



Article Coal Feed-Dependent Variation in Fly Ash Chemistry in a Single Pulverized-Combustion Unit

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Abstract: Four suites of fly ash, all generated at the same power plant, were selected for the study of the distribution of rare earth elements (REE). The fly ashes represented two runs of single-seam/single-mine coals and two runs of run-of-mine coals representing several coal seams from several mines. Plots of the upper continental crust-normalized REE, other parameters derived from the normalization, and the principal components analysis of the derived REE parameters (including the sum of the lanthanides plus yttrium and the ratio of the light to heavy REE) all demonstrated that the relatively rare earth-rich Fire Clay coal-derived fly ashes have a different REE distribution, with a greater concentration of REE with a relative dominance of the heavy REE, than the other fly ashes. Particularly with the Fire Clay coal-derived fly ashes, there is a systematic partitioning of the overall amount and distribution of the REE in the passage from the mechanical fly ash collection through to the last row of the electrostatic precipitator hoppers.

Keywords: lanthanides; sustainability; critical elements; coal combustion

1. Introduction

The concentration of the lanthanide—also known as the rare earth elements (REE)—and other critical elements during coal combustion has made fly ash a potential target for the extraction of metals. Whether through the incidental use of fly ash produced in the routine utility combustion of coal [1–5] or of fly ash produced for the secondary or even express purpose of recovering critical elements [6–9], the latter being a novel addition to the typical power-generation uses of the region's coals, fly ash has some advantages compared to coal in terms of the removal of most of the carbon, the fine size of the material, and the potential availability of decades of fly ash production in landfills at or near the power plants.

The chemistry of the feed coal influences the chemistry of the fly ash. In consideration of Meij's [10] Venn diagram of element partitioning from the feed coal to the ash products, particularly for the low volatility trace elements that tend to concentrate in the fly ash and bottom ash, it is noted that the concentrations of the REE do not vary substantially from the feed coal ash to the combustion fly ash. Some partitioning may occur because of the redistribution of REE-bearing minerals [11]. In this study, we discuss the differences in rare earth elements inherent in the differences between the coal sources fed into a single 100-MW boiler with an unchanging ash-collection system through the years of our studies.

2. Methods

2.1. Sample Sources

All fly ash samples were collected from the series of ash collection units for boiler unit 1 of Kentucky power plant I (letters were assigned to Kentucky power plants to anonymize



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). their identity). Ash Series 1 (92645 to 92647) was collected as an exclusive run of the Manchester coal from a single mine [12]; series 2 (93855 to 93859) was part of the Center for Applied Energy Research's (CAER) 2012 sampling of the coal-fired utility power plants in Kentucky [13]; series 3 (93953 to 93960) was collected as an exclusive run of the Fire Clay coal from a single mine [14]; and series 4 (94012 to 94019) was from a previously unpublished 2016 collection. The 2012 and 2016 fuels were the routine run-of-mine coal feeds typically used at the power plant.

2.2. Basic Chemistry and X-ray Fluorescence

For the basic analyses performed at the CAER, total sulfur analyses followed ASTM Standard D4239-18e1 [15], and the ultimate analysis was performed based on ASTM Standards D3176-15 [16]. Major oxide and non-REE minor element—including Se—chemistry at the CAER was analyzed by X-ray fluorescence on a Philips PW2404 X-ray spectrometer (Philips, Amsterdam, The Netherlands), following procedures originally outlined by Hower and Bland [17] and modified as needed for newer generations of XRF units. Mercury was analyzed on a LECO AMA254 Advanced Mercury Analyzer (St. Joseph, MI, USA).

2.3. Inductively Coupled Plasma-Mass Spectroscopy

Gallium, Ge, As, Sc, Y, and the lanthanides were analyzed using an Agilent 7900 Inductively coupled plasma-mass spectroscopy (ICP-MS) (Agilent Technologies, Santa Clara, CA, USA) at the CAER. Samples were digested following the ASTM D6357-21b [18] digestion method, utilizing heating the sample with a combination of nitric, hydrochloric, and hydrofluoric acids. The method was modified to include an additional nitric acid step at the end to handle any potential solid residue that might be present, and a sample weight of 0.1 g was utilized. The available standards were the certified reference material NIST 1633b, the primary method control sample, and the U.S. Geological Survey Brush Creek Shale (SBC-1) [19]; LGC Standards (https://www.lgcstandards.com/US/en; accessed on 24 August 2022) Brown Coal Ash (BF BE1); and available round-robin certified samples. The reference standards are digested in parallel with the samples to ensure that the digestion is complete. The certified values of the reference standard were in good agreement with the measured results. Instrument integrity is routinely monitored with random blanks and analytical standards throughout each sequence. The analysis signal for ¹⁵³Eu via ICP-MS overlapped with the signals for barium oxide polyatomic species $(^{137}Ba^{16}O, ^{136}Ba^{17}O, ^{135}Ba^{18}O, and ^{134}Ba^{18}OH)$ [20]. If samples with Ba/Eu > 1000 (mass basis), slightly more than $3 \times$ the world average for Ba/Eu [21], are flagged as unreliable, as suggested by Dai et al. [20] for the interpretation of Eu anomalies, then most of the samples in this study would have suspect Eu values.

The REE in the series 3 samples were analyzed by ICP-MS at Duke University using techniques described in Taggart et al. [14].

2.4. Notes on the Comparison of ICP Methods

One suite of series 4 samples (94012–94014, 94017–94019) was originally run on an inductively coupled plasma-optical emission spectroscopy (ICP-OES) instrument at the CAER (samples were digested following the ASTM D6357-11 [22] digestion method, which utilizes heating the sample with a combination of nitric, hydrochloric, and hydrofluoric acids). The method was modified to include an additional nitric acid step at the end to handle any potential solid residue that might be present, and a sample weight of 0.1 g was utilized. The certified reference material NIST 1633b was utilized as the primary method control sample). The samples were re-examined with ICP-MS for this study. In consideration of the known issues with the comparisons between ICP-OES and ICP-MS, studies have been made of the results from the two methods [3,23] and between ASTM D6357-11 22 (mixed acid digestion with heat); ASTM D4503 [23] (lithium borate fusion); and the ASTM D6357-11 [22] method, and with the addition of boric acid to neutralize the HF [24]. For these six fly ashes, except for five fly ashes for the Nd analysis and one

ash for the La analysis, the comparison of the analyses of the light REE vs. the cluster of the heavier REE (including Pr and Sm) gave the impression of a reasonable correlation between the two techniques (Figure 1A). A closer examination of the results for Pr, Sm, and the heavy REE illustrated the uncertainties in the comparison of those elements (Figure 1B). Given the problems with high Tm analyses on the CAER's ICP-OES, the non-detection of Ho, and the general wider range of ICP-OES analyses than the corresponding ICP-MS analyses, with Ce being an exception (Figure 1A), ICP-OES is generally considered to be a less reliable technique than ICP-MS.



Figure 1. (**A**) Comparison of ICP-OES and ICM-MS analyses for rare earth element contents in samples 94012–94019 (series 4). (**B**) A subset of the data, within blue outline in panel (**A**), focused on the lower abundance (and heavier) REE. Note that La, Ce, and Nd do not appear in this portion of the graph.

2.5. Notes on Rare Earth Nomenclature, Normalization, and the Expressions of Normalized Data

In this study, we used REE to describe the lanthanide elements, REY for REE + Y, and REYSc for REY + Sc. The light REE (LREE) are defined as La through Sm and the heavy REE (HREE) are defined as Eu through Lu [25,26]. Following the normalization of REE abundances to crustal averages (indicated by the suffix "N") [27], the normalized distribution can be divided into L-type (light type; $La_N/Lu_N > 1$); M-type (medium type; $La_N/Sm_N < 1$,

 $Gd_N/Lu_N > 1$); and H-type (heavy type; $La_N/Lu_N < 1$) enrichment patterns [28]. Ratios based on the upper continental crust (UCC) corrections after Taylor and McLennan [27] are used to decouple Ce, Eu, and Gd from the other REE in the distribution patterns [20,29–31]:

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

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

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

3. Results and Discussion

3.1. Basic Element Trends

The chemistry of the four series of fly ashes is shown in Tables 1–6. Among the non-REE, the general trend for an increase in volatile elements towards the last rows of the electrostatic precipitator (ESP) array, a function of both the decreasing particle size and the cooler flue gas temperatures in the back rows, has been noted by Sakulpitakphon et al. [12], Mardon and Hower [32], Hower et al. [33], and Hood et al. [34], among others. In these samples, As, V, Mo, Zn, Cu, Ge, Ga, and Pb generally exhibit an increase in concentration toward the last ESP rows. Selenium also increases toward the third-row ESP in the series 3 fly ashes. Mercury concentration also increases towards the cooler end of the ash-collection system, but Hg capture is complicated by Hg's dependence upon the amount and form of carbon for efficient capture [35,36].

Table 1. Series, sample type, collection date, coal seam, ultimate analysis. dl—detection limit.

				%; Mois—As-Rec., Others—Dry Basis													
Series	Sample	Туре	Row	Date	Coal	Ash	Mois.	С	Н	Ν	S	0					
1	92645	ESP	2	May-99	Manchester	90.01		6.93									
1	92646	ESP	3	May-99		92.25		5.96									
1	92647	ESP	3	May-99		91.05		6.53									
2	93855	mech	1	Dec-12	blend	93.75	0.10	1.83	0.11	dl	0.10	4.21					
2	93856	mech	1	Dec-12		92.41	0.12	9.74	0.62	0.73	0.12	dl					
2	93857	ESP	1	Dec-12		94.71	0.20	6.16	0.24	0.05	0.26	dl					
2	93858	ESP	2	Dec-12		94.57	0.32	6.03	0.24	0.01	0.36	dl					
2	93859	ESP	3	Dec-12		94.85	0.76	3.83	0.22	dl	1.05	0.05					
3	93953	mech	1	Oct-14	Fire Clay	94.46	0.09	8.23	0.30	dl	1.09	dl					
3	93954	mech	1	Oct-14		93.19	0.08	9.85	0.25	dl	1.09	dl					
3	93955	ESP	1	Oct-14		93.34	0.22	8.11	0.27	dl	1.49	dl					
3	93956	ESP	1	Oct-14		92.39	0.23	9.35	0.29	dl	1.36	dl					
3	93957	ESP	2	Oct-14		94.00	0.26	7.82	0.35	dl	1.47	dl					
3	93958	ESP	2	Oct-14		92.57	0.20	8.52	0.27	dl	1.63	dl					
3	93959	ESP	3	Oct-14		91.98	0.55	8.26	0.34	dl	1.92	dl					
3	93960	ESP	3	Oct-14		94.27	0.35	6.05	0.33	dl	1.94	dl					
4	94017	mech	1	Dec-16	blend	94.56	dl	5.94	0.09	dl	0.04	dl					
4	94018	mech	1	Dec-16		92.61	dl	8.11	0.1	0.01	0.1	dl					
4	94019	mech	1	Dec-16		91.29	dl	8.83	0.09	dl	0.09	dl					
4	94012	ESP	1	Dec-16		92.87	dl	6.48	0.13	dl	0.37	0.15					
4	94013	ESP	1	Dec-16		92.59	dl	6.58	0.1	0.01	0.18	0.54					
4	94014	ESP	2	Dec-16		85.05	1.24	6.66	0.17	dl	1.61	6.51					

Table 2. Major oxides. dl-detection limit.

			%; Asl	n Basis								
Sample	Туре	Row	Na ₂ O	MgO	Al_2O_3	SiO ₂	P_2O_5	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	SO_3
92645	ESP	2	0.78	0.23	25.50	47.40	0.33	2.45	1.88	1.43	13.67	0.13
92646	ESP	3	0.63	0.20	25.99	48.13	0.26	2.50	1.87	1.45	14.39	0.14
92647	ESP	3	0.72	0.15	24.99	46.49	0.59	2.39	3.82	1.40	14.26	0.07

		%; Asł	n Basis								
Туре	Row	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P_2O_5	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	SO ₃
mech	1	0.14	1.14	28.56	53.08	0.13	2.57	0.98	1.17	13.35	dl
mech	1	0.11	1.14	28.84	51.88	0.13	2.57	0.98	1.18	13.15	dl
ESP	1	0.20	1.27	30.58	52.46	0.27	2.91	1.09	1.25	10.22	dl
ESP	2	0.21	1.32	29.83	50.42	0.32	3.01	1.12	1.23	10.71	0.08
ESP	3	0.19	1.24	30.03	49.54	0.50	2.85	1.29	1.40	10.34	0.89
mech	1	0.18	0.78	30.10	54.21	0.26	1.75	1.46	1.68	9.27	dl
mech	1	0.18	0.77	30.02	54.60	0.25	1.72	1.51	1.66	9.30	dl
ESP	1	0.25	0.94	30.76	52.81	0.52	1.90	1.72	1.75	7.54	0.12
ESP	1	0.24	0.93	30.74	55.96	0.52	1.96	1.76	1.78	7.58	0.06
ESP	2	0.26	0.98	30.60	52.59	0.67	1.99	1.84	1.81	8.31	0.27
ESP	2	0.26	0.99	30.65	53.32	0.69	2.01	1.87	1.81	8.22	0.22
ESP	3	0.27	1.01	30.22	51.29	0.77	1.99	1.92	1.83	9.18	0.51
ESP	3	0.28	1.04	29.56	50.12	0.89	2.02	2.01	1.78	9.87	0.96
mech	1	0.23	1.07	28.80	55.54	0.58	2.37	1.68	1.48	9.62	0.08
mech	1	0.23	1.08	29.04	55.56	0.60	2.35	1.72	1.49	9.50	0.09
mech	1	0.23	1.06	28.87	55.20	0.60	2.32	1.74	1.49	9.63	0.09
ESP	1	0.29	1.16	29.89	52.64	1.36	2.44	2.04	1.59	8.41	0.22
ESP	1	0.28	1.15	29.67	52.49	1.22	2.44	2.01	1.56	8.34	0.38
ESP	2	0.24	0.93	23.46	43.26	0.67	2.04	1.50	1.29	26.05	1.69
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Ash Basis Type Row Na ₂ O MgO Al ₂ O ₃ SiO ₂ P ₂ O ₅ K ₂ O CaO TiO ₂ Fe ₂ O ₃ mech 1 0.14 1.14 28.56 53.08 0.13 2.57 0.98 1.17 13.35 mech 1 0.11 1.14 28.84 51.88 0.13 2.57 0.98 1.18 13.15 ESP 1 0.20 1.27 30.58 52.46 0.27 2.91 1.09 1.25 10.22 ESP 2 0.21 1.32 29.83 50.42 0.32 3.01 1.12 1.23 10.71 ESP 3 0.19 1.24 30.03 49.54 0.50 2.85 1.29 1.40 10.34 mech 1 0.18 0.77 30.02 54.60 0.25 1.72 1.51 1.66 9.30 ESP 1 0.25 0.94 30.76 52.81 0.5

Table 2. Cont.

Table 3. Minor elements (ash basis with the exception of Se and Hg on the whole-sample basis). dl—detection limit.

			ppm; A	sh Basis											
Sample	Туре	Row	V	Cr	Mn	Со	Ni	Cu	Zn	Ga	Ge	As	Rb	Sr	Zr
92645	ESP	2	471	266	322	168	328	284		124	118	576			196
92646	ESP	3								82	73	361			140
92647	ESP	3	456	258	325	176	339	253		102	90	420			157
93855	mech	1	322	133	200	48	110	120	182	53	19	112	46	911	313
93856	mech	1	331	135	200	47	110	120	190	44	16	96	41	954	269
93857	ESP	1	416	160	227	44	134	161	353	74	35	284	13	1211	229
93858	ESP	2	448	168	278	46	144	161	417	100	51	463	13	1147	246
93859	ESP	3	557	191	243	52	180	431	410	134	64	491	14	1352	207
93953	mech	1	461	149	111	45	88	178	74	51		57	369	964	365
93954	mech	1	440	151	108	41	121	160	64	45		45	390	928	366
93955	ESP	1	622	203	132	75	147	271	183	143		218	dl	1035	327
93956	ESP	1	639	206	131	74	149	282	174	136		212	dl	1261	391
93957	ESP	2	713	233	149	90	173	331	236	179		325	dl	1297	381
93958	ESP	2	723	234	148	90	179	322	234	180		325	dl	1312	384
93959	ESP	3	814	259	175	96	196	392	289	223		550	dl	1359	403
93960	ESP	3	831	265	196	103	210	398	333	215		582	dl	1254	359
94017	mech	1	374	137	130	44	92	116	81	33	9	64	380	1500	198
94018	mech	1	375	136	127	45	89	115	79	44	14	81	376	1550	277
94019	mech	1	372	136	127	45	89	119	79	35	10	66	412	1507	210
94012	ESP	1	496	182	149	67	142	190	206	72	22	270	dl	1767	185
94013	ESP	1	480	180	148	66	135	185	202	86	27	312	dl	1560	214
94014	ESP	2	433	214	1086	67	180	248	233	84	31	249	dl	910	179
			ppm; A	sh Basis									ppm;	Whole S	Sample
Sample	Туре	Row	Nb	Mo	Cd	9	Sb	Ba	Р	'b	Th	U	Se		Hg
92645	ESP	2	29		16				46	61			391		0.45
92646	ESP	3	21						-	-			÷		0.52
92647	ESP	3	25		17				46	60			400		0.92
93855	mech	1	36	35	1		3	885	7	' 4					
93856	mech	1	28	37	1		2	875	7	'5					

			ppm; A	sh Basis							ppm; Wh	ole Sample
Sample	Туре	Row	Nb	Mo	Cd	Sb	Ba	Pb	Th	U	Se	Hg
93857	ESP	1	28	63	1	1	1029	173				
93858	ESP	2	29	63	1	1	1107	218				
93859	ESP	3	28	67	1	1	1349	262				
93953	mech	1		140	dl	6	1139	82	44	16	13	0.27
93954	mech	1		142	dl	6	1113	79	45	15	13	0.24
93955	ESP	1		122	dl	dl	1573	149	49	31	61	1.36
93956	ESP	1		188	dl	6	1601	135	46	29	59	1.82
93957	ESP	2		193	1	6	1913	196	47	36	67	1.42
93958	ESP	2		195	1	6	1908	198	48	37	76	1.90
93959	ESP	3		209	1	7	2502	247	50	46	110	2.31
93960	ESP	3		168	1	4	2583	224	43	44	215	0.94
94017	mech	1	26	120	dl	9	1726	77				
94018	mech	1	40	118	dl	9	1734	78				
94019	mech	1	29	110	dl	8	1735	73				
94012	ESP	1	25	117	dl	6	2112	183				
94013	ESP	1	29	103	dl	4	2010	172				
94014	ESP	2	25	dl	2	8	1634	150				

Table 3. Cont.

Table 4. Sc, Y, rare earth elements.

Sample	Type	Row	550 Ash	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
92645	ESP	2	90.74	26	65	77	168	20	81	17	3.4	16	2.4	15	2.9	7.9	1.1	6.8	0.9
92646	ESP	3	93.29	10	21	48	112	14	58	12	2.3	11	1.6	10	1.9	5.2	0.7	4.3	0.6
92647	ESP	3	91.67	14	25	51	126	15	62	12	2.5	11	1.6	10	1.9	5.3	0.7	4.4	0.6
93855	mech	1	93.43	39	81	121	265	31	122	25	4.2	23	3.4	22	4.2	12.0	1.7	11.0	1.5
93856	mech	1	92.44	17	29	70	162	19	78	15	2.5	13	1.9	12	2.3	6.5	0.9	5.7	0.8
93857	ESP	1	94.89	30	65	82	175	21	83	18	3.2	17	2.6	17	3.3	9.3	1.3	8.9	1.2
93858	ESP	2	94.50	38	81	93	204	23	96	20	3.7	20	3	19	3.8	11.0	1.6	10.0	1.4
93859	ESP	3	95.28	32	66	76	168	19	78	17	3.3	17	2.6	17	3.3	9.6	1.4	8.7	1.2
93953	mech	1		40	106	117	261	28	110	22	3.6	25	3.4	19	3.9	11.0	1.6	9.9	1.5
93954	mech	1		39	102	117	261	28	110	23	3.5	25	3.4	19	3.8	10.7	1.6	9.5	1.5
93955	ESP	1		53	129	119	265	29	113	24	4.2	27	4.0	23	4.8	13.4	2.0	12.3	1.8
93956	ESP	1		52	127	114	252	28	109	22	4.0	26	3.7	22	4.5	12.9	1.9	11.4	1.7
93957	ESP	2		55	130	113	252	28	109	23	4.3	26	3.9	22	4.6	13.2	1.9	11.7	1.8
93958	ESP	2		55	133	116	257	28	111	23	4.3	27	3.9	23	4.7	13.4	2.0	12.2	1.8
93959	ESP	3		57	138	117	259	29	113	24	4.6	28	4.1	24	5.0	14.2	2.1	12.7	1.9
93960	ESP	3		54	132	110	246	27	106	23	4.5	26	3.9	23	4.7	13.5	2.0	12.0	1.8
94017	mech	1	94.41	25	62	88	192	21	87	18	3.6	17	2.5	16	3.0	8.6	1.2	8.0	1.1
94018	mech	1	93.87	39	95	106	218	25	99	20	4	19	2.8	18	3.4	9.5	1.4	9.0	1.2
94019	mech	1	92.92	24	59	93	198	22	90	18	3.7	18	2.6	16	3.1	8.9	1.3	8.3	1.1
94012	ESP	1	92.50	28	61	84	180	20	81	17	3.4	17	2.5	16	3.1	8.7	1.2	8.0	1.1
94013	ESP	1	92.18	34	75	95	207	23	95	20	4.1	20	2.9	19	3.7	10.0	1.5	9.6	1.3
94014	ESP	2	87.69	26	54	76	156	18	72	15	3.2	15	2.2	14	2.8	7.9	1.1	7.2	1.0

 Table 5. Upper continental crust-normalized rare earth elements.

UCC-Normalized REE																
			La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Sample	Туре	Row	30	64	7.1	26	4.5	0.9	3.8	0.6	3.5	0.8	2.3	0.3	2.2	0.32
92645	ESP	2	2.57	2.63	2.82	3.12	3.78	3.86	4.21	4.00	4.29	3.63	3.43	3.67	3.09	3.00
92646	ESP	3	1.60	1.75	1.97	2.23	2.67	2.61	2.89	2.67	2.86	2.38	2.26	2.33	1.95	2.00
92647	ESP	3	1.70	1.97	2.11	2.38	2.67	2.84	2.89	2.67	2.86	2.38	2.30	2.33	2.00	2.00

			UCC-I	Normaliz	ed REE											
			La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
Sample	Туре	Row	30	64	7.1	26	4.5	0.9	3.8	0.6	3.5	0.8	2.3	0.3	2.2	0.32
93855	mech	1	4.03	4.14	4.37	4.69	5.56	4.77	6.05	5.67	6.29	5.25	5.22	5.67	5.00	5.00
93856	mech	1	2.33	2.53	2.68	3.00	3.33	2.84	3.42	3.17	3.43	2.88	2.83	3.00	2.59	2.67
93857	ESP	1	2.73	2.73	2.96	3.19	4.00	3.64	4.47	4.33	4.86	4.13	4.04	4.33	4.05	4.00
93858	ESP	2	3.10	3.19	3.24	3.69	4.44	4.20	5.26	5.00	5.43	4.75	4.78	5.33	4.55	4.67
93859	ESP	3	2.53	2.63	2.68	3.00	3.78	3.75	4.47	4.33	4.86	4.13	4.17	4.67	3.95	4.00
93953	mech	1	3.90	4.07	3.97	4.23	4.96	4.09	6.54	5.34	5.53	4.93	4.78	4.83	4.49	3.42
93954	mech	1	3.89	4.08	3.98	4.23	5.03	4.00	6.53	5.23	5.44	4.75	4.65	4.70	4.31	3.40
93955	ESP	1	3.97	4.14	4.08	4.36	5.27	4.75	7.17	6.19	6.62	5.96	5.82	5.96	5.60	4.21
93956	ESP	1	3.79	3.94	3.90	4.18	4.99	4.51	6.94	5.85	6.22	5.62	5.59	5.62	5.16	4.03
93957	ESP	2	3.77	3.94	3.92	4.20	5.12	4.87	6.97	6.02	6.42	5.77	5.75	5.86	5.32	4.08
93958	ESP	2	3.86	4.01	3.99	4.28	5.16	4.93	7.14	6.08	6.52	5.90	5.83	5.96	5.53	4.18
93959	ESP	3	3.89	4.04	4.06	4.34	5.27	5.23	7.35	6.40	6.91	6.25	6.19	6.29	5.76	4.41
93960	ESP	3	3.67	3.85	3.82	4.09	5.02	5.10	6.96	6.05	6.52	5.90	5.86	5.94	5.47	4.23
94017	mech	1	2.93	3.00	2.96	3.35	4.00	4.09	4.47	4.17	4.57	3.75	3.74	4.00	3.64	3.67
94018	mech	1	3.53	3.41	3.52	3.81	4.44	4.55	5.00	4.67	5.14	4.25	4.13	4.67	4.09	4.00
94019	mech	1	3.10	3.09	3.10	3.46	4.00	4.20	4.74	4.33	4.57	3.88	3.87	4.33	3.77	3.67
94012	ESP	1	2.80	2.81	2.82	3.12	3.78	3.86	4.47	4.17	4.57	3.88	3.78	4.00	3.64	3.67
94013	ESP	1	3.17	3.23	3.24	3.65	4.44	4.66	5.26	4.83	5.43	4.63	4.35	5.00	4.36	4.33
94014	ESP	2	2.53	2.44	2.54	2.77	3.33	3.64	3.95	3.67	4.00	3.50	3.43	3.67	3.27	3.33

Table 5. Cont.

Table 6. Rare earth-related parameters.

Sample	Туре	Row	Eu_N/Eu_N^*	Ce_N/Ce_N^*	$\mathrm{Gd}_N/\mathrm{Gd}_N^*$	dist.	REE	REY	REYSc	LREE/HREE
92645	ESP	2	1.00	0.98	1.07	Н	419	484	510	6.44
92646	ESP	3	0.98	0.98	1.09	Н	282	303	313	6.49
92647	ESP	3	1.07	1.03	1.09	Н	304	329	343	7.00
93855	mech	1	0.85	0.99	1.08	Н	647	728	767	6.80
93856	mech	1	0.87	1.01	1.06	Н	390	419	436	7.54
93857	ESP	1	0.88	0.96	1.06	Н	443	508	538	5.94
93858	ESP	2	0.91	1.01	1.09	Н	510	591	629	5.93
93859	ESP	3	0.95	1.01	1.08	Н	422	488	520	5.59
93953	mech	1	0.80	1.04	1.25	L	617	723	763	6.80
93954	mech	1	0.79	1.04	1.26	L	616	719	758	6.93
93955	ESP	1	0.85	1.03	1.22	Н	643	772	825	5.92
93956	ESP	1	0.86	1.03	1.25	Н	613	740	792	5.95
93957	ESP	2	0.90	1.03	1.22	Н	616	746	800	5.81
93958	ESP	2	0.90	1.02	1.24	Н	628	761	816	5.81
93959	ESP	3	0.93	1.02	1.22	Н	638	775	833	5.60
93960	ESP	3	0.95	1.03	1.22	Н	604	737	791	5.59
94017	mech	1	1.01	1.02	1.09	Н	467	529	554	6.66
94018	mech	1	1.01	0.97	1.09	Н	536	631	670	6.85
94019	mech	1	1.02	1.00	1.12	Н	484	543	567	6.68
94012	ESP	1	0.99	1.00	1.11	Н	443	504	532	6.26
94013	ESP	1	1.02	1.01	1.12	Н	512	587	621	6.10
94014	ESP	2	1.06	0.96	1.11	Н	391	445	471	6.19

3.2. Principal Components Analysis on REY and Selected Major Oxides and Minor Elements

A principal components analysis (PCA; JMP[®] Pro 16.0.0, SAS Institute, Cary, NC, USA) was implemented to further understand the distributions of the major oxides and minor elements. The elements and combinations of selected elements and oxides were REY, LREE/HREE, and K₂O/(SiO₂ + Al₂O₃) as an indicator of clay minerals, and Zr and TiO₂/(TiO₂ + Al₂O₃) as indicators of detrital minerals. The results, shown in Figure 2 with details on the statistics on the PCA tab in Table S1, demonstrate that the Zr and REY axes are in close proximity to each

other, opposite the K₂O/(SiO₂ + Al₂O₃) axis, and orthogonal to the opposing LREE/HREE and TiO₂/(TiO₂ + Al₂O₃) axes. The first principal component, with nearly co-equal contributions from Zr, REY, and, in the opposite direction, K₂O/(SiO₂ + Al₂O₃), accounts for 62.51% of the variation. The first three principal components account for 96.80% of the variation. All of the eigenvectors make sense geologically. While not always specifically for REE or in the context of PCA, the nature of geochemical associations in eastern Kentucky and other coals has been discussed elsewhere [17,20,26,30,32,37–39]. For example, Y is an accessory element in zircons; therefore, Zr and REY are related. The nature of the REY associations with clays is different from the association in detrital minerals. Moreover, clays can act as a diluent of the REY-bearing clastic minerals, and TiO₂/(TiO₂ + Al₂O₃) indicates a strictly clastic source in contrast to the broader array of sources encompassed by the LREE/HREE.



Figure 2. Plot of principal component analysis axes (**right**) and individual points (**left**). The inset shows the detail of the Fire Clay source (93953–93960) series 3 ESP data. The detailed key to the symbols is on Table S1.

The PCA analysis, as shown in Figure 2, also demonstrates that the series-3 Fire Clayderived ashes are distinct from the other series, a function of their higher concentrations of Zr and REY than the other three series of fly ashes. Further, the mechanical ashes occupy a distinct area from the ESP ashes with the ESP rows showing a sequential distribution (Figure 2 inset). In the first case, the differentiation is a function of the higher LREE/HREE and lower $TiO_2/(TiO_2 + Al_2O_3)$ in the mechanical ashes vs. the ESP ashes. A similar differentiation drives the partition between the ESP rows. While this seems to contradict the inference of subtle, if any, REY variations between ashes from the same source [11], the differentiation in the amount and nature of the mineral inclusions seems to be sufficient to segregate the ashes. Of course, Liu et al. [11] focused on REY distributions, not a wider spectrum of major oxides and minor elements. They also examined the size fractions of a few single series-1 ashes with less emphasis on the discrete nature of the ashes from individual mechanical and ESP hoppers, as in this study. The nature of the ashes with respect to REY is further discussed below.

3.3. Lanthanide Elements

Apart from two fly ashes in the Manchester coal-derived series 1, all of the fly ashes have more than 390-ppm REE. The series-3 Fire Clay coal-derived ashes are all in the 604- to 638-ppm REE range. The series-3 Fire Clay-derived mechanical-collection fly ashes are the only ones in the study to show an L-type (normalized La > Lu) distribution ("dist." column in Table 6). The LREE/HREE distributions differ, with the mechanical ashes from the latter series having an LREE/HREE from 6.80 to 6.93, while the ashes from the 1st- to 3rd-row ESPs steadily decrease from 5.92–5.95 to 5.81 to 5.59–5.60. The mechanical ashes from series 2 and 4 also have higher LREE/HREE than the ESP ashes in those series. The overall order mimics the trend seen for the series-3 Fire Clay principal components (Figure 2), demonstrating the influence of the LREE/HREE on the trends and emphasizing the importance of REE distributions as a tool in understanding their behavior in combustion systems.

The upper continental crust-normalized REE distribution after Taylor and McLennan (1985) (Figure 3; Table 5) is cluttered. In consideration of the two single-source-coal-feed sets (Figure 4), it is evident that the trends seen in the PCA plots are also clearly seen in the normalized data. While both the ESP and mechanical ashes from the Fire Clay coal-derived series show negative Eu and positive Gd anomalies, the ESP ashes have a higher Tb through Lu distribution. Note that, while some of the lithotypes contributing to the Manchester coal-derived ash have high ash-basis REE contents, the ash contents of those lithotypes are low, therefore, they are not major contributors to the overall REE concentration of the fly ash [37,38].



Figure 3. Upper continental crust-normalized REE distribution after Taylor and McLennan [27]. All of the fly ash series are shown on this graph.

The distribution of the decoupled Ce_N/Ce_N^* , Eu_N/Eu_N^* , and Gd_N/Gd_N^* distributions (Figures 5–7) all show the segregation of the Fire Clay-derived mechanical and ESP fly ashes both from each other and, particularly, for the Gd_N/Gd_N^* vs. Eu_N/Eu_N^* (Figure 6) and Gd_N/Gd_N^* vs. Ce_N/Ce_N^* (Figure 7) distributions from the other three series. The latter trends are largely driven by the high Gd_N/Gd_N^* in the Fire Clay-derived ashes, an indicator of their high HREE concentration, compared to the other fly ashes. Series 2 is separated from the Manchester-coal-derived fly ashes and from the series 4 fly ashes in the Ce_N/Ce_N^* vs. Eu_N/Eu_N^* (Figure 5) and Gd_N/Gd_N^* vs. Eu_N/Eu_N^* (Figure 6) distributions, owing to their low Eu_N/Eu_N^* .



Figure 4. Upper continental crust-normalized REE distribution after Taylor and McLennan [27] for the Fire Clay- and Manchester-coal-derived fly ashes.



Figure 5. Eu_N/Eu_N^* vs. Ce_N/Ce_N^* for all of the samples.

3.4. Discussion

By focusing on a single 100-MW unit at a power plant, we were able to focus on variations in fly ash chemistry, as they are influenced by variations in the feed coal. From the PCA of several parameters, plots of the decoupled Ce_N/Ce_N^* , Eu_N/Eu_N^* , and Gd_N/Gd_N^* distributions, and spider plots of the upper continental crust-normalized REE values, we observed that the Fire Clay coal-derived fly ashes were distinctive in composition compared to the other three series. (Although, note that the spider-plot contrast is only evident in the comparison of the Fire Clay- and Manchester-derived fly ashes). Largely, this contrast is a function of the increased presence of REY-bearing minerals in the Fire Clay coal [26,32,38,39] compared to other coals in the region. The other coals are not necessarily depleted of REY. For example, the Manchester coal in the mine supplying the coal for Sakulpitakphon

et al.'s [12] study of the series-1 fly ash has several benches with >1600-ppm REY (ash basis) [38]. Nevertheless, none of them have the lateral continuity of the Fire Clay coal.



Figure 6. Eu_N/Eu_N^* vs. Gd_N/Gd_N^* for all of the samples.



Figure 7. Ce_N/Ce_N^* vs. Gd_N/Gd_N^* for all of the samples.

Using the Fire Clay-derived fly ashes as an example, it was noted above that the LREE/HREE ratio decreases from the mechanical rows through to the third-ESP row. The PCA analysis demonstrated a subtle partitioning between the three ESP rows. This is confirmed for Ce_N/Ce_N^* vs. Eu_N/Eu_N^* (Figure 5) and Gd_N/Gd_N^* vs. Eu_N/Eu_N^* (Figure 6), owing to the Eu_N/Eu_N^* increases from the first to the third ESP rows. Further, the Eu_N/Eu_N^* for

the mechanical fly ash is lower than for the ESP ashes. As with Liu et al.'s [11] examination of REY partitioning in fly ashes from the Series 1 fly ashes point towards the variations in LREE/HREE and the decoupled element distributions being a function of (1) petrographic variations between the samples from the individual collection times; (2) partitioning of the REY-bearing minerals; (3) variations in the chemistry of certain minerals.

4. Summary

The chemistry of four series of fly ashes generated in the same boiler but with different feed coal—either single-mine/single-seam coals in two cases or run-of-mine blends of coals from multiple mines and multiple seams—was examined with special attention to the concentration and distribution of the rare earth elements.

1/The principal components analysis demonstrated that series 3, the fly ashes derived from the combustion of the Fire Clay coal, were (1) distinctly partitioned from the other fly ash series; (2) internally divided between the mechanical hoppers and the three rows of ESP hoppers; (3) the ESP rows showed a subtle separation. The separation of the series-3 Fire Clay-derived ashes from the other series was driven by the higher Zr and REY in the series 3 ashes and the partitioning between the mechanical and ESP fly ashes, and among the ESP ashes is a function of the variations in the LREE/HREE and the TiO₂/(TiO₂ + Al₂O₃) ratios.

2/Upper continental crust normalization [27], particularly the plot of just the two single-mine/single-seam-coal-derived fly ashes, demonstrated the differentiation of (1) the Manchester coal-derived ash from the Fire Clay coal-derived ash; (2) in the REE abundances and distributions between ESP rows (Manchester coal source, series 1 fly ashes), and between the mechanical and ESP rows (Fire Clay coal source, series 3).

3/The decoupled Ce_N/Ce_N^* , Eu_N/Eu_N^* , and Gd_N/Gd_N^* distributions are complicated due to the Ba interferences with Eu. Nevertheless, the Ce_N/Ce_N^* vs. Eu_N/Eu_N^* and, in particular, the Gd_N/Gd_N^* vs. Eu_N/Eu_N^* distributions confirm the distinction between the Fire Clay coal-derived ashes and the remainder of the fly ashes, and the Fire Clay coal-derived mechanical and ESP ashes from each other. Both trends are also evident in the plot of Gd_N/Gd_N^* vs. Ce_N/Ce_N^* , although the differentiation between the ESP rows is not as distinct as in the Ce_N/Ce_N^* vs. Eu_N/Eu_N^* and the Gd_N/Gd_N^* vs. Eu_N/Eu_N^* plots.

4/The chemistry of the feed coal, while not specifically addressed here, is an obvious factor in the concentration and distribution of REE in the fly ash. Specifically, the Fire Clay coal-derived series 3 fly ash has distinctly different distribution patterns than the other single-seam or coal blend series. In addition, there is evidence that the distribution of REE progressively changes from the mechanical ash collection system through the ESP rows. While this might seem to differ from the conclusions of Liu et al. [11], it is noted that this study focused on sized fractions of single fly ashes, not the differentiation associated with the temperature and particle size gradients in the passage from the mechanical hoppers to the third row of the ESP array.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12091071/s1, Table S1: Supporting information for PCA test.

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