Article

Notes on the Potential for the Concentration of Rare Earth Elements and Yttrium in Coal Combustion Fly Ash

James C. Hower [1,*], John G. Groppo [1], Kevin R. Henke [1], Madison M. Hood [1], Cortland F. Eble [2], Rick Q. Honaker [3], Wencai Zhang [3] and Dali Qian [1,4]

[1] Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511, USA; E-Mails: john.groppo@uky.edu (J.G.G.); kevin.henke@uky.edu (K.R.H.); madison.hood@uky.edu (M.M.H.); dali.qian@uky.edu (D.Q.)

[2] Kentucky Geological Survey, Lexington, KY 40506, USA; E-Mail: eble@uky.edu

[3] Department of Mining Engineering, University of Kentucky, Lexington, KY 40506, USA; E-Mails: rick.honaker@uky.edu (R.Q.H.); wencai.zhang@uky.edu (W.Z.)

[4] Electron Microscopy Center, Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506, USA

* Author to whom correspondence should be addressed; E-Mail: james.hower@uky.edu; Tel.: +1-859-257-0261.

Abstract: Certain Central Appalachian coals, most notably the Fire Clay coal with a REY-enriched volcanic ash fall tonstein, are known to be enriched in rare earth elements. The Fire Clay tonstein has a greater contribution to the total coal + parting REY than would be inferred from its thickness, accounting for about 20%–35% of the REY in the coal + parting sequence. Underground mining, in particular, might include roof and floor rock and the within-seam partings in the mined product. Beneficiation, necessary to meet utility specifications, will remove some of the REY from the delivered product. In at least one previously published example, even though the tonstein was not present in the Fire Clay coal, the coal was enriched in REY. In this case, as well as mines that ship run-of-mine products to the utility, the shipped REY content should be virtually the same as for the mined coal. At the power plant, however, the delivered coal will be pulverized, generally accompanied by the elimination of some of the harder rock, before it is fired into the boiler. Overall, there are a wide range of variables between the geologic sample at the mine and the power plant, any or all of which could impact the concentration of REY or other critical materials in the coal combustion products.

1. Introduction

Central Appalachian coals, in particular the Middle Pennsylvanian Fire Clay coal in Eastern Kentucky and Southern West Virginia, are known to be relatively enriched in rare earth elements (REE); or rare earth + yttrium (REY) if Yttrium is included. The Fire Clay coal stands out because it includes a volcanic ash-derived parting or tonstein [1], which has a high REY content [2,3]. Portions of the coal above and, in particular, below the tonstein are also enriched in REY [2]. In some cases where the tonstein is not present, the coal is still enriched in REY [3]. Comparing average ash-basis REYs from five major coals (Table 1, after Bragg *et al*. [4]), it can be seen that the Fire Clay coal and its correlatives have a higher total REY than the other coals.

Table 1. Averages (ash-basis ppm) of rare earth elements and yttrium for five major eastern Kentucky coals. Based on data compiled by [4]. The Clintwood Gd average contains one value of 173 ppm, far higher than the other Gd values. Avg: average; st dev: standard deviation.

Coal Bed		Dry Ash	Whole Coal Basis															Ash Basis	
			Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y + REE	Y + REE
Coalburg	avg	11.28	8.7	11.1	21.2	6.5	11.3	1.9	0.4	1.7	0.4	2.1	0.6	1.0	0.4	1.2	0.2	68.6	668.3
(no. = 104)	*st dev*	*5.41*	*4.3*	*5.0*	*9.1*	*3.9*	*5.3*	*0.7*	*0.2*	*1.2*	*0.1*	*1.4*	*0.3*	*0.6*	*0.2*	*0.4*	*0.1*	*26.1*	*241.6*
Leatherwood	avg	11.02	10.0	13.1	24.7	6.0	13.8	2.2	0.5	1.8	0.4	2.2	0.6	1.1	0.4	1.4	0.2	78.3	789.5
(no. = 38)	*st dev*	*6.22*	*5.2*	*8.0*	*13.8*	*3.9*	*9.9*	*1.2*	*0.2*	*1.2*	*0.2*	*1.4*	*0.3*	*0.9*	*0.2*	*0.6*	*0.1*	*40.3*	*287.2*
Fire Clay	avg	11.46	11.8	17.9	33.9	7.1	17.9	2.9	0.5	2.7	0.6	2.8	0.6	1.4	0.4	1.7	0.2	102.5	921.9
(no. = 41)	*st dev*	*5.64*	*8.1*	*9.9*	*18.9*	*4.8*	*15.6*	*1.4*	*0.2*	*3.4*	*0.3*	*2.0*	*0.4*	*1.2*	*0.3*	*0.7*	*0.1*	*58.8*	*319.9*
Pond Creek	avg	7.24	5.0	6.4	12.2	4.2	6.0	1.1	0.3	1.1	0.2	1.3	0.4	0.6	0.2	0.8	0.1	39.8	550.5
(no. = 46)	*st dev*	*4.13*	*3.2*	*5.4*	*9.5*	*2.9*	*6.7*	*0.8*	*0.2*	*1.0*	*0.1*	*0.8*	*0.2*	*0.5*	*0.1*	*0.4*	*0.0*	*29.4*	*213.2*
Clintwood	avg	6.89	5.4	7.2	13.1	3.6	6.9	1.2	0.3	1.4	0.2	1.2	0.3	0.6	0.2	0.8	0.1	42.5	676.9
(no. = 40)	*st dev*	*4.05*	*2.8*	*4.5*	*8.1*	*2.1*	*4.4*	*0.7*	*0.2*	*2.1*	*0.1*	*0.6*	*0.2*	*0.5*	*0.1*	*0.4*	*0.0*	*21.5*	*271.0*
all	avg	9.91	7.9	10.5	20.1	5.6	10.3	1.8	0.5	1.7	0.4	1.9	0.6	1.0	0.4	1.2	0.2	63.2	687.6
(no. = 788)	*st dev*	*5.60*	*4.7*	*7.3*	*14.1*	*4.1*	*8.1*	*1.7*	*1.4*	*2.1*	*1.4*	*1.8*	*1.4*	*1.5*	*1.4*	*1.5*	*1.4*	*37.1*	*296.2*

The potential for the concentration of REY in coal combustion products (CCPs) has been investigated in a number of coal fields [3,5–7]. In principal, the REY are conserved in the combustion process, meaning that they are not among the volatile elements and not particularly vulnerable to loss with flue gas. The concentration of REY in the feed coal should be proportional to the REY in the coal combustion products, therefore, coals with high REY, such as the Pennsylvanian Fire Clay coal in Eastern Kentucky, should yield CCPs with high REY [2,3]. Indeed, for the Fire Clay-coal-derived CCP's investigated by Mardon and Hower [3], the REY content of the bottom ash did not differ greatly from the concentrations in the fly ash and the REY concentrations in fly ashes from individual rows in the ash collection system were similar, all generally within 10%–20% of each other. In contrast, volatile trace elements can vary by several 100% from the first electrostatic precipitator row to the last row [3].

For the current investigation, coal and a composite fly ash were collected at two power plants. In addition, a composite bottom ash sample was collected at one plant. In both cases, the power plant was burning a coal blend dominated by the eastern Kentucky Fire Clay coal.

2. Methods

The samples were analyzed for moisture and ash following American Society for Testing and Materials (ASTM) standard methods. The REY content was analyzed by Inductively Coupled Plasma—Mass Spectroscopy using sinter methods adapted from U.S. Geological Survey procedures [8].

Elemental studies of selected samples were conducted on a Zeiss EVO-MA10 SEM (Zeiss, Jena, Germany), coupled with back-scatter electron (BSE) detector and a Bruker energy-dispersive (EDS) detector, which was operated at 20/25 keV. In some cases, potential mineral grains were first identified using optical microscopy in the CAER Applied Petrology Laboratory. For this purpose, the ash was mounted in 2.54-cm diameter pellets and prepared to a 0.05-micron final polish. The pellets were examined using reflected-light, oil-immersion optics at a final magnification of 500×. Promising grains were circled using a diamond-tip indenter and photographed using a Spot Insight 4 digital camera.

Selected samples were examined by powder X-ray diffraction (XRD) at the University of Kentucky Center for Applied Energy Research. If required, the samples were ground by hand in a ceramic mortar and pestle just before XRD analysis. The powdered samples were then dry mounted in aluminum holders. The samples were scanned at 8°–60° 2θ with copper K-α radiation on a Philips X'Pert diffractometer (model PW3040-PRO, Amsterdam, The Netherlands) operating at 45 kilovolts (kV) and 40 milliamps (mA). Crystalline substances or "minerals" were identified in the diffractograms with an International Centre for Diffraction Data (ICDD, Newtown Square, PA, USA) powder diffraction (PDF) database.

Coal and fly ash petrology was using oil-immersion, reflected-light optics on epoxy-bound 2.54-cm diameter particulate pellets prepared to a final 0.05-micron polish. Maceral nomenclature followed International Committee for Coal Petrology (ICCP) [9,10] and fly ash nomenclature followed Hower [11].

3. Results and Discussion

The Mardon and Hower [3] study has proven to be something of a benchmark for US-based REY-enrichment investigations. The study was originally planned as a single-seam, single-mine investigation of the partitioning of mercury; the added focus on rare earth elements was serendipitous, a function of the use of a Fire Clay coal correlative as the source coal. There are unique features of the study which need to be considered when comparing the results with REY concentrations in fly ash from other power plants. Unlike most other Fire Clay sites, the Mardon and Hower [3] Fire Clay coal site did not have the REY-rich tonstein. Instead, the part of the coal where the parting would usually be found had a high concentration of REY. In one sense, the presence or absence of the tonstein in the coal made no difference since the utility contracted to purchase unbeneficiated, run-of-mine coal from the mine. As long as the run-of-mine coal met the contracted ash/sulfur/heating value (and, in some cases, other parameters, such as chlorine and grindability) specifications, it would have been shipped to the utility. The utility does pulverize the coal, so some rock would have been rejected by the pulverizer. In contrast, the underground mines producing Fire Clay coal will typically mine some of the roof and floor rock in addition to all of the partings. The coal + rock is beneficiated, leaving the REY-enriched

tonstein with the refuse at the power plant. Rock shipped with the coal to the power plant might be rejected in pulverization, as noted above. Therefore, the Mardon and Hower [3] Fire Clay coal would have had a higher concentration of REY than the Fire Clay coal typically burned by power plants.

In order to understand the influence of the different geologic settings and mining/beneficiation scenarios, we examined three examples of the distribution of REY within the Fire Clay coal bed (Table 2). In the KCER-5499 to -5504 sequence from the Mardon and Hower [3] study, the flint clay parting is absent but the REY signature is present in the lower four benches of the coal. The KCER-4754 to -4767 is an example of the flint clay tonstein directly overlaying coal while the tonstein overlays an illitic clay in the KCER-4706 to -4714 sequence [2]. In both of the latter two sequences, the coal benches, with one exception, have a higher *ash-basis* REY than the flint clay. The flint clay parting, however, always has higher *whole-sample* REY content than the coals. In the KCER-4754 to -4767 sequence, the flint clay, with less than 10% of the total seam thickness, accounts for over 20% of the total REY. Therefore, the flint clay parting, despite having a REY concentration diluted by the abundance of minerals with negligible REY content, still makes a significant contribution of REY to the overall amount of REY in the entire coal + parting sequence.

For the current study, the power plant feed coals have different sources, as indicated by the vitrinite maximum reflectances (Table 3). The higher reflectance (higher rank) of the plant W feed coal is known to have been mined in Southern Leslie County, Kentucky, closer to the higher-rank portions of the coalfield. The plant I coal was mined further to the north-northwest, a lower rank region. The maceral percentages are not unique enough to be diagnostic indicators of the coal source.

The fly ash petrology (Table 4) is dominated by glass, much of it rounded, as is typical of pulverized-coal-derived fly ashes, but with a small percentage of angular glassy particle, as seen on the left-center of Figure 1. Fly ash carbons, including both inertinite passed along from the feed coal and neoformed carbons from the melting and re-polymerization of macerals, are significantly more abundant in the plant I fly ash than in the plant W ash.

The REY concentrations in the feed coal and combustion products for the two power plants are shown in Table 5. As noted above, the coal blends were dominated by Fire Clay coal. However, the utilities, in contracting for the coal, did specify that the Fire Clay should constitute the majority of blend, but they had less control of the coal and mine selection process than was present for the Mardon and Hower [3] study. The feed coal REY concentrations are lower than published REY values for the Fire Clay coal (for example, the average Fire Clay REE and REY in Table 1 from Bragg *et al*. [4] and Table 2 values from Hower *et al*. [2] and Mardon and Hower [3]). Caution must be exercised in comparing geologic samples to the mined, beneficiated (or not beneficiated), and shipped product. While thicker partings should be excluded from the geologic sample, even the thin partings could be beneficiated out of the coal destined for a power plant. As noted above, the objective of the beneficiation is to produce a coal product meeting or slightly exceeding the contract specifications. To date, for US coals and utilities, the REY concentration has not been a contracted parameter. In addition to the exclusion (or inclusion as misplaced material) of in-seam or of out-of-seam rock in the shipped product, the Fire Clay-derived REY concentration could also be diluted through the inclusion of other coals with lower REY concentrations. Despite these caveats, the ash-basis fly ash REY concentrations of 774 and 899 ppm, while lower than the range seen in the Mardon and Hower [3] fly ashes, are among the best REY concentrations observed in our studies to date.

Table 2. Rare earth elements and yttrium for three distinct settings of the Fire Clay coal: (1) samples 5499-5504—no tonstein parting but high REY concentrations [3], (2) samples 4706-4714—tonstein overlying an illitic clay parting [2], and (3) samples 4754-4767—tonstein without an illitic clay parting.

| KCER # | Bench # | Ad Ash | Sample Thickness (cm) | % of Total Thickness | % of Total Thickness without Partings | Rare Earth Element (Ash Basis; ppm) | | | | | | | | | | | | | | REY | Ash (weighted averages) | whole sample Y + REE (ppm) |
						Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb			
5499	1 of 6 (top)	19.78	17.0	16.6	16.6	56.1	80.7	148	17	63	13.1	2.4	10.1	1.8	12.4	2.6	7.5	1.8	7	424		84
5500	2 of 6	4.55	19.8	19.4	19.4	143	114	256	31.8	129	32.3	4.3	25.7	4.5	30.2	6.1	16.6	3.8	13.9	811		37
5501	3 of 6	2.41	23.1	22.6	22.6	351	499	1020	121	449	90.3	7.6	65.8	11.2	70.6	13.3	37.9	8.9	33.4	2779		67
5502	4 of 6	5.67	16.0	15.6	15.6	328	407	851	101	375	76.8	6.8	60	10.4	67.3	13	37.1	8.8	31.9	2374		135
5503	5 of 6	10.35	17.0	16.6	16.6	232	399	822	94.6	349	71.3	6	52.4	9	58.7	11	31.9	7.4	27.3	2172		225
5504	6 of 6	11.48	9.4	9.2	9.2	208	366	755	89.8	323	67.1	5.4	50.1	9	59.1	11.5	34.2	8.2	31.6	2018		232
whole channel ash (as determined basis, weighted average)																					8.37	
total whole-coal basis Y + REE (ppm)																						116
total ash-basis Y + REE																				1384		
4706	1 of 7 (top)	2.24	20.6	16.1	20.9	630	220	390	47	190	46	10	60	10	78	17	55	8	54	1815		41
4707	2 of 7	3.47	12.4	9.8	12.6	210	240	460	53	200	40	5	40	5	33	6	19	3	17	1331		46
4708	3 of 7	4.78	15.0	11.8	15.2	210	200	100	49	180	40	5	40	6	36	7	20	3	17	913		44
4709	4 of 7	5.76	7.6	6.0	7.7	230	190	360	44	170	38	4	40	6	38	7	22	3	19	1171		67
4710	5 of 7	16.84	7.9	6.2	8.0	120	170	310	36	130	26	3	20	4	25	7	14	2	13	880		148
4711	6 of 7	9.73	22.6	17.7	22.9	330	430	820	96	350	71	6	70	10	67	13	40	6	38	2347		228
4712	flint clay	83.14	14.0	11.0		47	90	190	24	90	19	1	20	2	14	2	6	0.8	5	511		425
4713	illitic clay	91.85	15.0	11.8		15	70	120	14	50	11	2	9	1	8	2	4	0.7	4	311		285
4714	7 of 7	11.05	12.4	9.8	12.6	320	240	500	60	240	53	9	50	9	64	13	43	7	43	1651		182
whole channel ash (as determined basis, weighted average)																					25.35	

Table 2. *Cont.*

| KCER # | Bench # | Ad Ash | Sample Thickness (cm) | % of Total Thickness | % of Total Thickness without Partings | Rare Earth Element (Ash Basis; ppm) | | | | | | | | | | | | | | | Ash (weighted averages) | whole sample Y + REE (ppm) |
						Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	REY		
whole channel ash, excluding partings (as determined basis, weighted average)																					7.05	
total whole-coal-basis Y + REE with partings (ppm)																						168
total whole-coal-basis Y + REE without partings (ppm)																						113
% total whole-coal basis Y + REE without partings/% total whole-coal basis Y + REE with partings																						*67.6*
4754	1 of 11 (top)	3.87	10.4	8.3	9.2	390	140	270	33	130	36	8	40	9	58	12	36	5	33	1200		46
4755	2 of 11	10.26	10.4	8.3	9.2	97	60	110	12	50	10	2	10	2	10	2	6	0.8	5	377		39
4756	3 of 11	3.68	9.9	7.9	8.7	190	250	470	54	190	42	5	40	6	37	7	20	3	18	1332		49
4757	4 of 11	13.14	13.0	10.3	11.4	79	140	240	28	90	20	3	20	3	18	4	11	2	10	668		88
4758	5 of 11	6.58	9.4	7.5	8.3	210	180	370	44	160	36	4	30	6	35	6	19	3	17	1120		74
4759	6 of 11	4.79	12.7	10.1	11.2	340	240	470	57	210	49	5	50	8	51	10	30	4	27	1551		74
4760	7 of 11	10.29	18.0	14.3	15.9	200	270	500	58	200	44	4	40	7	46	9	30	5	29	1442		148
4761	flint clay	83.85	12.4	9.9		49	110	200	24	90	19	1	20	2	13	2	6	0.8	4	541		453
4762	8 of 11	10.01	9.4	7.5	8.3	430	790	1500	100	660	150	13	130	22	130	25	75	11	72	4108		411
4763	9 of 11	25.26	11.4	9.1	10.1	110	110	210	25	90	22	4	20	4	28	6	18	3	17	667		168
4765	10 of 11	25.08	4.6	3.6	4.0	120	110	200	26	100	36	6	20	4	24	5	15	2	13	681		171
4767	11 of 11	9.69	4.1	3.2	3.6	320	160	360	47	190	51	12	50	10	61	12	36	5	34	1348		131
whole channel ash (as determined basis, weighted average)																					20.44	
whole channel ash, excluding partings (as determined basis, weighted average)																					13.62	
total whole-coal-basis Y + REE with partings (ppm)																						155
total whole-coal-basis Y + REE without partings (ppm)																						123
% total whole-coal basis Y + REE without partings/% total whole-coal basis Y + REE with partings																						*79.3*

Table 3. Feed coal petrology. Macerals not encountered are not listed in the table. Note that the vitrinite maceral subgroups are totaled along with the total vitrinite percentage. The inertinite, liptinite, and mineral percentages are listed along with the individual percentages of the macerals and minerals. Vitrinite maximum (Rmax) and random (Rrandom) reflectances and their respective standard deviations are also listed for each coal.

Plant	Sample #	Telinite	Collotelinite	Total Telovitrinite	Total Detrovitrinite	Total Gelovitrinite	Total Vitrinite	Fusinite	Semifusinite	Micrinite	Macrinite	Total Inertinite	Sporinite	Cutinite	Resinite	Total Liptinite	Silicate	Sulfide	Carbonate	Other	Total Mineral	Rmax	st dev	Rrandom	st dev
W	93931	10.4	35.6	46.0	11.4	8.0	65.4	9.0	7.4	5.4	0.2	22.0	8.0	0.6	0.6	9.2	2.8	0.6	0.0	0.0	3.4	0.91	0.06	0.84	0.06
		10.8	36.9	47.6	11.8	8.3	67.7	9.3	7.7	5.6	0.2	22.8	8.3	0.6	0.6	9.5									
I	93939	10.0	43.4	53.4	10.6	3.4	67.4	5.8	7.2	2.2	1.6	16.8	6.2	2.4	0.4	9.0	5.4	1.2	0.0	0.2	6.8	0.76	0.09	0.69	0.09
		10.7	46.6	57.3	11.4	3.6	72.3	6.2	7.7	2.4	1.7	18.0	6.7	2.6	0.4	9.7									

Table 4. Fly ash petrology (volume percent; t = trace).

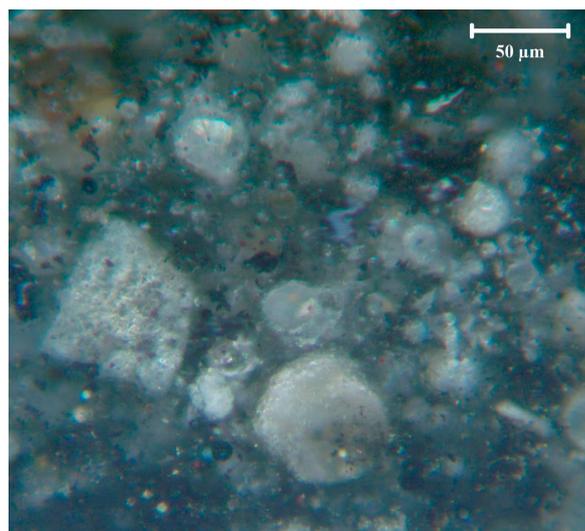| Sample	93932	93951
Plant	Plant W	Plant I
Material type	fly ash	fly ash
glass	89.6	64.5
mullite	0.0	2.0
spinel	1.2	8.5
quartz	2.0	0.0
sulfide	0.8	1.0
rock fragment	t	0.0
isotropic coke	0.4	6.5
anisotropic coke	4.8	13.5
inertinite	1.2	4.0

Figure 1. Plant W fly ash with both rounded and angular glass particles. Image 93932 FA 06.

An SEM image of fly ash from the plant W fly ash with the element analysis results is shown in Figure 2. Using Ce as a proxy for the entire REY suite, detectable amounts of REY are seen in what appears to be a Fe oxide. Hower *et al.* [12] and Dai *et al.* [7] have also demonstrated that REY can be detected in the fly ash glass, at least as part of the glass, if not as mineral phases included within the glass. REY elements were observed in the bottom ash glass from another sampling date at plant I.
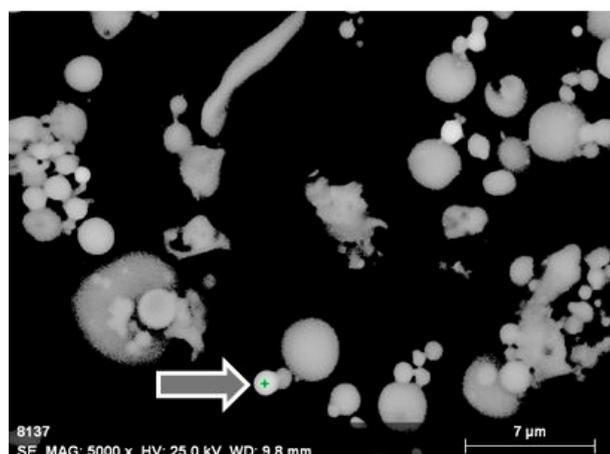

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Spectrum: MA73764-Williams flyash_EDS_point#2.spx

Element      Series   unn. C norm. C Atom. C Error
                      [wt.%]  [wt.%]  [at.%]   [%]
--------------------------------------------------
Oxygen     K-series   29.78   34.71   59.37  28.9
Aluminium  K-series    6.89    8.03    8.15   0.4
Silicon    K-series    7.46    8.69    8.47   0.4
Potassium  K-series    0.33    0.39    0.27   0.0
Calcium    K-series    0.74    0.86    0.59   0.1
Titanium   K-series    0.16    0.19    0.11   0.0
Iron       K-series   40.27   46.92   23.00   1.1
Cerium     L-series    0.18    0.21    0.04   0.0
--------------------------------------------------
           Total:     85.82  100.00  100.00
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Figure 2. Scanning electron microscope image of plant W fly ash with accompanying element analysis.

The XRD runs show the major minerals in relative concentrations. No attempt was made to separate or concentrate minerals by density or other parameters. For example, the plant W Appalachian feed coal only shows the presence of quartz and clay minerals (kaolinite and illite). The fly ash XRD patterns are dominated by glass, which, as a non-crystalline material, is represented as a broad, amorphous background pattern. Quartz and mullite were the prominent minerals in the plant W fly ash. In addition to the latter minerals, hematite and possibly lime were detected in the plant I unit 1 fly ash. Without extensive separation and concentration methods, XRD is not sensitive enough to detect trace amounts (<<1 wt %) of REE-bearing and other minerals.

Table 5. Moisture (% as-received basis), ash (% dry basis), major oxides (% ash basis), minor elements (ppm, ash basis) and rare earth elements and yttrium (ppm, ash basis) for two power plants burning coal blends dominated by the Fire Clay coal.

Sample	Plant	Unit	Sample Type	Moisture	Ash	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	Na$_2$O	K$_2$O	P$_2$O$_5$	TiO$_2$	SO$_3$
93931	W	1	Feed Coal	5.24	13.40	54.17	29.53	7.09	1.80	1.00	0.32	2.29	0.50	1.71	0.90
93932	W	1	Fly Ash	0.19	96.12	54.21	28.43	7.60	4.01	1.07	0.32	2.26	0.54	1.60	0.09
93933	W	1	Bottom Ash	8.29	100.00	49.96	28.62	11.54	3.85	1.13	0.17	2.12	0.67	1.20	<0.1
93939	I	1	Feed Coal	6.00	12.45	48.09	26.25	15.46	2.97	1.21	0.19	2.64	0.21	1.12	2.15
93951	I	1	Fly Ash	11.24	95.67	53.47	29.91	8.46	1.50	0.82	0.20	1.81	0.36	1.72	0.20

Sample	Plant	Unit	Sample Type	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Zr	Mo	Cd	Sb	Ba	Pb
93931	W	1	Feed Coal	536	170	212	90	147	235	174	60	324	1213	304	170	<1	6	1182	84
93932	W	1	Fly Ash	486	156	223	82	137	181	177	73	355	1175	302	152	1	6	1273	81
93933	W	1	Bottom Ash	322	130	393	63	130	102	92	2	510	1624	260	47	1	1	2198	76
93939	I	1	Feed Coal	301	152	200	44	159	136	177	162	226	672	255	68	2	8	839	115
93951	I	1	Fly Ash	516	168	114	55	110	204	113	124	221	1047	360	153	<1	5	1253	100

Sample	Plant	Unit	Sample Type	Y	La	Ce	Pr	Nd	Sm	*LREE*	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	*HREE*	REY (1)	REY (2)	LREE/HREE
93931	W	1	Feed Coal	102	99	208	67	99	26	*499*	6	14	11	18	14	20	7	10	6	*105*	95	706	4.76
93932	W	1	Fly Ash	110	108	224	79	111	28	*551*	7	15	12	20	15	22	7	11	6	*113*	744	774	4.85
93933	W	1	Bottom Ash	123	114	247	84	128	33	*606*	8	19	12	21	2	20	6	12	8	*108*	834	837	5.64
93939	I	1	Feed Coal	129	133	276	52	99	49	*607*	5	36	23	26	13	26	11	15	5	*161*	112	897	3.76
93951	I	1	Fly Ash	124	141	304	66	121	34	*667*	5	29	8	24	5	14	2	15	5	*108*	860	899	6.18

(1) ppm whole sample basis

(2) ppm ash basis

4. Summary

Some Central Appalachian coals are known to be enriched in rare earth elements; the Fire Clay coal in eastern Kentucky, with a REY-enriched volcanic ash fall tonstein, is among the best-known REE source in the region. The tonstein has a greater contribution to the total coal + parting REY than would be immediately inferred from its thickness, accounting for about 20%–35% of the REY in the coal + parting sequence. In cases where the coal is beneficiated, much of the partings and the roof and floor rocks mined with the coal are removed from the shipped clean coal product, leaving their portion of the REY at the preparation plant. In some cases, such as seen in the Mardon and Hower [3] study, even though the tonstein is not present in the Fire Clay coal, the REY were still enriched compared to most other coal seams in the region. In this case, as well as mines that ship run-of-mine products to the utility, the shipped REY content should be virtually the same as for the mined coal. At the power plant, the delivered coal will be pulverized, generally accompanied by the elimination of some of the harder rock, before it is fired into the boiler.

The scenarios described above describe some of the constraints inherent in translating data from a whole-seam section, with or without partings, to the delivered coal at the power plant and then to the pulverized coal combusted in the boiler. The Bragg *et al*. [4] data for US coals generally do not include rock partings thicker than a prescribed amount, usually 0.375 inches (0.95 cm). For this reason and because we cannot fully account for misplaced material at the preparation plant, we must treat the geologic information as a first approximation of the bottom ash and fly ash chemistry. Therefore, the reported REY concentrations of +/−1500 ppm [3] for the CCP's of burn of run-of-mine, no-tonstein, high-REY Fire Clay coal actually compare favorably with the 775–900-ppm fly ashes produced by plants burning beneficiated Fire Clay coal.

Author contributions

All of the authors have had roles in one or more aspects of the study. James C. Hower and Cortland F. Eble conducted the early-1990s sampling Reference [2]. Hower conducted the Reference [3] sampling and collected samples for the Kentucky portion of Reference [4]. Hower, John G. Groppo, Kevin R. Henke, Cortland F. Eble, Wencai Zhang, and Madison M. Hood were all part of the most recent sampling efforts. James C. Hower and Madison M. Hood were responsible for petrographic data, Kevin R. Henke was responsible for the mineralogy, and Dali Qian was responsible for the microbeam studies. Rick Q. Honaker, John G. Groppo, and Wencai Zhang were responsible for processing of the fly ash. Basically, this is a three-organization effort within the university and all authors have been part of the various discussions that underlie this contribution.

Conflicts of Interest

The authors declare no conflict of interest.

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