



Full Length Article

Distribution of rare earth elements in fly ash derived from the combustion of Illinois Basin coals

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ABSTRACT

This study examined rare earth element (REE) trends for Illinois Basin coal-sourced fly ashes, with the goal of understanding the elemental composition and resource potential for various fly ash fractions. Illinois Basin coals have a high volatile C through A bituminous rank with a moderate ash content (slightly >12% ash (dry basis)), about 3% sulfur, and, in general, lower concentrations of hazardous and other trace elements than many Central Appalachian coals. Fly ash from the combustion of Illinois Basin coals tends to have a high Fe₂O₃ content owing to the amount of pyrite in the feed coals. The rare earth element (REE) concentrations in Illinois Basin coal-sourced fly ashes are less than that for fly ashes from the combustion of Central Appalachian coals. The Upper continental crust-corrected fly ashes show an H-type enrichment, a positive Eu_N/Eu_N^{*}, and, in some cases, a sharp Gd peak. For comparison, a suite of fly ashes from the combustion of a blend of eastern Kentucky coals had an H-type enrichment, a positive Eu_N/Eu_N^{*}, but only a minimal Gd peak. In contrast, fly ash from the combustion of the Fire Clay coal, a REE-rich coal, had a negative Eu_N/Eu_N^{*} and a sharp Gd peak. These results highlight the importance of feed coal composition on trace element contents of respective combustion fly ash fractions and also the unique REE enrichment patterns of the Illinois Basin fly ashes relative to the better studied fly ashes of eastern Kentucky and Central Appalachia.

1. Introduction

In the overall analysis of the potential for the extraction of Rare earth elements (REE) from coal combustion ashes, justified attention has been paid to ashes produced from the combustion of Appalachian bituminous coals [1–9] and western US lignites and subbituminous coals [10,11]. Illinois Basin coal-derived fly ashes have been analyzed [5], but they have not been investigated as a REE resource to the same depth compared to fly ashes derived from other coal sources.

The Illinois Basin comprises the coal fields in Illinois, Indiana, and western Kentucky. While some Mississippian coals are known [12] and Permian strata with no coals are found in a graben in Union County, Kentucky [13,14], all of the major coals are of Pennsylvanian age, with the bulk of the coal production centered on Asturian-age coals. Aspects of the depositional environments of the major coals are found in Greb et al. [15,16], Nelson et al. [17], and Fielding et al. [18].

Studies of the basic geochemistry of coal have benefited from the

contributions of the three state geological surveys, the U.S. Geological Survey, and numerous university-based researchers. Among the many geochemical studies are Zubovic [19], Gluskoter et al. [20], Ward, [21] Fiene et al., [22] Kuhn et al., [23] Hower et al., [24–26] Mastalerz and Drobnik, [27] and Valian et al. [28] Basically, the major coals have a high-S content (Table 1), with 1.48% S_{py} (dry basis) in the pulverized feed coal to the power plants studied here (coincidentally, the average S_{org} plus S_{sulfate} is also 1.48%; the pulverizer rejects, the hard, mineral-rich portion of the delivered coal, accounting for < 1% of the feed coal at most power plants, have 29.30% S_{py}). In spite of the high amount of sulfides, as reflected in pyritic S contents, the trace element content of the Illinois Basin-sourced feed coals is less than that of Central Appalachian-sourced feed coals with similar levels of sulfur (i.e., 1–2% S) [29]. One exception to that trend lies within the southwestern portion of the coalfield, located in western Kentucky, where the high volatile A bituminous coals (in contrast to high volatile C bituminous throughout most of the rest of the basin) have elevated concentrations of As, Ni, V,

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Table 1

Average, standard deviation, and count for compositional analyses of pulverized coal, pulverizer rejects, 1st- through 3rd-row ESP fly ashes, and bottom ash for Illinois Basin feed coals and combustion ashes.

		As-rec.		Dry	Dry, ash-free										mmmf		Whole coal
Type	Row	Mois, %	Ash, %	VM, %	FC, %	C, %	H, %	N, %	O, %	S, %	Spy, %	Ssulf, %	Sorg, %	HV, MJ/kg	Cl, ppm		
Pulv coal	Avg.	3.55	12.16	37.14	47.15	66.83	5.04	1.34	11.66	2.97	1.48	0.11	1.37	28.20	213		
	St. dev.	0.92	2.01	1.43	0.93	1.84	0.17	0.25	3.08	0.47	0.31	0.06	0.32	0.53	351		
	Count	15	15	15	15	15	15	15	15	15	15	15	15	15	14		
Rejects	Avg.	2.05	49.77	28.81	19.37	26.00	2.24	0.56	*	29.30	23.06	0.49	5.81		96		
	St. dev.	1.36	11.24	3.34	8.31	14.47	1.09	0.34		12.44	10.04	0.37	3.91		182		
	Count	13	13	13	13	13	13	11		13	13	13	13		12		
ESP fly ash	1	Avg.	0.26	96.20			3.79	0.36	0.08	0.60	0.62						
	St. dev.	0.20	4.31			3.98	0.14	0.06	0.67	0.52							
	Count	53	53			43	52	25	29	53							
ESP fly ash	2	Avg.	0.36	93.88			5.65	0.36	0.13	0.86	0.61						
	St. dev.	0.29	7.27			6.60	0.11	0.10	1.02	0.37							
	Count	46	46			41	45	19	29	46							
ESP fly ash	3	Avg.	0.55	94.16			4.60	0.47	0.11	1.30	1.17						
	St. dev.	0.48	6.55			5.81	0.45	0.14	1.29	0.62							
	C	24	24			23	24	7	12	23							
Bottom ash	Avg.	0.46	94.14			7.40	0.68	0.12	0.73	1.09							
	St. dev.	0.57	9.13			12.00	1.15	0.16	0.67	2.17							
	Count	11	11			8	11	9	4	10							
Coal & rejects same plant																	
Pulv coal	Avg.	3.76	11.68	37.38	47.18	66.59	5.05	1.31	3.00	12.37	1.47	0.12	1.40	12130.83	109.24		
	St. dev.	0.90	1.83	1.40	1.00	2.00	0.17	0.27	0.50	2.98	0.30	0.06	0.35	240.10	205.48		
	count	12	12	12	12	12	12	12	12	12	12	12	12	12	11		
Rejects	avg.	2.05	49.77	28.81	19.37	26.00	2.24	0.56	*	29.30	23.06	0.49	5.81		96.20		
	St. dev.	1.36	11.24	3.34	8.31	14.47	1.09	0.34		12.44	10.04	0.37	3.91		182.45		
	Count	13	13	13	13	13	13	11		13	13	13	13		12		

		Ash basis													
Type	Row		SiO2, %	Al2O3, %	Fe2O3, %	CaO, %	MgO, %	Na2O, %	K2O, %	P2O5, %	TiO2, %	SO3, %			
Pulv coal	Avg.		48.70	21.48	18.58	3.53	1.12	0.54	2.46	0.19	1.03	3.68			
	St. dev.		2.41	1.70	3.35	1.56	0.18	0.15	0.27	0.13	0.05	2.47			
	Count		15	15	15	15	15	15	15	15	15	15	15		
Rejects	Avg.		16.28	5.45	59.44	6.58	1.42	0.52	0.65	0.38	0.37	9.28			
	St. dev.		7.36	2.51	17.80	5.32	1.26	0.23	0.34	0.54	0.11	7.18			
	Count		13	13	13	13	13	13	13	13	12	13	12		
ESP fly ash	1	Avg.	48.46	21.20	20.17	4.01	1.09	0.67	2.37	0.17	1.02	1.40			
	St. dev.		2.92	2.02	3.56	2.55	0.17	0.89	0.37	0.08	0.08	1.73			
	Count		53	53	53	53	53	53	53	53	53	53	51		
ESP fly ash	2	Avg.	48.25	21.63	19.73	4.08	1.14	0.47	2.45	0.20	1.05	1.46			
	St. dev.		2.36	2.33	3.88	2.77	0.17	0.21	0.38	0.09	0.09	1.41			
	Count		46	46	46	46	46	46	46	46	46	46	43		
ESP fly ash	3	Avg.	44.78	19.96	20.39	6.82	1.03	0.41	2.21	0.21	0.96	3.38			
	St. dev.		5.44	3.42	5.92	4.41	0.18	0.20	0.62	0.09	0.17	2.38			
	Count		24	24	24	24	24	24	24	24	24	24	23		
Bottom ash	Avg.		46.18	19.56	26.24	3.64	1.12	0.40	2.11	0.19	0.97	1.40			
	St. dev.		3.66	2.35	3.84	2.35	0.30	0.12	0.34	0.13	0.10	1.81			
	Count		11	11	11	11	11	11	11	11	11	11	7		
Coal & rejects same plant															
Pulv coal	Avg.		48.65	21.36	19.05	3.54	1.06	0.56	2.47	0.19	1.03	3.67			
	St. dev.		2.68	1.77	3.25	1.75	0.11	0.16	0.26	0.13	0.06	2.77			
	Count		12	12	12	12	12	12	12	12	12	12	12		
Rejects	Avg.		16.28	5.45	59.44	6.58	1.42	0.52	0.65	0.38	0.37	9.28			
	St. dev.		7.36	2.51	17.80	5.32	1.26	0.23	0.34	0.54	0.11	7.18			
	Count		13	13	13	13	13	13	13	13	13	12	13	12	

		Ash basis																Whole sample		
Type	Row	V, ppm	Cr, ppm	Mn, ppm	Co, ppm	Ni, ppm	Cu, ppm	Zn, ppm	As, ppm	Rb, ppm	Sr, ppm	Zr, ppm	Mo, ppm	Cd, ppm	Sb, ppm	Ba, ppm	Pb, ppm	Se, ppm	Hg, ppm	
Pulv coal	Avg.	442	168	261	57	109	75	233	96	46	220	24	28	1	5	622	50	2.32	0.16	
	St. dev.	177	35	48	10	23	24	68	29	28	138	39	19	0	1	326	12		0.22	
	Count	15	15	15	15	15	14	15	15	10	15	15	15	15	15	15	15		14	
Rejects	Avg.	87	140	388	149	105	23	135	340	66		45		1	16	477	51	8.22	1.58	
	St. dev.	63	32	248	40	31	21	140	167	86		68		0	3	348	42		0.69	
	Count	13	13	13	13	13	9	11	13	5		13		13	13	13	12		13	
ESP fly ash	1	Avg.	494	167	263	63	131	67	259	115	50	244	26	31	1	6	601	53	15.59	0.08
	St. dev.	356	29	41	11	69	17	101	42	38	137	38	19	0	1	221	17	10.50	0.13	
	Count	53	53	53	53	53	51	53	53	47	53	53	40	53	53	53	53	4	13	
	2	Avg.	552	174	266	62	144	74	302	140	47	270	28	40	1	6	614	63	21.09	0.20

(continued on next page)

Table 1 (continued)

Type	Row	Ash basis																	Whole sample			
		V, ppm	Cr, ppm	Mn, ppm	Co, ppm	Ni, ppm	Cu, ppm	Zn, ppm	As, ppm	Rb, ppm	Sr, ppm	Zr, ppm	Mo, ppm	Cd, ppm	Sb, ppm	Ba, ppm	Pb, ppm	Se, ppm	Hg, ppm			
ESP fly ash		St. dev.	434	35	45	12	84	22	112	61	34	158	39	28	0	1	214	25	8.94	0.45		
ESP fly ash	3	Count	46	46	46	46	46	44	46	37	46	46	39	46	46	46	46	5	13			
		Avg.	401	149	258	84	126	67	323	146	66	241	31	48	1	7	579	63	39.03	0.46		
		St. dev.	134	19	53	102	34	32	129	72	32	167	41	33	0	2	259	33	24.32	0.88		
Bottom ash		Count	24	24	24	24	24	24	24	18	24	24	16	24	24	24	24	3	13			
		Avg.	364	168	328	76	111	53	127	65	53	159	48	4	1	9	605	23	25.53	0.32		
		St. dev.	89	26	50	10	36	15	35	15	35	86	70		0	2	244	8	30.36	0.39		
Coal & rejects same plant		Count	11	11	11	11	11	10	11	11	10	10	11	1	11	11	11	2	2			
		Avg.	467	167	266	59	114	68	242	96	43	185	26	25	1	5	575	49	2.32	0.17		
		St. dev.	190	27	53	10	24	12	67	31	29	124	43	13	0	2	311	12		0.24		
Rejects		Count	12	12	12	12	12	11	12	12	7	12	12	12	12	12	12		11			
		Avg.	87	140	388	149	105	23	135	340	66		45	1	16	477	51	8.22	1.58			
		St. dev.	63	32	248	40	31	21	140	167	86		68	0	3	348	42		0.69			
		Count	13	13	13	13	13	9	11	13	5		13	13	13	13	12		13			
Ash basis																						
Type	Row	Sc, ppm	Y, ppm	La, ppm	Ce, ppm	Pr, ppm	Nd, ppm	Sm, ppm	Eu, ppm	Gd, ppm	Tb, ppm	Dy, ppm	Ho, ppm	Er, ppm	Tm, ppm	Yb, ppm	Lu, ppm	REE, ppm	REY, ppm	REYSc, ppm	LREE/	
ESP Fly ash	1	Avg.	28	53	54	112	13	50	10	2.3	10	1.6	9	1.8	5.2	0.8	4.8	0.7	276	330	359	6.57
		St. dev.	6	12	10	20	2	12	3	0.6	3	0.4	2	0.4	0.9	0.1	0.7	0.1	55	65	73	0.38
		Count	10	11	11	11	11	11	11	11	11	11	11	11	11	11	10	11	11	10	11	
ESP Fly ash	2	Avg.	29	55	54	113	13	51	11	2.3	11	1.6	9	1.9	5.4	0.8	5.0	0.8	280	334	364	6.42
		St. dev.	9	16	13	26	3	15	4	0.7	4	0.5	3	0.5	1.4	0.2	1.1	0.2	70	83	95	0.38
		Count	11	12	12	12	12	12	12	12	12	12	12	12	12	12	11	12	12	11	11	
ESP Fly ash	3	Avg.	28	54	54	112	13	50	10	2.3	10	1.6	9	1.8	5.3	0.8	4.8	0.7	275	328	358	6.54
		St. dev.	3	10	6	12	1	8	2	0.4	2	0.3	2	0.3	0.8	0.1	0.7	0.1	34	40	44	0.45
		Count	9	10	10	10	10	10	10	10	10	10	10	10	10	10	9	10	10	9	10	

*The ASTM procedure calls for the use of the total S in the determination of the O content; for any coal, the resulting O is suspect. For super-high-S coals, the reported O can be negative.

Zn, Hg, and Cl, among other elements [24,25,30]

From 2007 through 2016, power plants in central Kentucky and the Ohio River Valley shifted the types of coal sources from the low-S Central Appalachian coals to the high-S Illinois Basin coals [31,32]. This change was driven by the requirements for all major coal-fired units in the eastern US to install high-efficiency flue-gas desulfurization equipment [33,34] (note, these rules have been amended but these were the version in place or anticipated at the time of the sampling [35]) and further motivated by the increasing costs of Central Appalachian coals, a function of the diminishing reserves and quality of the region's coals [36].¹

Rare earth elements (REE) are a vital resource in the modern, technology-driven economy [3,5,9,11]. The concentration of REE in Central Appalachian coal-derived fly ashes has been addressed

¹ As stated decades ago by James Cobb, later the Kentucky State Geologist. "We've already mined out the best of the best. We're mining the worst of the best. Soon we'll be mining the best of the worst. The key question is, do we have at least one generation – 20 years – of high-level, cost-effective mining left. We need to know at least a generation in advance when it will become too costly to produce, so we can prepare for the economic changes that will result." [37] While the timing of his prediction was accurate; the level of planning by the region and the state was not in line with his hopes.

elsewhere [2–9,29,38]. With the exception of some analyses by Taggart et al. [5], a detailed presentation of REE from the combustion of Illinois Basin coals has not been presented. In this study, analyses from fly ashes collected from Kentucky power plants from 2007 through 2016 is presented. Some samples were collected in conjunction with a pent-annual collection of coals and ashes from Kentucky power plants [31,32], with the remainder collected as part of federally-funded studies of REE in fly ashes.

2. Methods

2.1. Nomenclature surrounding rare earth element distributions

Seredin and Dai [39] described four genetic modes of REY (REE + Y; REYSc is REE + Y + Sc) emplacement on coals: detrital, tuffaceous (volcanic), infiltrational/leaching, and hydrothermal. Organic associations, common in low-rank coals and perhaps into the high volatile C bituminous rank range (which would cover much of the Illinois Basin), are a fifth category. In many, if not all, cases, REY enrichment in coal is a function of multiple modes of enrichment [40,41]. With no known ash-fall events represented in the Illinois Basin coals, the tuffaceous mode seems to be eliminated from consideration; eliminating just one possibility still leaves a complex array of potential enrichment events.

In the usage here, light rare earth elements (LREE) include La

through Sm and the heavy rare earth elements (HREE) include Eu to Lu [42–46], with the use of LREE/HREE in the evaluation of the distribution following Balashov [47] and Seredin [42]. The relative concentrations of select elements after McLennan and Taylor's [48] Upper Continental Crust (UCC) corrections are:

- L-type ($\text{La}_N/\text{Lu}_N > 1$; N indicates a value corrected against a standard distribution, such as the Upper Continental Crust),
- M-type ($\text{La}_N/\text{Sm}_N < 1$, $\text{Gd}_N/\text{Lu}_N > 1$), and
- H-type ($\text{La}_N/\text{Lu}_N < 1$) enrichment patterns [39].

The following ratios, based on the UCC corrections, as indicated by the N subscript following the element symbol, decouple Ce, Eu, and Gd from the other REE in the distribution patterns: [46,49,50,51]

$$\text{Eu}_N/\text{Eu}_N^* = \text{Eu}_N/(0.67\text{Sm}_N + 0.33\text{Tb}_N) \quad (1)$$

$$\text{Ce}_N/\text{Ce}_N^* = \text{Ce}_N/(0.5\text{La}_N + 0.5\text{Pr}_N) \quad (2)$$

$$\text{Gd}_N/\text{Gd}_N^* = \text{Gd}_N/(0.33\text{Sm}_N + 0.67\text{Tb}_N) \quad (3)$$

2.2. Sample and data collection

Every five years from 1992 to 2012, with supplemental collections made in the intervening years and up to 2016, the University of Kentucky Center for Applied Energy Research (CAER) sampled 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 coal-fired power plants in Kentucky. Through that time, as many as 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. As best as possible, fly ash was collected from multiple rows (including cyclone (mechanical), baghouse/fabric filter (FF), and electrostatic precipitator (ESP) systems (ESPs are the sole means of fine ash collection at the studied plants)) and from multiple ash-collection hoppers in each row. For the 2002, 2007, and 2012 collections, as well as any collections between those times and for all post-2012 collections, an effort was made to sample the same hoppers every time. In addition to the physical collections, information was gathered on the source of the coal, the tonnages of coal combustion products, and the utilization versus disposal practices. The 2007 and 2012 results are discussed by Hower et al. [31,32] (earlier collections were discussed by Hower et al. [43,44,52,53]) and a discussion of the partitioning of select elements between the pulverized feed coal and the fly ash is found in Hower et al. [29] Rather than identify power plants in publications, a letter code system was developed in 1992 at the start of our collection efforts.

The samples investigated here represent the units burning Illinois Basin coal, with an emphasis on the 33 fly ash samples for which REE analyses are available. Due to the availability of samples and the constraints on the analytical process imposed by time and budgets, the analyzed samples tend to be from the later years of the overall sampling program. The complete data set is in the [Supplementary Information](#) (tab 7 on the Excel file), with Illinois Basin sources listed on rows 3–233 and 395–409.

The proximate, heating value, and sulfur forms analyses of the feed coals and the ultimate analysis and major oxide and select minor element, both done by X-ray fluorescence, determinations were performed at the CAER following ASTM standards for the various techniques. The REE analyses were conducted by via inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700x) at Duke University [5].

2.3. Data analysis

[Supplementary data](#) analysis was conducted using the Principal

Components Analysis (PCA) package of JMP Pro 14 (SAS, Cary, North Carolina). Analyzed parameters included Zn, Zr, $100^*\text{TiO}_2/\text{Al}_2\text{O}_3$, REY (lanthanides + Y), and LREE/HREE mass ratio ((La through Sm)/(Eu through Lu)). The parameters (from tables in the [Supplementary Information](#) and from Bragg et al. [54] were selected based on at least a partial association with hydrothermal mineralization (Zn) and detrital input (Zr and $\text{TiO}_2/\text{Al}_2\text{O}_3$), in addition to the Rare Earth parameters (REY and LREE/HREE).

3. Results and discussion

3.1. Historic coal chemistry data

Fly ash chemistry is a function of the chemistry of the feed coal or the blend of feed coals. A coal with low concentrations of As, Hg, or REE will not produce a fly ash with high concentrations in those elements. This is a rather unforgiving caveat in broad comparisons of element trends from multiple power plants; such assessments cannot be made outside of the context of the variation in the feed coal chemistry. For Hg, this is further complicated by the fact that, aside from Hg-collection additives to the flue gas stream, Hg collection is driven by the amount of carbon in the fly ash [55].

The feed coals are from mines in western Kentucky, Illinois, and Indiana. Coal supplies are contracted on the basis of the traditional major parameters such as ash, sulfur, and heating value with some consideration given to the chlorine content and the Hardgrove grindability index (HGI). In some cases, utilities may allow a harder-to-grind coal (lower HGI) with an allowance that the heating value must be increased by, for example, 200 Btu/lb. (0.465 MJ/kg) for every HGI point below HGI = 50. This is a logical tradeoff, since lower grindabilities imply a lessened throughput in the pulverizers; a higher heating value offsets the delay in grinding the harder coal. Multiple mines and, potentially, multiple coal seams are represented in the feed coal at each of the power plants. In addition, the coal supply shifted over time as mines closed and new mines opened. As a result, even if specifications of the feed coals (e.g., ash content, S content, heating value) remained the same over multiple years, the 2007 feed coal to an individual plant is likely to have had a somewhat different source than the 2012 coal delivered to the same plant.

An extensive data set for the examination of coals in the Illinois Basin states is the Bragg et al. [54] database. The limitations of the database are that the samples represent coal mined and sampled in the 1970's and 1980's and the analyses were done in the same period. Technology changes, for example, the modern ICP-MS instrumentation for REE analysis is considered to be more reliable and precise than what was available decades ago. As an advantage, though, the coverage of mines was much better decades ago that it is now, so locations not available at this time are averaged into the total coalfield set.

For this analysis, data from the Springfield (Western Kentucky No. 9, Illinois 5, Indiana V), Herrin (Western Kentucky No. 11, Illinois 6, Herrin (Indiana)), and Baker (Western Kentucky No. 13, Jamestown (Illinois), Hymera VI (Indiana)) coals, among the most important resources in the basin, were selected as a subset (106 analyses out of the 298 Illinois Basin coals in the database) for further examination. The selected data from Bragg et al. [54] starts in column BA on tab 2 of the [Supplementary Information](#). The Principal Components Analysis (PCA), based on Zn, Zr, $100^*\text{TiO}_2/\text{Al}_2\text{O}_3$, REY, and LREE/HREE (or transforms of those parameters), is shown on [Fig. 1](#) with more details on tab 2 of the [Supplementary Information](#). The latter parameters were used by Hower et al. [41] based on the assumption that Zn can be a proxy for hydrothermal mineralization, Zr and $\text{TiO}_2/\text{Al}_2\text{O}_3$ for detrital influences, and REY and LREE/HREE for aspects of the REE and REY distribution. Overall, the PCA trends are somewhat diffuse, with the detrital contributors having a near orthogonal relationship. The points are clustered, with only five points, four high- and one low-REY points (the ash-basis values are shown with the points on [Fig. 1](#)) out of the >100 analyzed samples

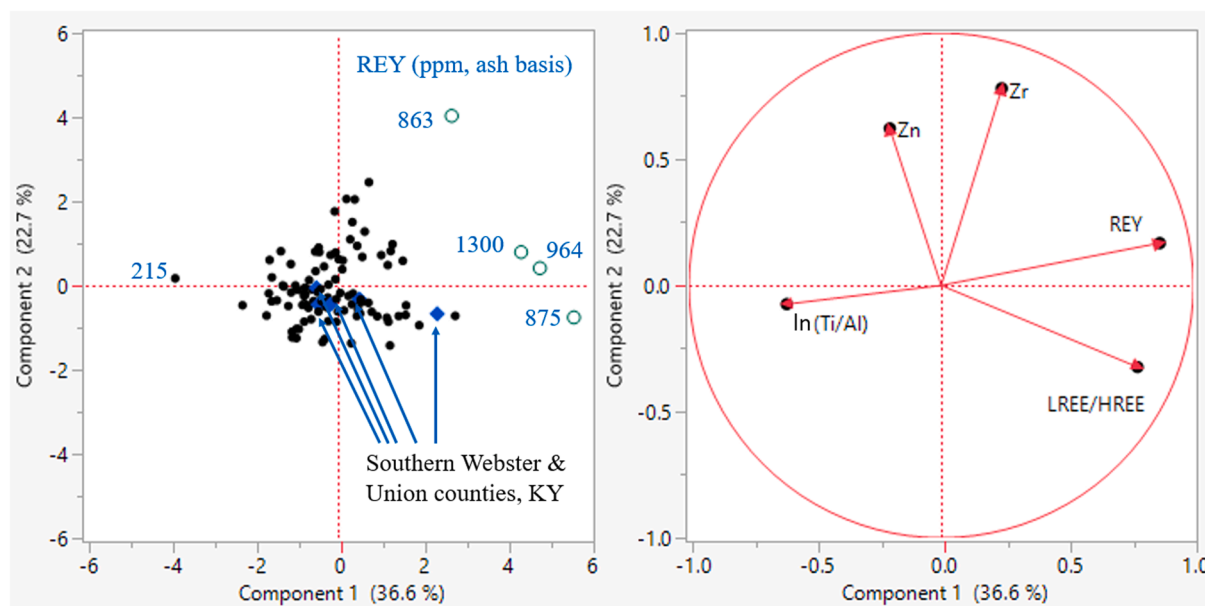


Fig. 1. Principal components analysis of Springfield, Herrin, and Baker coals (and correlatives) in the Illinois Basin. The four high-REY and one low-REY data points are shown along with the REY value (ppm, ash basis). Data from Bragg et al. [54]

falling outside of the central cluster. Even samples from southern Webster and Union counties, Kentucky, with a presumed hydrothermal influence, [25] fall within the largely undifferentiated central cluster.

3.2. Chemistry of feed coal

For the sake of comparison, the pulverized coal is used as the baseline because it is a direct representation of the fuel fed to the boiler. The pulverization process rejects a hard, rocky, high-S waste stream from the fuel. Hower et al. [29] discussed element partitioning between the pulverized coal, pulverizer rejects, and the first two ash collection rows, both FF and ESP, from Kentucky power plants.

As seen in Table 1 and on tabs 5 and 7 in the [Supplementary Information](#), the pulverized coal is, on average, a moderate-ash content (12.16% dry), high-S (2.97% dry, ash-free) product. In contrast, the pulverizer rejects, colloquially called the “pyrites”, has 49.77% ash; 29.30% S; and a much higher concentration of potentially hazardous elements such as Hg, Se, and As. The feed coal has 70.18% $\text{SiO}_2 + \text{Al}_2\text{O}_3$ and 18.58% Fe_2O_3 (ash basis) compared to 21.73% $\text{SiO}_2 + \text{Al}_2\text{O}_3$ and 59.44% Fe_2O_3 in the pulverizer rejects.

3.3. Coal combustion products

3.3.1. Distribution of non-Rare earth elements

The chemistry of the coal combustion products, collectively the fly ash and bottom ash for the purpose of this study, is given on Table 1 and tabs 1 and 5–7 in the [Supplementary Information](#). The bottom ash is not nearly as well represented as the fly ashes, so this fraction will not be considered further in this study.²

In the fly ash-collection system, the first-row collectors experience the hottest flue gas, with the temperature decreasing as the gas passes through the collection system. As a rule of thumb, the first ESP row collects about 80% of the ash reaching that point (keeping in mind that some ash could be removed by the economizer and by the cyclone collection systems). Each successive row collects about 80% of the ash

entering that row. In our experience, the ash-collection systems have from two to five rows. Only the first three rows are considered here because collection from the fourth and fifth rows, where present, is not consistently reliable; the ash volumes are often low to non-existent. The particle size decreases from the first to last row; [4,45,56,57] therefore, the cooler ESP rows also contain smaller/higher-surface-area particles, an optimal recipe for the collection of volatile trace elements. As noted above, Hg, while highly volatile, is subject to different parameters in its collection by fly ash; Hg collection will increase with both a drop in flue gas temperature and an increase in the fly ash carbon. [29,55] Variations in the fly ash petrology between ash-collection rows can impact the relative abundance of the non-volatile elements in fly ash [58].

The emphasis in this study is the distribution of the REY, but the row-by-row variation in other elements is noteworthy. The average S and SO_3 , As, Zn, Se, and Hg increase from the 1st to 3rd rows. The increase in Hg from 0.08 to 0.46 ppm (whole ash) is accompanied by an increase in carbon from 3.79% in the 1st row to 5.65% in the 2nd row and 4.60% in the 3rd row. Such a trend, seemingly driven by the combination of the increase in C along with a decrease in flue gas T, is tempered by the difficulty in making broad comparisons without a thorough comparison of the Hg content of the coal source or the configuration of the individual plants [55,59].

3.3.2. Distribution of the rare earth elements

In contrast to the between-row variation in the volatile elements, the average REE, REY, REYSc, and LREE/HREE show a non-significant change from the 1st through 3rd rows. Such a fundamental comparison aside, the next step in the overall evaluation was to look for representative trends in the distribution of major and minor elements. As part of this evaluation, the relationship between select parameters was examined on scatter plots (after JMP; see [Supplementary Information](#), tab 4). This included the five direct and derived parameters noted for the PCA analysis in section 3.1 plus SiO_2 , Al_2O_3 , Fe_2O_3 , P_2O_5 , TiO_2 , Y, Ba, Sr, Ba + Sr, and $\text{SiO}_2/\text{Al}_2\text{O}_3$. Most of the relationships are fairly random, but a few were selected for a closer examination. The PCA and scatter plots together were used as starting points for the evaluation of trends. Neither is definitive in themselves. A thorough analysis must be grounded in the knowledge of the coal and the fly ash in order to avoid spurious interpretations.

Since Y can be a trace constituent in zircon, the relationship between

² At many plants, the pulverizer rejects are mixed with the bottom ash prior to our sampling point. In this case, the “bottom ash” is not representative of the combustion process. Such operations are not considered in the Table 1 average.

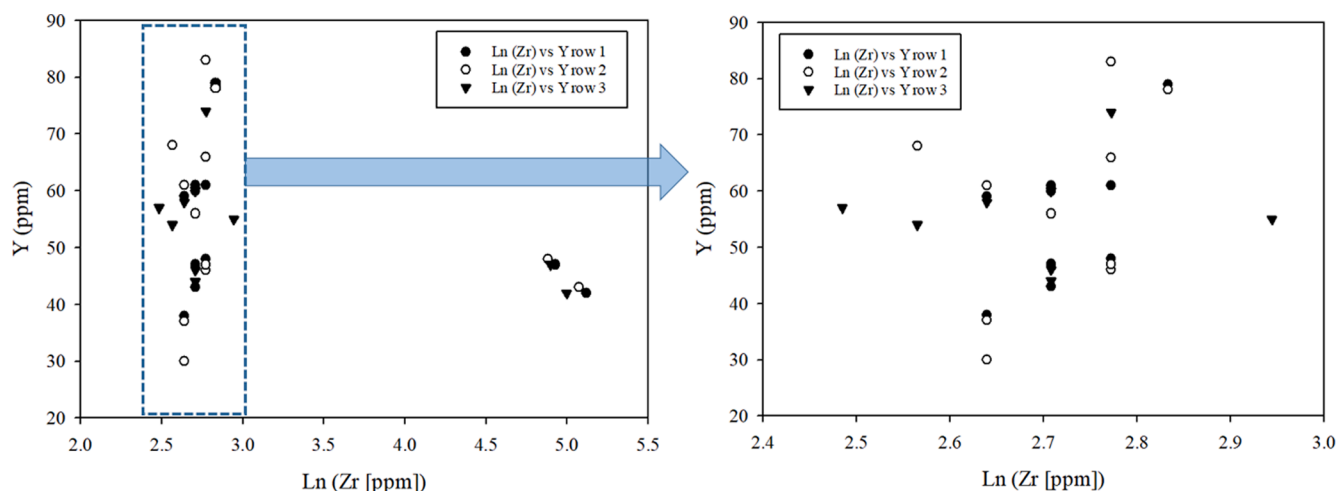


Fig. 2. Natural log transform $\ln(\text{Zr} [\text{ppm}])$ vs. $\text{Y} (\text{ppm})$ contents in fly ash from all three ESP rows of the power plants. Left: All data; right: data for select $\ln(\text{Zr})$ range.

Y content and Zr content (as the natural log transform $\ln(\text{Zr})$) is of potential interest (Fig. 2). The distribution of the points represent a classic problem in correlations for two reasons: (1) the cluster of points in the 2.4 to 3.0 $\ln(\text{Zr})$ region does not show a resolved trend and (2) the smaller, distant cluster of points at $\pm 5 \ln(\text{Zr})$ lines up with the midpoint of the left previous group. The $\ln(\text{Zr})$ values vs. REY, $\text{Sr} + \text{Ba}$ vs. $\text{TiO}_2/\text{Al}_2\text{O}_3$, P_2O_5 vs. $\text{TiO}_2/\text{Al}_2\text{O}_3$, and REY vs. $\text{TiO}_2/\text{Al}_2\text{O}_3$, all shown on tab 8 in the [Supplementary Information](#), show similar diffuse trends.

The relationship between $\ln(\text{Zr})$ and $\text{TiO}_2/\text{Al}_2\text{O}_3$ (Fig. 3) with a better resolved trend ($r^2 = 0.67$ for the 1st-row points), is based on the zircon and Ti-oxide minerals (rutile, anatase) potentially being part of the detrital mineral suites in the coals. The point with higher $\ln(\text{Zr})$ values show that the relationship with $\text{TiO}_2/\text{Al}_2\text{O}_3$ can be specific to the power plant, thus, to the source of the coals rather than to the ESP row. Plants P and R have individual (relatively) tight clusters and the ESP row has no bearing on the concentration of any of the elements. The plot of $\text{Sr} + \text{Ba}$ vs. $(\text{SiO}_2 + \text{Al}_2\text{O}_3)/\text{Fe}_2\text{O}_3$ (Fig. 4) is marginally significant; the 3rd-row correlation is significant at the 5% level of confidence while the 1st and 2nd rows fall below this threshold.

Based on the importance of REY, LREE/HREE, and $\text{TiO}_2/\text{Al}_2\text{O}_3$ parameters from the PCA assessment of the coal quality information (Fig. 1) and the $\text{Ba} + \text{Sr}$ and $(\text{SiO}_2 + \text{Al}_2\text{O}_3)/\text{Fe}_2\text{O}_3$ parameters from the Fig. 4 regression, those variables were chosen for the PCA assessment of the fly ash composition. Fig. 5, with more data on tab 3 of the

[Supplementary Information](#), shows all three rows (points for each of the rows are labeled). The first eigenvector is dominated by $\text{Ba} + \text{Sr}$ and $(\text{SiO}_2 + \text{Al}_2\text{O}_3)/\text{Fe}_2\text{O}_3$, with lesser negative contributions from REY and $\text{TiO}_2/\text{Al}_2\text{O}_3$. The second eigenvector is dominated by negative $\text{TiO}_2/\text{Al}_2\text{O}_3$ and positive REY and LREE/HREE. The 1st- and 2nd-row samples from Plant O, each with over 1600-ppm $\text{Ba} + \text{Sr}$ (dry), and the 3rd-row Plant H sample, with the lowest $\text{TiO}_2/\text{Al}_2\text{O}_3$ are the outliers.

The spider plot of the Upper continental crust-corrected REE distribution [48], shown on Fig. 6 (with the corrected data on tab 6 of the [Supplementary Information](#)), reveals two features: (1) a clear Gd peak for certain samples and (2) $\text{La}_N/\text{Lu}_N < 1$ for most samples, indicating an H-type enrichment pattern [39]. In order to better resolve the Gd peaks, Fig. 7 shows just the 1st-row ESP fly ashes. In this case, it is evident that Plants E and H are the sources of the highest Gd peaks. Fig. 8 shows all rows in Plants E and H, indicating that, for Plant H, the fly ash from two collections, June 2012 and July 2013, each had some of the higher Gd peaks with the 1st- and 2nd-row samples all having a UCC-corrected value > 4 . It is known from other studies [2,3] that Gd exhibits a high concentration in the magnetic concentrates of fly ash, suggesting an association with the magnetic particles (magnetite and other Fe-rich spinels). The decrease in Gd and Gd_N from the 2nd to 3rd ESP row is likely due to a combination of factors from change in the nature of the fly ash petrography as the coarser particles were removed by the 1st and 2nd ESP's to, simply, the overall lower concentration of REE in the 3rd-

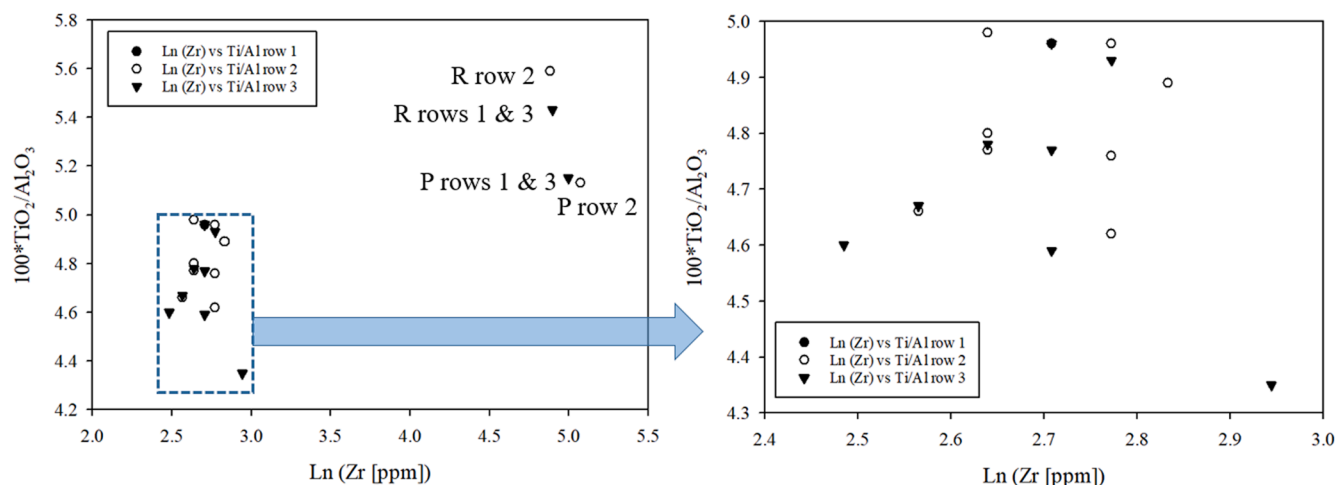


Fig. 3. $\ln(\text{Zr} [\text{ppm}])$ vs. $100 \cdot \text{TiO}_2/\text{Al}_2\text{O}_3$ contents for fly ash from all three ESP rows of the power plants. Left: All data; right: data for select $\ln(\text{Zr})$ range.

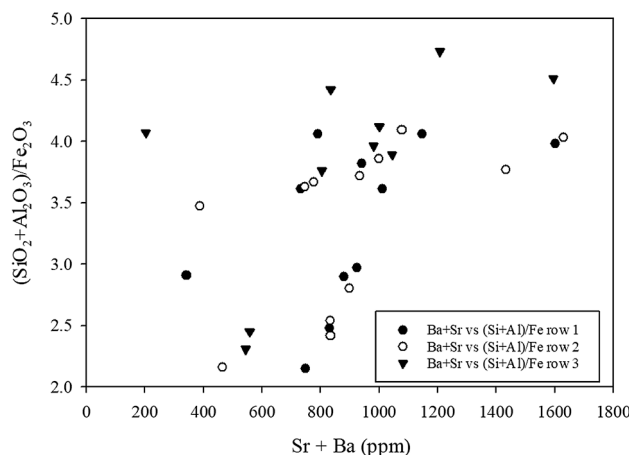


Fig. 4. Fly ash Ba + Sr (ppm) vs. $(\text{SiO}_2 + \text{Al}_2\text{O}_3)/\text{Fe}_2\text{O}_3$ contents for samples from all three ESP rows of the power plants.

row samples in Plants E and H.

Central Appalachian coals, particularly the Fire Clay coal in eastern Kentucky, are, in some respects, the standard to which other fly ashes of eastern U.S. coals are compared for REE content and speciation [1,4,5]. Two fly ash collections from Plant I, traditionally burning a mix of eastern Kentucky coals, are detailed on Table 2 and on tab 9 in the Supplementary Information. Both sets were analyzed on the same instrument in the same laboratory by the same operator as the Illinois Basin-sourced fly ashes discussed above. The 2007 fly ash from both units was sourced from a mix of moderate-S, high volatile A bituminous eastern Kentucky coals. The 2014 fly ash collection from unit 1 (unit 2 was reconfigured, thus, it was no longer possible to collect unadulterated fly ash) was from a pre-arranged burn of the Fire Clay coal. The spider plot of the UCC-corrected REE's (Fig. 9) shows that the two runs have distinctly different patterns. The Fire Clay-derived fly ash has a negative $\text{Eu}_N/\text{Eu}_N^*$, with values ranging from 0.83 to 0.93, and a distinct Gd peak. The Fire Clay coal, particularly the ash-fall tonstein and lithotypes adjacent to the tonstein, has a significant negative Eu anomaly [41]. The mixed-source fly ash from the 2007 collection has a positive $\text{Eu}_N/\text{Eu}_N^*$, with values ranging from 1.02 to 1.06, and a muted-to-nonexistent Gd peak. In both cases, the $\text{La}_N/\text{Lu}_N < 1$, indicating an H-

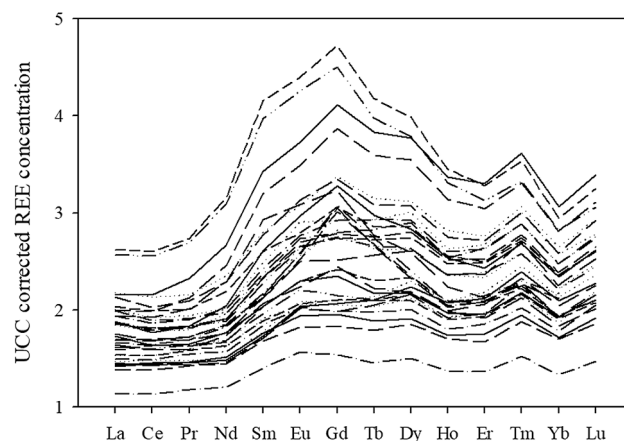


Fig. 6. Spider plot of Upper continental crust-corrected REE data [48] for all fly ash samples collected from all three ESP rows of the power plants.

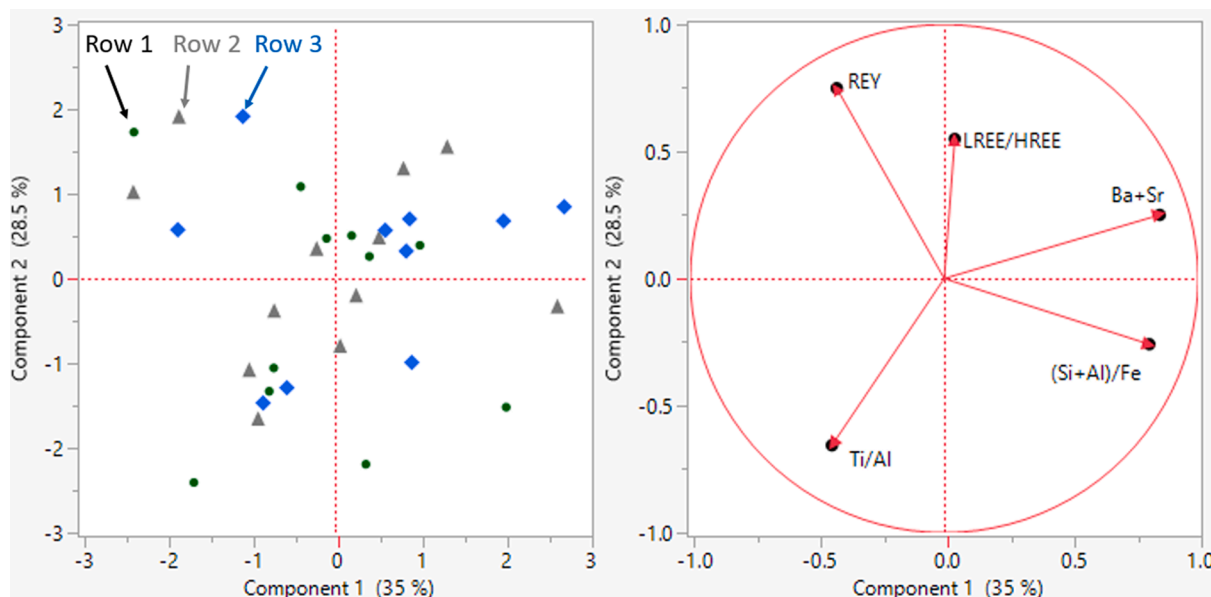


Fig. 5. Principal components analysis of fly ash data for all three ESP rows of the power plants.

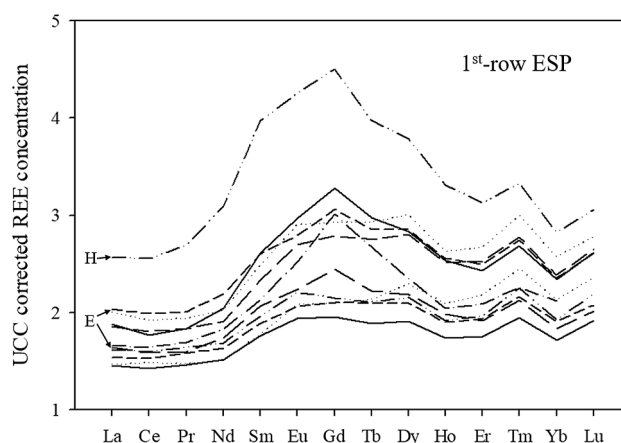


Fig. 7. Spider plot of Upper continental crust-corrected REE data [48] for fly ash samples from the first ESP row of each of the power plants.

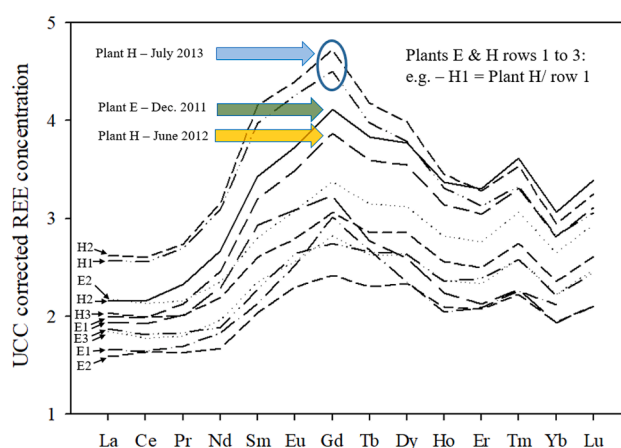


Fig. 8. Spider plot of Upper continental crust-corrected REE data [48] for fly ash power plants E and H.

type enrichment pattern. Aside from the higher REE/REY/REYSc in the eastern Kentucky-sourced fly ashes versus the Illinois Basin-sourced ashes, the distributions are somewhat distinct with (1) the Illinois Basin fly ashes having a positive $\text{Eu}_N/\text{Eu}_N^*$ and, in some cases, distinct Gd peaks, (2) the mixed-source Plant I fly ashes having a positive $\text{Eu}_N/\text{Eu}_N^*$ and a poorly defined Gd peak, and (3) the Fire Clay-derived Plant I ashes showing a $\text{Eu}_N/\text{Eu}_N^*$ and a sharp Gd peak. Aside from the Plant E and H fly ashes, the Illinois Basin-sourced fly ash patterns resemble the mixed-source Plant I fly ashes.

4. Summary

Several utility power plants in Kentucky burn Illinois Basin coals. Detailed collections of pulverized coal and fly ash from 2007 to 2016 enabled comparisons of elemental compositions, including the rare earth elements. For the fly ashes, comparisons could be made for multiple ash-collection rows.

The high volatile C through high volatile A bituminous pulverized feed coals have, on average, 12.16% ash (dry), nearly 3% S_{total} (dry, ash-free), over 70% $\text{SiO}_2 + \text{Al}_2\text{O}_3$, and 18.58% Fe_2O_3 (oxides on ash basis). The higher rank coals have higher Cl, Ni, V, Cr, Zn, As, and Hg than the high volatile C bituminous coals.

Within the fly ashes, while, in accordance with the increased surface area (the result of a smaller particle size) and the decrease in flue gas T, the S and SO_3 , As, Zn, Se, and, with caveats related to the amount of carbon in the fly ash, Hg increase from the 1st to 3rd rows, non-volatile elements, such as Zr, Ti, and the rare earths, show no discernable

changes in concentration between the ESP rows. While Y is a trace constituent in zircon, no relationship between Y and Zr was observed. The correlation between Zr and $\text{TiO}_2/\text{Al}_2\text{O}_3$, representing different minerals within the detrital-mineral suite, is significant. The relationship between $\text{Sr} + \text{Ba}$ and $(\text{SiO}_2 + \text{Al}_2\text{O}_3)/\text{Fe}_2\text{O}_3$, with the former representing elements associated, in part, with phosphates and, indirectly, with REE, is marginally significant.

The spider plots of the Upper continental crust-corrected REE distributions show that Plants E and H have distinct Gd peaks and that the normalized La is less than the normalized Lu ($\text{La}_N/\text{Lu}_N < 1$), indicating an H-type distribution of the REE. Overall, the REE concentrations for Illinois Basin coal-sourced fly ashes are about one-third less than that for fly ashes from the combustion of Central Appalachian coals. For the sake of comparison, spider plots of the corrected REEs from two sets of Central Appalachian coal-sourced fly ashes were created: one set is from a blend of coals and the other from an exclusive run of the Fire Clay coal, both from the same power plant (Plant I in our code). The Fire Clay-derived fly ash has a negative $\text{Eu}_N/\text{Eu}_N^*$ and a distinct Gd peak. The Eu anomaly is a notable reflection of the character of the Fire Clay coal. The mixed-source fly ash has a positive $\text{Eu}_N/\text{Eu}_N^*$ and minimal Gd peak. Both sets of ashes have H-type enrichment patterns. Aside from the Plant E and H fly ashes with the sharp Gd peaks, the Illinois Basin-sourced fly ash patterns resemble the mixed-source Plant I fly ashes.

While their REE contents are less than that for fly ashes produced in the combustion of Central Appalachian coals, the relative availability of Illinois Basin-derived fly ashes may make them an attractive resource.

Table 2

Major and trace element contents for fly ashes samples collected from 1st- through 3rd-row ESP during 2007 and 2014 collection events from Plant I.

				Ash basis; ppm																				
Unit	Row	Bin	Sample	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	REE	REY	REYSc	LREE/ HREE	
1	1	12	93375	46	104	87	189	22	83	19	4.1	19	3.1	18	3.7	11	1.5	9.2	1.4	471	558	604	5.63	
1	2	10	93376	47	100	80	173	20	79	18	3.9	18	2.9	17	3.5	10	1.4	8.9	1.3	437	517	564	5.50	
1	3	8	93377	50	96	79	172	20	78	17	3.8	17	2.8	16	3.4	10	1.4	8.4	1.3	431	510	560	5.69	
2	1	12	93382	38	82	82	175	20	77	16	3.5	16	2.5	15	2.9	8	1.2	7.3	1.1	428	510	549	6.45	
2	1	10	93383	37	84	82	176	20	77	16	3.4	16	2.5	15	3.0	8	1.2	7.5	1.1	429	511	548	6.36	
2	2	8	93384	39	83	78	167	19	74	16	3.5	16	2.5	14	3.0	8	1.2	7.6	1.1	411	488	527	6.16	
2	2	6	93385	39	85	76	164	19	73	16	3.4	16	2.5	15	3.0	9	1.2	7.6	1.1	406	483	522	6.02	
2	3	4	93386	44	91	77	169	19	75	16	3.6	17	2.6	15	3.2	9	1.3	7.9	1.2	417	494	538	5.88	
2	3	2	93387	42	97	81	179	21	80	18	3.8	18	2.8	16	3.4	10	1.4	8.5	1.3	443	524	567	5.82	
1	1	11	93955	53	129	119	265	29	113	24	4.2	27	4.0	23	4.8	13	2.0	12.3	1.8	643	762	814	5.92	
1	1	12	93956	52	127	114	252	28	109	22	4.0	26	3.7	22	4.5	13	1.9	11.4	1.7	613	727	778	5.95	
1	2	9	93957	55	130	113	252	28	109	23	4.3	26	3.9	22	4.6	13	1.9	11.7	1.8	616	729	783	5.81	
1	2	10	93958	55	133	116	257	28	111	23	4.3	27	3.9	23	4.7	13	2.0	12.2	1.8	628	743	798	5.81	
1	3	7	93959	57	138	117	259	29	113	24	4.6	28	4.1	24	5.0	14	2.1	12.7	1.9	638	754	812	5.60	
1	3	8	93960	54	132	110	246	27	106	23	4.5	26	3.9	23	4.7	13	2.0	12.0	1.8	604	715	769	5.59	
UCC-corrected REE																								
Unit	Row	Bin	Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu							
				30	64	7.1	26	4.5	0.88	3.8	0.64	3.5	0.8	2.3	0.33	2.2	0.32			Eu _N /Eu _N *	Ce _N /Ce _N *	Gd _N /Gd _N *		
1	1	12	93375	2.90	2.95	3.04	3.21	4.13	4.62	5.08	5.09	5.21	4.61	4.57	4.95	4.20	4.59	1.04		1.00		1.06		
1	2	10	93376	2.66	2.71	2.83	3.03	3.99	4.38	4.78	4.78	4.89	4.39	4.38	4.69	4.04	4.46	1.03		0.99		1.06		
1	3	8	93377	2.64	2.69	2.81	2.98	3.78	4.32	4.52	4.66	4.71	4.27	4.17	4.63	3.84	4.20	1.06		0.99		1.03		
2	1	12	93382	2.74	2.73	2.83	2.96	3.62	3.98	4.27	4.14	4.15	3.63	3.59	3.89	3.31	3.71	1.05		0.98		1.08		
2	1	10	93383	2.73	2.75	2.82	2.95	3.62	3.91	4.31	4.24	4.21	3.72	3.66	3.98	3.42	3.82	1.02		0.99		1.07		
2	2	8	93384	2.58	2.60	2.70	2.85	3.55	3.93	4.17	4.18	4.09	3.70	3.65	4.00	3.44	3.69	1.05		0.98		1.05		
2	2	6	93385	2.54	2.57	2.66	2.81	3.56	3.91	4.18	4.19	4.15	3.75	3.73	3.98	3.46	3.79	1.04		0.99		1.05		
2	3	4	93386	2.57	2.63	2.73	2.88	3.61	4.08	4.36	4.34	4.37	3.98	3.92	4.24	3.58	3.98	1.06		0.99		1.06		
2	3	2	93387	2.71	2.80	2.89	3.06	3.89	4.35	4.67	4.65	4.69	4.25	4.20	4.53	3.85	4.29	1.05		1.00		1.06		
1	1	11	93955	3.97	4.14	4.08	4.36	5.27	4.75	7.17	6.60	6.62	5.96	5.82	6.56	5.60	6.03	0.83		1.03		1.16		
1	1	12	93956	3.79	3.94	3.90	4.18	4.99	4.51	6.94	6.24	6.22	5.62	5.59	6.19	5.16	5.77	0.84		1.03		1.19		
1	2	9	93957	3.77	3.94	3.92	4.20	5.12	4.87	6.97	6.42	6.42	5.77	5.75	6.45	5.32	5.85	0.88		1.03		1.16		
1	2	10	93958	3.86	4.01	3.99	4.28	5.16	4.93	7.14	6.49	6.52	5.90	5.83	6.56	5.53	6.00	0.88		1.02		1.18		
1	3	7	93959	3.89	4.04	4.06	4.34	5.27	5.23	7.35	6.82	6.91	6.25	6.19	6.92	5.76	6.32	0.90		1.02		1.16		
1	3	8	93960	3.67	3.85	3.82	4.09	5.02	5.10	6.96	6.46	6.52	5.90	5.86	6.53	5.47	6.07	0.93		1.03		1.16		
				As-rec.		Dry		Dry, ash-free				Ssh basis												
Unit	Row	Bin	Sample	Mois, %	Ash, %	C, %	H, %	N, %	O, %	S, %	SiO2, %	Al2O3, %	Fe2O3, %	CaO, %	MgO, %	Na2O, %	K2O, %	P2O5, %	TiO2, %	SO3, %				
1	1	12	93375	0.37	92.08	6.59	0.10	dl	0.91	0.32	51.79	30.40	9.63	1.61	1.14	0.17	3.07	0.58	1.49	0.08				
1	2	10	93376	0.41	90.58	7.65	0.12	0.02	1.18	0.45	50.82	29.92	10.07	1.67	1.16	0.18	3.09	0.65	1.50	0.12				
1	3	8	93377	1.87	87.36	5.26	0.23	dl	6.21	0.94	48.77	28.86	13.17	1.66	1.16	0.19	2.97	0.82	1.48	0.42				
2	1	12	93382	0.17	96.48	2.95	0.05	dl	0.41	0.11	54.21	28.13	11.12	1.15	1.13	0.16	3.02	0.30	1.31	0.03				
2	1	10	93383	0.18	95.48	3.80	0.05	dl	0.55	0.12	53.67	28.30	10.98	1.18	1.12	0.16	3.01	0.31	1.34	0.02				
2	2	8	93384	0.19	94.99	4.14	0.06	dl	0.64	0.17	52.38	27.74	12.80	1.28	1.15	0.17	3.03	0.35	1.33	0.05				
2	2	6	93385	0.35	92.41	6.45	0.07	0.01	0.82	0.24	52.22	28.38	12.43	1.34	1.17	0.17	3.06	0.39	1.35	0.05				
2	3	4	93386	0.55	93.03	4.58	0.15	dl	1.83	0.41	51.09	28.57	12.74	1.47	1.22	0.18	3.17	0.52	1.39	0.15				
2	3	2	93387	0.52	90.09	7.51	0.12	0.03	1.76	0.49	50.79	29.02	12.40	1.54	1.23	0.18	3.17	0.59	1.43	0.14				
1	1	11	93955	0.22	93.34	8.11	0.27	dl	dl	1.49	52.81	30.76	7.54	1.72	0.94	0.25	1.90	0.52	1.75	0.12				
1	1	12	93956	0.23	92.39	9.35	0.29	dl	dl	1.36	55.96	30.74	7.58	1.76	0.93	0.24	1.96	0.52	1.78	0.06				
1	2	9	93957	0.26	94.00	7.82	0.35	dl	dl	1.47	52.59	30.60	8.31	1.84	0.98	0.26	1.99	0.67	1.81	0.27				

(continued on next page)

Table 2 (continued)

Unit	Row	Bin	Sample	As-rec.		Dry		Dry, ash-free				Ssh basis				Whole sample, ppm									
				Mois, %	Ash, %	C, %	H, %	N, %	O, %	S, %	SiO2, %	Al2O3, %	Fe2O3, %	CaO, %	MgO, %	Na2O, %	K2O, %	P2O5, %	TiO2, %	SO3, %					
1	2	10	93958	0.20	92.57	8.52	0.27	dl	1.63	53.32	30.65	8.22	1.87	0.99	0.26	2.01	0.69	1.81	0.22						
1	3	7	93959	0.55	91.98	8.26	0.34	dl	1.92	51.29	30.22	9.18	1.92	1.01	0.27	1.99	0.77	1.83	0.51						
1	3	8	93960	0.35	94.27	6.05	0.33	dl	1.94	50.12	29.56	9.87	2.01	1.04	0.28	2.02	0.89	1.78	0.96						
Unit	Row	Bin	Sample	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Zr	Mo	Cd	Sb	Ba	Pb	Se	Hg				
1	1	12	93375	491	183	183	37	158	337	285	361	dl	1421	38	242	1	2	1155	191	24.18	0.72				
1	2	10	93376	519	199	199	39	170	357	322	469	dl	1364	43	243	1	3	1212	235	30.49	1.17				
1	3	8	93377	542	214	316	50	185	364	357	1266	dl	1203	69	181	1	4	1284	536	47.00	0.60				
2	1	12	93382	353	136	201	36	109	219	138	127	25	1034	67	139	1	3	1020	83	6.99	0.12				
2	1	10	93383	361	134	192	36	109	225	138	124	6	1073	62	153	1	3	1020	82	10.60	0.18				
2	2	8	93384	379	147	220	42	121	235	151	183	18	1017	75	120	1	4	1064	100	11.06	0.22				
2	2	6	93385	402	149	218	42	129	243	173	222	29	1024	75	124	1	4	1098	117	18.70	0.52				
2	3	4	93386	449	173	247	46	154	298	240	371	1	1101	71	149	1	4	1159	176	24.28	0.33				
2	3	2	93387	476	174	238	46	165	318	266	425	dl	1177	64	175	1	4	1218	201	35.66	0.77				
1	1	11	93955	622	203	132	75	147	271	183	218	dl	1035	327	122	dl	dl	1573	149	1.36					
1	1	12	93956	639	206	131	74	149	282	174	212	dl	1261	391	188	dl	6	1601	135	1.82					
1	2	9	93957	713	233	149	90	173	331	236	325	dl	1297	381	193	1	6	1913	196	1.42					
1	2	10	93958	723	234	148	90	179	322	234	325	dl	1312	384	195	1	6	1908	198	1.90					
1	3	7	93959	814	259	175	96	196	392	289	550	dl	1359	403	209	1	7	2502	247	2.31					
1	3	8	93960	831	265	196	103	210	398	333	582	dl	1254	359	168	1	4	2583	224	0.94					

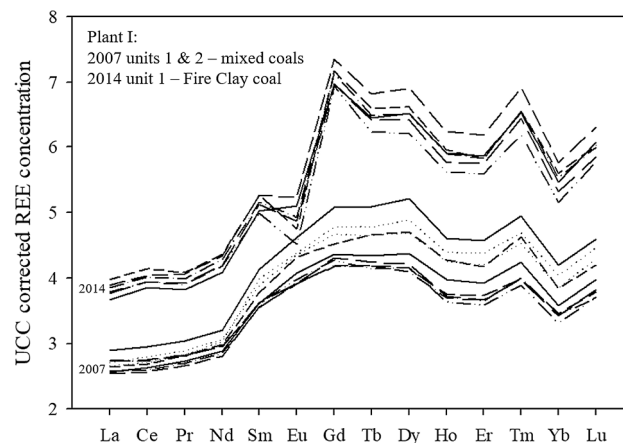


Fig. 9. Spider plot of Upper continental crust-corrected REE data [48] for fly ash the 2007 and 2014 fly ash collections from Plant I. The 2007 feed coal was a blend of eastern Kentucky (Central Appalachian) coals and the 2014 feed coal was the Fire Clay coal, also from eastern Kentucky.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Conflicts of interest

The authors declare no conflicts of interest.

Responsibilities

All authors were responsible for the writing and editing of the manuscript. Hower and Groppo, among others at the CAER, collected the samples; Hower managed the CAER-based portion of the project; Hsu-Kim managed the Duke University portion of the project; and Taggart was responsible for the ICP-MS analyses.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2020.119990>.

References

- [1] Hower JC, Groppo JG, Henke KR, Hood MM, Eble CF, Honaker RQ, et al. Notes on the potential for the concentration of rare earth elements and Yttrium in coal combustion fly ash. *Minerals* 2015;5:356–66.
- [2] Hower JC, Groppo JG, Henke KR, Graham UM, Hood MM, Joshi P, et al. Pondered and landfilled fly ash as a source of rare earth elements from a Kentucky power plant. *Coal Combust Gasification Prod* 2017;9:1–21. <https://doi.org/10.4177/CCGP-D-17-00003.1>.
- [3] Hower JC, Groppo JG, Joshi P, Preda DV, Gamliel DP, Mohler DT, et al. Distribution of Lanthanides, Yttrium, and Scandium in the pilot-scale beneficiation of fly ashes derived from eastern Kentucky coals. *Minerals* 2020;10:105. <https://doi.org/10.3390/min10020105>.
- [4] Hood MM, Taggart RK, Smith RC, Hsu-Kim H, Henke KR, Graham UM, et al. Rare earth element distribution in fly ash derived from the Fire Clay coal, Kentucky. *Coal Combust Gasification Prod* 2017;9:22–33. <https://doi.org/10.4177/CCGP-D-17-00002.1>.

- [5] Taggart RK, Hower JC, Dwyer GS, Hsu-Kim H. Trends in the rare-earth element content of U.S.-based coal combustion fly ashes. *Environ Sci Technol* 2016;50: 5919–26.
- [6] Taggart RK, Hower JC, Hsu-Kim H. Effects of roasting and leaching parameters on extraction of rare earth elements from coal fly ash. *Int. J. Coal Geology* 2018;196: 106–14. <https://doi.org/10.1016/j.coal.2018.06.021>.
- [7] Taggart RK, Rivera NA, Levard C, Ambrosi JP, Borschneck D, Hower JC, et al. Differences in Bulk and Microscale Yttrium Speciation in Coal Combustion Fly Ash. *Environ Sci Processes Impacts* 2018;20:1390–403.
- [8] King JF, Taggart RK, Smith RC, Hower JC, Hsu-Kim H. Aqueous acid and alkaline extraction of rare earth elements from coal combustion ash. *Int J Coal Geol* 2018; 195:75–83. <https://doi.org/10.1016/j.coal.2018.05.009>.
- [9] Smith RC, Taggart RK, Hower JC, Wiesner MR, Hsu-Kim H. Selective Recovery of Rare Earth Elements from Coal Combustion Product Leachates Using Liquid Membranes. *Environ Sci Technol* 2019;53:4490–9.
- [10] Huang Z, Fan M, Tian H. Rare earth elements of fly ash from Wyoming's Powder River Basin coal. *J Rare Earths* 2020;38:219–26.
- [11] Park D, Middleton A, Smith R, Deblonde G, Laudal D, Theaker N, Hsu-Kim H, Jiao Y. A biosorption-based approach for selective extraction of rare earth elements from coal byproducts. *Sep Purif Technol* 2020;241. art. no. 116726.
- [12] Hower JC, O'Keefe JMK, Eble CF. Mississippian (Serpukhovian; Chesterian Stage) coals from the Fluorspar District, Crittenden and Caldwell counties, Kentucky. *Int. J. Coal Geology* 2017;174:23–30.
- [13] Douglass, R.C. The distribution of fusulinids and their correlation between the Illinois Basin and the Appalachian Basin. In: Palmer, J.E., Dutcher, R.R., eds., *Depositional and structural history of the Pennsylvanian System of the Illinois Basin, Part 2: Invited papers. International Congress of Carboniferous Geology and Stratigraphy*, 9th, 26 May – 1 June 1979, Urbana, Illinois, Field trip 9, 15–20.
- [14] Nelson WJ, Elrick S, Williams DA. Permian outliers in Western Kentucky. *Int J Coal Geol* 2013;119:152–64.
- [15] Greb SF, Eble CF, Chesnut Jr DR. Comparison of the Eastern and Western Kentucky coal fields (Pennsylvanian), USA—why are coal distribution patterns and sulfur contents so different in these coal fields? *Int J Coal Geol* 2002;50:89–118.
- [16] Greb SF, Andrews WA, Eble CF, DiMichele W, Cecil CB, Hower JC. Desmoinesian coals of the Illinois and surrounding basins: the largest tropical peat mires in earth history. In: Chan MA, Archer AW, editors. *Extreme Depositional Environments: Mega-end members in Geologic Time*. Geological Society of America Special Publication 370; 2003. p. 127–50.
- [17] Nelson WJ, Greb SF, Weibel CP. Pennsylvanian subsystem in the Illinois Basin. *Stratigraphy* 2013;10:41–54.
- [18] Fielding CR, Nelson JW, Elrick SD. Sequence stratigraphy of the Late Desmoinesian to Early Missourian (Pennsylvanian) succession of southern Illinois: Insights into controls on stratal architecture in an icehouse period of earth history. *J Sediment Res* 2020;90:200–27.
- [19] Zubovic P. Physicochemical properties of certain minor elements as controlling factors in their distribution in coal, in *Coal Science*. In: Given PH, editor. *American Chemical Society Advances in Chemistry* 55. Washington, D.C.: Publications; 1966. p. 221–46.
- [20] Gluskoter HJ, Ruch RR, Miller WG, Cahill RA, Dreher GB, Kuhn JK. Trace elements in coal: Occurrence and distribution. *Illinois State Geological Survey Circular* 499 1977:154 p.
- [21] Ward, C.R. Mineral matter in the Springfield-Harrisburg (No. 5) coal member in the Illinois Basin. *Illinois State Geological Survey Circular* 498, 1977, 35 p.
- [22] Fiene, F.L.; Kuhn, J.K.; Gluskoter, H.J. Mineralogic affinities of trace elements in coal. In: Rogers, S.E., Lemmon Jr., A.W. (Eds.), *Symposium on Coal Cleaning to Achieve Energy and Environ. Coals Proc. Vol. 1*. EPA, Washington, DC, Rep. EPA600/7-79-098a, 1979, 29–58.
- [23] Kuhn JK, Fiene FL, Cahill RA, Gluskoter HJ, Shimp NF. Abundance of trace and minor elements in organic and mineral fractions of coal. *Illinois State Geological Survey Environmental Geology Notes* 1980;88:67.
- [24] Hower, J.C.; Wild, G.D.; Pollock, J.D.; Trinkle, E.J.; Bland, A.E.; Fiene, F.L. Petrography, geochemistry, and mineralogy of the Springfield (Western Kentucky No. 9) coal bed. *Journal of Coal Quality* 1990, 9, 90–100.
- [25] Hower JC, Greb SF, Cobb JC, Williams DA. Discussion on origin of vanadium in coals: parts of the Western Kentucky (USA) No. 9 coal rich in vanadium: *Special Publication No. 125*, 1997, 273–286. *Journal of the Geological Society* 2000;157: 1257–9.
- [26] Hower JC, Mastalerz M, Drobnik A, Quick JC, Eble CF, Zimmerer MJ. Mercury content of the Springfield coal bed, Indiana and Kentucky. *Int. J. Coal Geology* 2005;63:205–27.
- [27] Mastalerz M, Drobnik A. Arsenic, cadmium, lead, and zinc in the Danville and Springfield coal members (Pennsylvanian) from Indiana. *Int J Coal Geol* 2007;71: 37–53.
- [28] Valian, A.; Groppo, J.G.; Eble, C.F.; Hower, J.C.; Honaker, R.Q.; Greb, S.F. Rare earth elements in the Illinois Basin coals. *Mining, Metallurgy & Exploration* 2020, in press. 10.1007/s42461-020-00257-y.
- [29] Hower JC, Fu B, Dai S. Geochemical partitioning from pulverized coal to fly ash and bottom ash. *Fuel* 2020;279:118542.
- [30] Hower JC, Rimmer SM, Williams DA, Beard JG. Coal rank trends in the Western Kentucky coalfield and relationship to hydrocarbon occurrence. In: Nuccio VT, Barker CE, editors. *Applications of thermal maturity studies to energy exploration. Rocky Mountain Section: Society of Economic Paleontologists and Mineralogists*; 1990. p. 127–38.
- [31] Hower JC, Robl TL, Thomas GA, Hopps SD, Grider M. Chemistry of coal and coal combustion products from Kentucky power plants: Results from the 2007 sampling, with emphasis on selenium. *Coal Combust Gasification Prod* 2009;1:50–62.
- [32] Hower JC, Thomas GA, Hopps SG. Trends in coal utilization and coal-combustion product production in Kentucky: Results of the 2012 survey of power plants. *Coal Combust Gasification Prod* 2014;6:35–41.
- [33] Environmental Protection Agency. Mercury and Air Toxics Standards (MATS). 2012 <http://www.epa.gov/airquality/powerplanttoxics/basic.html> (accessed 25 February 2014); now at <https://www.epa.gov/mats> (accessed 3 September 2020).
- [34] Environmental Protection Agency. Cross-State Air Pollution Rule (CSAPR). 2013 <http://www.epa.gov/crossstaterule/> (accessed 25 February 2014); now at <https://www.epa.gov/csapr> (accessed 3 September 2020).
- [35] Hood MM, Groppo JG, Johnston MN, Hower JC, Clack HC, de Medeiros DS, et al. Influence of coal-fired power plant emissions regulations and consequent engineering controls and coal-supply modifications on fly ash chemistry and petrology: Examples from Kentucky power plants. *Coal Combust Gasification Prod* 2016;8:8–18.
- [36] Houser, T.; Bordoff, J.; Masters, P. Can Coal Make a Comeback? Columbia University School of International and Public Affairs, Center on Global Energy Policy. 2017 <http://energypolicy.columbia.edu/publications/report/can-coal-make-comeback> (accessed 3 September 2020).
- [37] Kentucky New Era. Geological study may set pricetag of unmined coal. 21 March 1988. <https://news.google.com/newspapers?nid=266&dat=19880319&id=QvsvAAAAIBAJ&sjid=J20FAAAIBAJ&pg=1308,2205730&hl=en> (accessed 3 September 2020).
- [38] Kolker A, Scott C, Hower JC, Vazquez JA, Lopano CL, Dai S. Distribution of Rare Earth Elements in Coal Combustion Fly Ash, Determined by SHRIMP-RG Ion Microprobe. *Int. J. Coal Geology* 2017;184:1–10. <https://doi.org/10.1016/j.coal.2017.10.002>.
- [39] Seredin VV, Dai S. Coal deposits as potential alternative sources for lanthanides and yttrium. *Int J Coal Geol* 2012;94:67–93.
- [40] Hower JC, Eble CF, Dai S, Belkin HE. Distribution of rare earth elements in eastern Kentucky coals: Indicators of multiple modes of enrichment? *Int J Coal Geol* 2016; 160–161:73–81.
- [41] Hower JC, Eble CF, Backus JS, Xie P, Liu J, Fu B, et al. Aspects of Rare Earth Element enrichment in Central Appalachian coals. *Appl Geochem* 2020;120 (104676):104676. <https://doi.org/10.1016/j.apgeochem.2020.104676>.
- [42] Seredin VV. Rare earth element-bearing coals from the Russian Far East deposits. *Int J Coal Geol* 1996;30:101–29.
- [43] Hower JC, Robl TL, Thomas GA. Changes in the Quality of Coal Combustion By-products Produced by Kentucky Power Plants, 1978 to 1997: Consequences of Clean Air Act Directives. *Fuel* 1999;78:701–12.
- [44] Hower JC, Robl TL, Thomas GA. Changes in the quality of coal delivered to Kentucky power plants, 1978 to 1997: Responses to Clean Air Act directives. *Int. J. Coal Geology* 1999;41:125–55.
- [45] Mardon SM, Hower JC. Impact of coal properties on coal combustion by-product quality: Examples from a Kentucky power plant. *Int. J. Coal Geol.* 2004;59:153–69.
- [46] Dai S, Graham IT, Ward CR. A review of anomalous rare earth elements and yttrium in coal. *Int J Coal Geol* 2016;159:82–95.
- [47] Balashov, Y.A. *Geochemistry of Rare Earth elements*. Nauka, Moscow, 1976, 267 p. (in Russian).
- [48] McLennan SM, Taylor SR. Sedimentary rocks and crustal evolution: tectonic setting and secular trends. *J. Geol.* 1991;99:1–21.
- [49] Bau M, Dulski P. Distribution of yttrium and rare-earth elements in the Penge and Kuruman Iron-Formations, Transvaal Supergroup. *South Africa. Precambrian Research* 1996;79:37–55.
- [50] Dai S, Xie P, Jia S, Ward CR, Hower JC, Yan X, et al. Enrichment of U-Re-V-Cr-Se and rare earth elements in the Late Permian coals of the Moxinpo Coalfield, Chongqing, China: Genetic implications from geochemical and mineralogical data. *Ore Geol Rev* 2017;80:1–17.
- [51] Dai S, Xie P, Ward CR, Yan X, Guo W, French D, et al. Anomalies of rare metals in Lopingian super-high-organic-sulfur coals from the Yishan coalfield, Guangxi, China. *Ore Geology Reviews* 2017;88:235–50.
- [52] Hower JC, Robertson JD, Thomas GA, Wong AS, Schram WH, Graham UM, et al. Characterization of fly ash from Kentucky power plants. *Fuel* 1996;75:403–11.
- [53] Hower JC, Robl TL, Anderson C, Thomas GA, Sakulpitakphon T, Mardon SM, et al. Characteristics of coal utilization products (CUBs) from Kentucky power plants, with emphasis on Mercury content. *Fuel* 2005;84:1338–50.
- [54] Bragg, L.J.; Oman, J.K.; Tewart, S.J.; Oman, C.L.; Rega, N.H.; Washington, P.M.; Finkelman, R.B. U.S. Geological Survey Coal Quality (COALQUAL) Database: Version 2.0. U.S. Geological Survey Open-file Report 97-134, 1998, CD-ROM.
- [55] Hower JC, Senior CL, Suuberg EM, Hurt RH, Wilcox JL, Olson ES. Mercury capture by native fly ash carbons in coal-fired power plants. *Prog Energy Combust Sci* 2010;36:510–29.
- [56] Hower JC, Trimble AS, Eble CF. Temporal and spatial variations in fly ash quality. *Fuel Process Technol* 2001;73:37–58.
- [57] Hower JC, Clack HC, Hood MM, Hopps SG, Thomas GH. Impact of coal source changes on Mercury content in fly ash: Examples from a Kentucky power plant. *Int. J. Coal Geol.* 2017;170:2–6.
- [58] Liu J, Dai S, He X, Hower JC, Sakulpitakphon T. Size-dependent variations in fly ash trace element chemistry: Examples from a Kentucky power plant and with emphasis on rare earth elements. *Energy Fuels* 2017;31:438–47.
- [59] Hower, J.C.; Valentim, B.; Kostova, I.J.; Henke, K.R. Discussion on “Characteristics of Fly Ashes from Full-Scale Coal-Fired Power Plants and Their Relationship to Mercury Adsorption” by Lu et al. *Energy & Fuels* 2008, 22, 1055–1058.