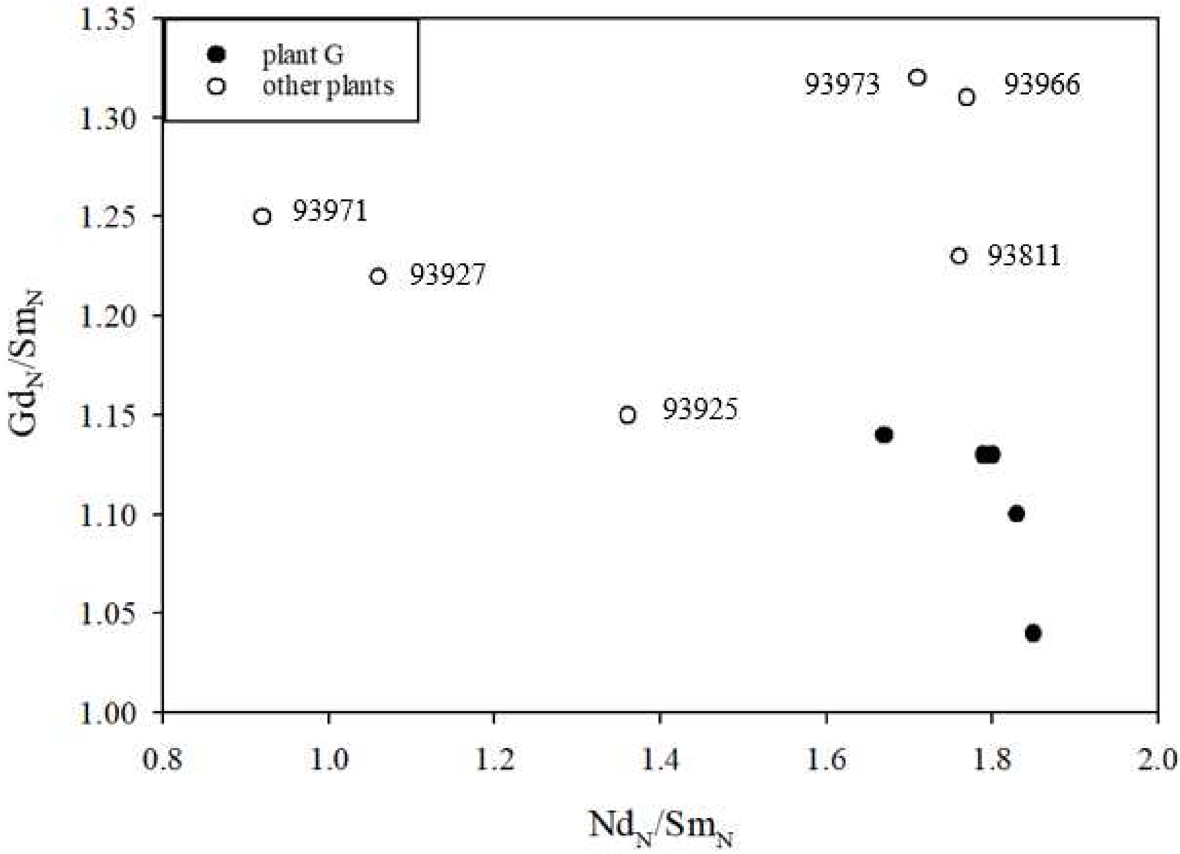
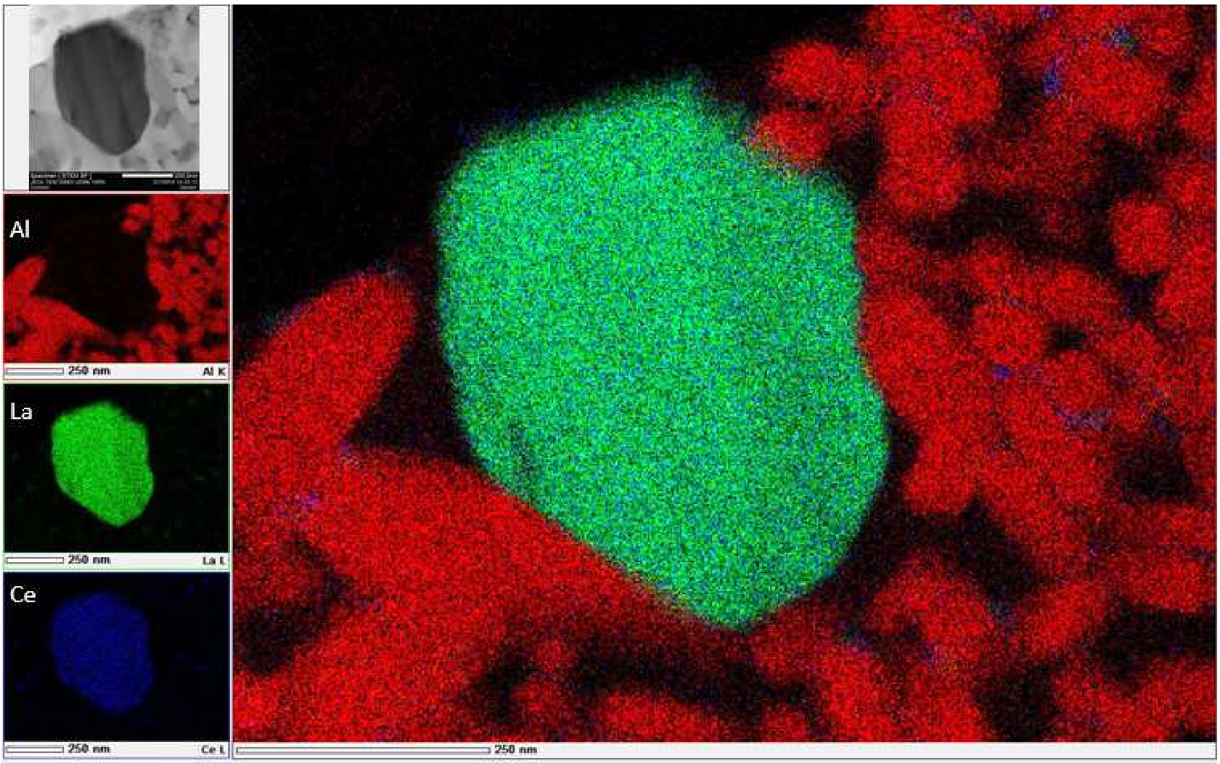
536 5. Eu$_N$ vs. Ba/Eu for Powder River Basin coal-derived fly ashes.



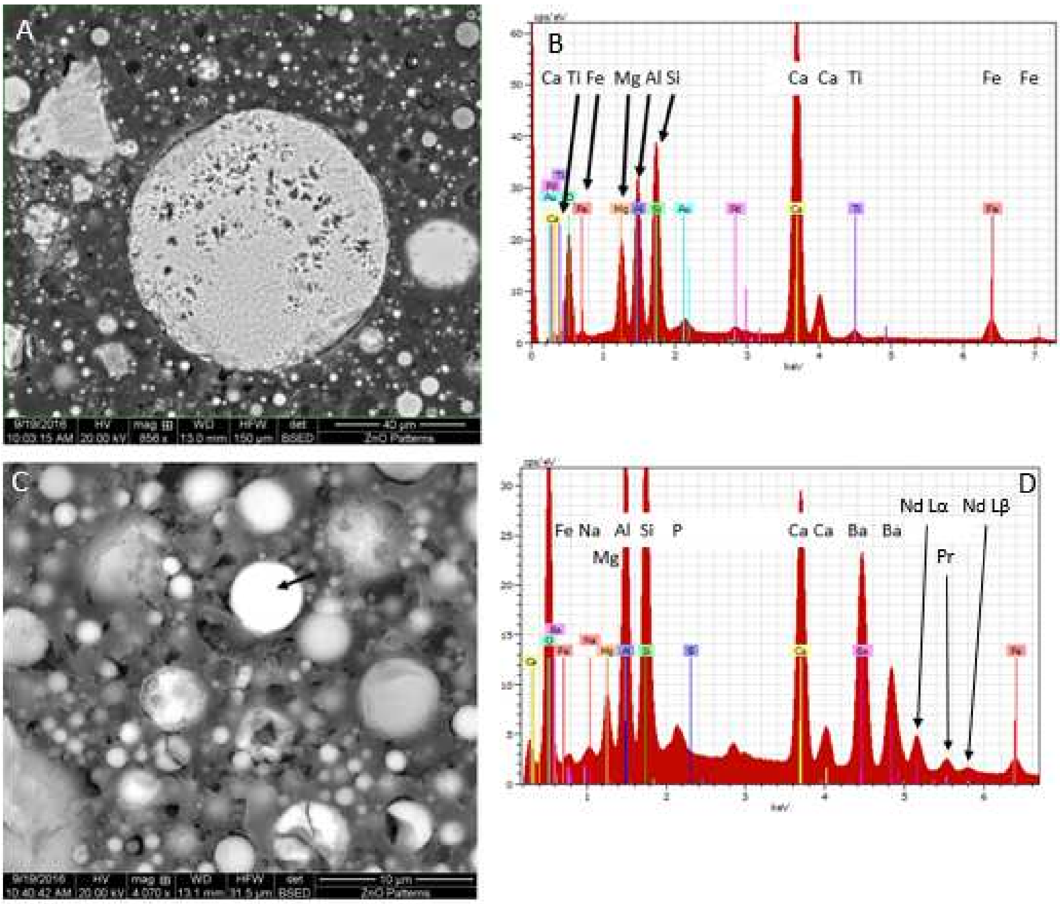
6. Upper continental crust-corrected rare earth concentrations (after McLennan and Taylor[38]) for the fly ashes from the combustion of subbituminous Powder River Basin coals.



7. Nd_N/Sm_N* vs. Gd_N/Sm_N* for the fly ashes from the combustion subbituminous Powder River Basin coals.



8. Cerium, La, and Al elemental map for a davidite crystal in a stoker ash from the combustion of a high-REE central Appalachian coal.[59]



9. Back-scatter image (A) and energy-dispersive spectroscopy scan (B) for Mg-Ca-Al-Si sphere from a Powder River Basin coal-derived fly ash. Back-scatter image (C) and energy-dispersive spectroscopy scan (D) for Nd- and Pr-bearing grain from a Powder River Basin coal-derived fly ash. Both from study by Hood et al.[51]

Supplementary data. Selected analyses from Taggart et al.,[33] supplemented by ultimate analysis, major oxide, and selected minor element data from the Center for Applied Energy Research.