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A Note on the Occurrence of Yttrium and Rare Earth Elements in Coal Combustion Products

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ABSTRACT

There is an international need for a variety of lanthanide elements (rare earth elements, or REEs) in modern electronic and related components. This has led to a desire to broaden production from both previously productive locations and to expand production to new sources, possibly including coal-derived fly ash. The concentration of lanthanides in coal-combustion fly ash depends on a number of factors, one of the most important being the concentration of the elements in the feed coal. Unlike some elements, such as Zn and As, the REE concentration is largely not a function of element volatility.

In this study, we review the concentrations of REEs in a power plant burning a variety of coals. Additionally, a power plant burning 2–3% tires in a cyclone boiler and a plant burning 30% pet coke were also investigated. In general, the Yttrium + REE concentrations do not systematically vary between electrostatic precipitator rows. However, the light REE/heavy REE ratio (LREE/HREE) generally decreases with a decrease in flue gas temperature. The element partitioning responsible for the LREE/HREE decrease is not fully understood.

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1. Introduction

The growing need for a variety of lanthanide elements (or rare earth elements, REEs) in modern electronic and related components, along with the concentration of production in China, has driven the need to broaden production from both previously productive locations (Bradsher, 2011; Margonelli, 2011) and to expand production to new sources, possibly including coal-derived fly ash. Long et al. (2010) and Henderson et al. (2011) discussed the occurrence and the need for enhanced development of lanthanide element sources in the United States and globally. Lanthanides occur in oxides, carbonates, phosphates, and silicates (Long et al., 2010).

Seredin and Dai (2012) summarized the occurrence of REY (lanthanides + yttrium) in coals and other deposits, describing three enrichment patterns: LREY, ($La_N/Lu_N > 1$); MREY, ($La_N/Sm_N < 1$, $Gd_N/Lu_N > 1$); and HREY, ($La_N/Lu_N < 1$). They further divided the lanthanides into critical (Nd, Eu, Tb, Dy, Y, and Er), uncritical (La, Pr, Sm, and Gd), and excessive (Ce, Ho, Tm, Yb, and Lu) groups (after Seredin, 2010). Lanthanides occur in four main types of

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Table 1
Pulverized coal, fly ash, and bottom ash REY data (ppm, whole coal or whole ash) from the Mardon and Hower (2004) study

		Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Pulverized feed coal		180	255	510	59	226	48	4.6	37	6.3	42	8.2	23	5.6	21
Fly ash	Economizer	203	246	502	59	223	46	4.8	34	6.0	39	7.8	22	5.2	20
Fly ash	Mech/1st row	212	261	535	63	233	48	4.9	36	6.3	41	7.9	23	5.6	21
Fly ash	Mech/2nd row	199	221	447	53	197	40	4.2	30	5.3	34	6.7	19	4.6	17
Fly ash	ESP/1st row	253	239	487	58	211	47	4.9	31	6.3	42	8.5	26	5.7	23
Fly ash	ESP/2nd row	259	264	535	64	235	52	5.4	35	7.0	47	9.7	29	6.4	26
Fly ash	ESP/3rd row	238	231	458	56	211	44	5.8	34	6.4	43	8.8	26	6.4	24
Bottom ash		184	211	419	50.3	186	38.4	3.9	28	4.9	32.2	6.3	18.2	4.2	16.1

						Seredin (2010) classes							
		LREE	HREE	Y+REE	LREE/HREE	LREY	MREY	HREY	Critical	Uncritical	Excessive	La/Yb	$\mathrm{REY_{critical}}/\mathrm{REY_{total}}$
Pulverized feed coal		1103	142	1425	7.75	1097.9	269.2	57.7	481.4	398.7	544.7	12.20	33.8
Fly ash	Economizer	1081	135	1418	8.03	1075.8	286.8	55.5	498.1	384.7	535.3	12.12	35.1
Fly ash	Mech/1st row	1144	140	1495	8.17	1138.8	299.7	57.3	519.6	407.6	568.7	12.61	34.7
Fly ash	Mech/2nd row	962	118	1279	8.16	957.4	273.0	48.0	459.1	343.6	475.7	12.71	35.9
Fly ash	ESP/1st row	1046	141	1440	7.42	1041.0	336.4	62.6	542.3	374.3	523.5	10.46	37.7
Fly ash	ESP/2nd row	1155	160	1573	7.24	1149.2	353.2	70.9	582.5	414.4	576.4	10.21	37.0
Fly ash	ESP/3rd row	1006	148	1391	6.76	999.8	327.6	64.6	530.2	365.2	496.7	9.83	38.1
Bottom ash		909	110	1203	8.27	904.7	253.0	44.8	429.2	327.7	445.6	13.11	35.7

Mech = mechanical.

enrichment: terrigenous (Dai et al., 2006, 2008, 2012), tuffaceous (Hower et al., 1999; Mardon and Hower, 2004), infiltrational (Arbuzov and Mashen'kin, 2007), and hydrothermal (Seredin, 2004). The older twofold divisions into light and heavy rare earths, the trifold divisions of REY, the critical/uncritical/excessive REY divisions, and the La/Yb ratio (the latter three after Seredin, 2010) are included in the tables in this paper.

The concentration of lanthanides in coal combustion fly ash depends on a number of factors, perhaps the most important being the concentration of the elements in the feed coal. For some trace elements, the combustion and ash collection systems are important, with the more volatile elements, such as Zn and As, being preferentially captured in the cooler ash collection rows where the lower flue gas temperature is complemented by the greater surface area (the coarser fly ash being preferentially captured in the first ash collection rows) (Sakulpitakphon et al., 2003, 2004; Mardon and Hower, 2004; Hower et al., 2006).

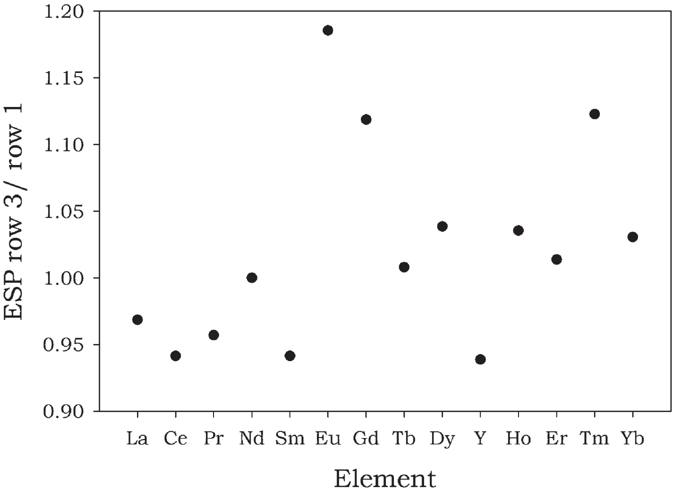

Fig. 1. Based on REY trends discussed by Mardon and Hower (2004), the ESP row 3 data is plotted and normalized to the ESP row 1 data. In other words, the cooler fly ash data (row 3) is normalized to the hotter fly ash data (row 1), showing that Y + the lighter REE are depleted in the third row ESP relative to the first row ESP. In contrast, the heavier REE are enriched in the third row vs. first row ESP fly ashes.

Fly ash from coal and coal + other fuel (such as petroleum coke, tires, and biomass) combustion represents a growing and potentially available source of raw material needed for the extraction of REY and other valuable trace elements. In 2010, U.S. utilities produced 61.4 Mt (metric tons) of fly ash (American Coal Ash Association, 2011), of which 38.7 Mt was not utilized. Therefore, with some annual variation expected, the U.S. resource of unused fly ash grows by 35–45 Mt each year.

The lanthanide levels of coals are not as well-known as some of the potentially hazardous elements. Traditionally, the more extensively studied elements have included S and, more recently, As, Hg, and other toxic trace elements. This is a function of the regulation-driven need to understand hazardous air pollutants, as well as the relative difficulty in analyzing lanthanides. The most extensive database of lanthanide (and other elements) in U.S. coals is the U.S. Geological Survey's data collection (Bragg et al., 1998). Because the sample collection is specific to mines and other sample sources that are, in general, several decades old, the data have to be treated as a guide to regions of interest. Even if mines operating in 1980 are still open, which is possible for the larger underground mines, the mine faces will be varying distances from the 1980 location.

In this study, we will review some previous studies and add data from new studies of lanthanides in coal and coal combustion fly ash.

2. Methods

Fly ash collection was generally done at electrostatic precipitator (ESP) hoppers. For the Mardon and Hower (2004) study, additional samples were collected from economizer and mechanical (cyclone) hopper rows, both collecting ash before the ESPs, thus at a hotter point in the pollution control system.

Table 2
Fly ash REY data (ppm, whole ash) from Chinese power plants (Silva et al., 2012b)

			As det. (dry basis)			Rare earth elements and Y (ppm in ash)														
Sample	Plant	Location	mois	Ash	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
69405	Diandong	E Yunnan 1	0.39	91.64	25	77	94	199	23	90	18	3.5	17.6	2.5	14.1	2.8	8.0	1.1	7.5	1.1
69406	Diandong	E Yunnan 2	0.35	89.09	25	83	96	206	24	93	18	3.7	18.6	2.6	15.1	3.0	8.6	1.2	8.0	1.2
69407	Diandong	E Yunnan 3	0.73	91.72	23	82	100	210	25	97	19	3.9	18.9	2.6	15.1	3.0	8.6	1.2	8.0	1.1
69408	Diandong	E Yunnan 4	1.13	91.29	26	86	110	225	27	106	20	4.1	20.1	2.8	15.8	3.1	9.0	1.3	8.4	1.2
69409	Anwen	SCDZ 1-2	1.06	86.08	17	67	107	219	23	81	15	2.3	16.2	2.3	12.9	2.5	7.2	1.0	6.6	0.9
69410	Anwen	SCDZ 2-2	1.08	84.01	17	67	107	218	23	81	15	2.4	16.1	2.3	13.0	2.5	7.3	1.0	6.6	1.0

			Chondrite corrected rare earth elements and Y (ppm in ash)													
			Y	La	Ce	Nd	Pr	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Sample	Plant	Location	2.12	0.32	0.82	0.62	0.12	0.20	0.08	0.27	0.05	0.33	0.08	0.22	0.03	0.22
69405	Diandong	E Yunnan 1	36	293	243	146	192	88	46	66	50	43	37	37	34	34
69406	Diandong	E Yunnan 2	39	301	251	151	199	92	49	70	53	46	39	40	37	36
69407	Diandong	E Yunnan 3	39	314	256	158	207	95	51	71	53	46	39	40	36	36
69408	Diandong	E Yunnan 4	41	346	275	172	226	102	54	75	56	48	41	41	38	38
69409	Anwen	SCDZ 1-2	32	334	267	132	190	74	30	61	46	39	33	33	30	30
69410	Anwen	SCDZ 2-2	32	334	266	132	190	74	31	60	46	39	33	34	31	30

							Seredin (2010) classes							
Sample	Plant	Location	LREE	HREE	Y+ REE	LREE/ HREE	LREY	MREY	HREY	Critical	Uncritical	Excessive	La/Yb	$REY_{critical}$/ REY_{total}
69405	Diandong	E Yunnan 1	427	55	558	7.81	423.4	114.3	20.5	194.5	152.1	211.7	12.48	34.8
69406	Diandong	E Yunnan 2	441	58	582	7.56	437.3	122.9	22.0	205.8	157.0	219.4	11.94	35.3
69407	Diandong	E Yunnan 3	456	58	596	7.80	451.7	122.5	21.8	209.2	163.3	223.5	12.61	35.1
69408	Diandong	E Yunnan 4	493	61	641	8.02	488.8	128.9	22.9	223.5	178.0	239.1	13.19	34.9
69409	Anwen	SCDZ 1-2	447	50	563	9.01	444.3	100.6	18.2	172.8	160.5	229.8	16.10	30.7
69410	Anwen	SCDZ 2-2	445	50	563	8.95	443.1	101.2	18.4	173.3	160.4	229.0	16.09	30.8

Except where indicated, the lanthanide analysis was done with inductively coupled plasma mass spectroscopy (ICP-MS) at the U.S. Geological Survey laboratories in Denver, Colorado (data from Mardon and Hower, 2004), or at China University of Mining and Technology (Beijing). With the separation in time and space between the historical (Mardon and Hower, 2004) and current data acquisition, no comparison between the two laboratories was made.

Detailed analysis of ICP-MS at the U.S. Geological Survey laboratories was described by Mardon and Hower (2004) and references therein. Detection of Tm can be problematical in ICP-MS because of limitations of acid leaching in sample preparation.

ICP-MS analysis (X series II) at China University of Mining and Technology, in a pulse counting mode (three points per peak), was used to determine trace elements in coal samples. This procedure and sample microwave digestion program, related to coal and coal-related materials, were outlined by Dai et al. (2011). Multielement standards (Inorganic Ventures, Christiansburg, VA: CCS-1, CCS-4, CCS-5, and CCS-6) were used for calibration of trace element concentrations. For ICP-MS analysis, samples were digested using an UltraCLAVE microwave high-pressure reactor (Milestone, Shelton, CT). The results from duplicate samples were within 5% of the mean to ensure precision.

The full sets of major oxide and minor and trace element data for the current and two previous fly ash studies (Mardon and Hower, 2004; Silva et al., 2012b) are in Appendix A.

3. Results and Discussion

3.1. Previous studies: Fire Clay coal bed, eastern Kentucky, USA

Hower et al. (1999) found that the high volatile A bituminous Fire Clay coal bed in eastern Kentucky had high lanthanide concentrations, particularly in portions of the coal immediately underlying the volcanic ash fall (tonstein) parting. As in western U.S. coals studied by Crowley et al. (1989, 1993), REE-bearing phosphates are found in the tonstein. In Crowley et al. (1989, 1993) and Hower et al. (1999), the lanthanide elements leached from the tonsteins into the underlying coal. Even though the tonstein was not observed in the Dean (Fire Clay–correlative) coal, the coal had the elevated REY signature found in the Fire Clay coal bed (Mardon and Hower, 2004).

Mardon and Hower (2004) arranged for the exclusive burn of the Dean coal in a 220-MW utility pulverized-coal unit and sampled the fly ash at the time of the burn (Table 1). The resulting fly ash showed REY levels in excess of 1500 ppm. Although total REY did not show any particular trend from the hotter mechanical ash collection hoppers to the cooler ESP rows (with ESP row 1 being hotter than ESP row 3), the light REE to heavy REE (LREE/HREE) ratio decreased toward the cooler end of the ash collection system (Figure 1). The critical REY/total REY percentage increases slightly toward the cooler end of the ash collection system (34.7% in the first mechanical row to 38.1% in the third ESP row). The latter percentages are higher than for the Anwen and Jungar fly ashes, to be discussed below (Tables 2 and 3).

3.2. Previous studies: China

Silva et al. (2012b) investigated the chemistry, petrology, and mineralogy of two suites of Chinese fly ashes (Table 2). The REY levels are about a third of the levels in the Fire Clay coal–derived fly ash discussed above. Particularly in the LREE/HREE, there is a distinction between the two power plants investigated, with the Anwen plant having a higher ratio than the Diandong plant. The Anwen fly ash has a lower critical REY/total REY percentage than the Diandong fly ash (30.7% vs. 35%).

Table 3
Coal and fly ash REY data (ppm, whole coal or whole ash) from the Jungar, China, power plant (Dai and Zhao, unpublished data, 2006; Dai et al., 2010)

Sample type	Date	Ash yield, %	LOI	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Coal	20-Jun-06	35.81		22.7	40.5	70.2	8.1	27.7	5.4	1.0	5.0	0.8	4.8	0.9	2.7	0.4	2.6	0.4
	21-Jun-06	35.64		20.1	46.2	80.1	8.9	29.7	5.5	1.0	4.8	0.7	4.2	0.8	2.4	0.4	2.3	0.3
	22-Jun-06	32.87		20.2	43.6	74.2	8.5	28.1	5.2	0.9	4.6	0.7	4.2	0.8	2.4	0.4	2.3	0.3
	23-Jun-06	30.36		18.5	37.1	65.5	7.3	25.2	4.9	0.8	4.3	0.7	3.8	0.8	2.1	0.3	2.0	0.3
	24-Jun-06	30.24		20.5	38.7	69.0	7.8	27.4	5.2	0.9	4.7	0.7	4.2	0.8	2.3	0.3	2.2	0.3
	Average			20.4	41.2	71.8	8.1	27.6	5.2	0.9	4.7	0.7	4.2	0.8	2.4	0.3	2.3	0.3
	St. dev.			1.5	3.7	5.6	0.6	1.6	0.2	0.1	0.2	0.0	0.3	0.1	0.2	0.0	0.2	0.0
Economizer Fly ash	20-Jun-06	93.48	6.52	47.4	90.0	154.0	18.3	64.9	12.0	2.0	10.0	1.5	9.3	1.8	5.2	0.8	5.1	0.7
	21-Jun-06	95.88	4.12	34.3	62.2	107.0	12.4	43.4	8.0	1.4	7.2	1.2	7.2	1.4	4.1	0.6	4.1	0.6
	22-Jun-06	95.65	4.35	42.2	80.8	126.0	16.4	54.4	9.6	1.7	8.4	1.3	8.3	1.7	5.0	0.7	4.7	0.7
	23-Jun-06	96.22	3.78	42.8	96.1	158.0	20.1	65.4	11.7	1.9	9.6	1.5	9.0	1.7	5.1	0.7	5.0	0.7
	24-Jun-06	95.93	4.07	43.9	97.7	160.0	19.5	64.2	11.8	2.0	10.4	1.5	9.2	1.8	5.2	0.7	4.9	0.7
	Average			42.1	85.4	141.0	17.3	58.5	10.6	1.8	9.1	1.4	8.6	1.7	4.9	0.7	4.8	0.7
	St. dev.			4.8	14.5	23.5	3.1	9.6	1.7	0.2	1.3	0.1	0.9	0.1	0.5	0.1	0.4	0.1
Wet fly ash	20-Jun-06	96.25	3.75	53.1	98.7	170.0	20.8	68.6	12.6	2.3	11.4	1.8	10.6	2.2	6.1	0.9	5.8	0.8
	21-Jun-06	96.29	3.71	51.7	101.0	162.0	20.9	66.3	12.7	2.1	11.2	1.7	10.4	2.1	6.0	0.9	5.8	0.9
	22-Jun-06	96.29	3.71	53.2	104.0	181.0	21.2	72.7	13.6	2.5	11.4	1.8	10.6	2.1	6.0	0.9	5.9	0.8
	23-Jun-06	96.37	3.63	60.9	118.0	208.0	24.8	83.3	15.9	2.7	13.4	2.2	12.1	2.4	6.8	1.0	6.6	0.9
	24-Jun-06	96.59	3.41	51.9	100.0	169.0	20.0	71.6	12.5	2.3	11.0	1.7	10.1	2.0	6.1	0.8	5.8	0.8
	Average			54.2	104.3	178.0	21.5	72.5	13.5	2.4	11.7	1.8	10.8	2.1	6.2	0.9	6.0	0.9
	St. dev.			3.8	7.9	18.1	1.9	6.5	1.4	0.2	1.0	0.2	0.8	0.2	0.4	0.1	0.3	0.0
Bottom ash	20-Jun-06	69.95	30.05	38.3	75.4	118.0	14.7	49.4	9.6	1.6	8.5	1.3	7.9	1.5	4.5	0.7	4.4	0.6
	21-Jun-06	87.58	12.42	34.9	69.8	119.0	14.4	47.8	8.7	1.4	7.7	1.1	7.3	1.4	4.0	0.6	4.1	0.6
	22-Jun-06	87.59	12.41	33.5	67.6	117.0	14.2	46.9	8.7	1.4	7.2	1.1	6.5	1.3	3.8	0.6	3.8	0.5
	23-Jun-06	85.85	14.15	30.7	63.7	115.0	13.4	44.8	8.4	1.4	7.0	1.1	6.5	1.3	3.8	0.5	3.6	0.5
	24-Jun-06	82.15	17.85	31.7	60.0	118.0	12.7	45.2	7.9	1.4	7.2	1.1	6.6	1.3	3.8	0.5	3.8	0.5
	Average			33.8	67.3	117.4	13.9	46.8	8.7	1.5	7.5	1.1	6.9	1.3	4.0	0.6	3.9	0.6
	St. dev.			3.0	5.9	1.5	0.8	1.9	0.6	0.1	0.6	0.1	0.6	0.1	0.3	0.1	0.3	0.0

						Seredin (2010) classes							
Sample type	Date	LREE	HREE	Y+REE	LREE/HREE	LREY	MREY	HREY	Critical	Uncritical	Excessive	La/Yb	$\mathrm{REY_{critical}}/\mathrm{REY_{total}}$
Coal	20-Jun-06	152.9	17.4	193.0	8.77	151.9	34.2	6.9	59.6	59.0	74.5	15.70	30.9
	21-Jun-06	171.3	15.8	207.2	10.83	170.4	30.7	6.2	58.1	65.3	83.8	20.53	28.0
	22-Jun-06	160.6	15.7	196.5	10.24	159.6	30.6	6.2	56.5	62.0	78.0	19.12	28.8
	23-Jun-06	140.9	14.3	173.6	9.87	140.0	28.1	5.5	51.1	53.7	68.9	18.19	29.4
	24-Jun-06	149.0	15.6	185.0	9.55	148.1	31.0	6.0	56.0	56.4	72.7	17.28	30.2
	Average	154.9	15.8	191.1	9.85	154.0	30.9	6.2	56.2	59.3	75.6	18.09	29.4
	St. dev.	11.6	1.1	12.6	0.77	11.5	2.2	0.5	3.2	4.6	5.7	1.83	1.14
Economizer Fly ash	20-Jun-06	341.2	34.4	423.1	9.91	339.2	70.3	13.6	130.4	130.3	162.4	17.54	30.8
	21-Jun-06	234.5	26.3	295.1	8.90	233.0	51.3	10.8	91.6	89.8	113.7	15.28	31.0
	22-Jun-06	288.9	30.8	361.9	9.40	287.2	61.9	12.7	112.9	115.2	133.7	17.19	31.2
	23-Jun-06	353.2	33.3	429.3	10.59	351.3	64.8	13.3	125.7	137.5	166.2	19.18	29.3
	24-Jun-06	355.2	34.4	433.5	10.32	353.2	66.9	13.3	126.0	139.4	168.1	19.82	29.1
	Average	314.6	31.9	388.6	9.83	312.8	63.0	12.7	117.3	122.4	148.8	17.90	30.2
	St. dev.	52.3	3.4	59.8	0.69	52.0	7.2	1.1	15.8	20.6	24.1	1.79	1.02
Wet fly ash	20-Jun-06	373.0	39.6	465.7	9.43	370.7	79.2	15.8	142.5	143.5	179.7	16.93	30.6
	21-Jun-06	365.0	38.9	455.6	9.39	362.9	77.2	15.6	138.2	145.8	171.6	17.44	30.3
	22-Jun-06	395.0	39.4	487.5	10.03	392.5	79.4	15.6	146.7	150.2	190.6	17.72	30.1
	23-Jun-06	452.7	45.3	558.9	10.00	450.0	91.3	17.6	168.0	172.1	218.8	18.02	30.1
	24-Jun-06	375.4	38.3	465.6	9.81	373.1	77.0	15.5	143.7	143.5	178.4	17.12	30.9
	Average	392.2	40.3	486.7	9.73	389.8	80.8	16.0	147.8	151.0	187.8	17.46	30.4
	St. dev.	35.6	2.8	42.0	0.30	35.4	5.9	0.9	11.7	12.1	18.6	0.44	0.34
Bottom ash	20-Jun-06	268.7	29.3	336.3	9.16	267.1	57.5	11.7	103.0	108.1	125.2	17.02	30.6
	21-Jun-06	261.1	26.6	322.6	9.83	259.7	52.4	10.5	96.5	100.6	125.5	17.23	29.9
	22-Jun-06	255.8	24.8	314.1	10.34	254.4	49.8	9.9	93.2	97.7	123.2	17.79	29.7
	23-Jun-06	246.8	24.4	301.9	10.12	245.3	46.7	9.8	88.3	92.6	121.0	17.55	29.2
	24-Jun-06	245.2	24.6	301.6	9.95	243.8	47.9	9.8	89.8	87.8	124.0	16.00	29.8
	Average	255.5	25.9	315.3	9.88	254.1	50.9	10.4	94.1	97.4	123.8	17.12	29.9
	St. dev.	9.8	2.1	14.7	0.45	9.8	4.3	0.8	5.9	7.8	1.8	0.69	0.50

St. dev. = standard deviation.

Dai and Zhao (unpublished data, 2006) and Dai et al. (2010) examined coal, economizer and wet fly ash, and bottom ash from the Junger power plant. Samples were collected for 5 days in June 2006. Overall, although the averages of the LREE, HREE, and REY vary considerably among the sample types, the LREE/HREE average is basically the same for all four sample types (Table 3). Sized fly ash (economizer fly ash of 21 June 2006) shows a progressive increase in LREE, HREE, and REY from the coarsest

Table 4
REY concentrations in sized fly ash (ppm, whole ash) from Jungar power plant (Dai and Zhao, unpublished data, 2006; Dai et al., 2010)

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
>120 mesh	30.7	60.1	104.0	11.7	39.1	7.1	1.3	6.4	1.0	6.0	1.2	3.6	0.5	3.4	0.5
120–160 mesh	34.8	57.9	104.0	11.8	40.2	7.5	1.4	6.9	1.2	6.9	1.4	4.0	0.6	3.7	0.6
160–300 mesh	43.3	77.9	112.0	15.8	53.7	9.9	1.8	9.4	1.5	8.7	1.8	5.0	0.7	4.7	0.7
300–360 mesh	52.8	103.0	167.0	21.0	71.4	12.9	2.3	11.9	1.9	10.4	2.1	5.9	0.9	5.4	0.8
360–500 mesh	57.5	121.0	206.0	24.6	84.7	14.6	2.6	13.3	2.0	11.2	2.3	6.3	0.9	5.9	0.8
<500 mesh	65.5	136.0	246.0	28.5	102.0	17.2	3.1	15.4	2.3	13.0	2.7	7.5	1.0	6.9	1.0

					Seredin (2010) classes							
	LREE	HREE	Y+REE	LREE/HREE	LREY	MREY	HREY	Critical	Uncritical	Excessive	La/Yb	$REY_{critical}$/ REY_{total}
>120 mesh	223.3	22.7	276.7	9.85	222.0	45.4	8.8	81.7	85.3	109.2	17.73	29.5
120–160 mesh	222.8	25.1	282.7	8.86	221.4	51.0	9.7	88.4	84.0	109.7	15.69	31.3
160–300 mesh	271.0	32.4	346.7	8.37	269.3	64.6	12.2	113.9	113.0	119.2	16.43	32.8
300–360 mesh	377.6	39.2	469.6	9.63	375.3	79.3	14.3	144.7	148.8	175.4	19.00	30.8
360–500 mesh	453.5	42.8	553.8	10.61	450.9	86.6	15.4	164.3	173.5	215.1	20.54	29.7
<500 mesh	532.8	49.8	648.1	10.69	529.7	99.3	18.1	193.5	197.1	256.6	19.77	29.9

(>120 mesh [>120 μm]) to the finest (<500 mesh [<25 μm]) fractions (Table 4). LREE/HREE, however, passes through a minimum in the 160 × 300 mesh fraction, with the highest LREE/HREE in the finest fraction. The critical REY increases from the coarse fraction to the finest fractions, but because total REY also increases, critical REY/total REY stays in the 29.5–32.8% range throughout the size range. As far as we know, this is the only study of rare earth elements in sized fly ash, so we cannot be certain whether the trends observed would be typical of any other fly ash.

The distribution patterns of REY in the Junger feed coal, economizer fly ash, wet fly ash, and bottom ash, as well as in the different size fractions, are similar (Figures 2 and 3), all showing light REY enrichment type and negative Eu, Ce, and Y anomalies, which are similar to those of the raw feed coals reported by Dai et al. (2006, 2008).

3.3. Current study

In this study, new fly ash data were obtained for two Bulgarian power plants burning low-rank coal (after discussion by Kostova et al., 2011a,b; Silva et al., 2012a), a Turkish power plant burning low-rank coal (multiple samples from same ESP row), Kentucky power plants burning eastern Kentucky and Illinois Basin high-volatile bituminous coal blends, a western Kentucky plant burning a blend of about 2–3% tire-derived fuel (tdf) with high-volatile C bituminous coal (after discussions by Hower et al., 2001, 2007), and a western Kentucky plant burning a blend of about 30% petroleum coke with a high-volatile C bituminous coal (after discussions by Hower et al., 2005b; Silva et al., 2013) (Table 5).

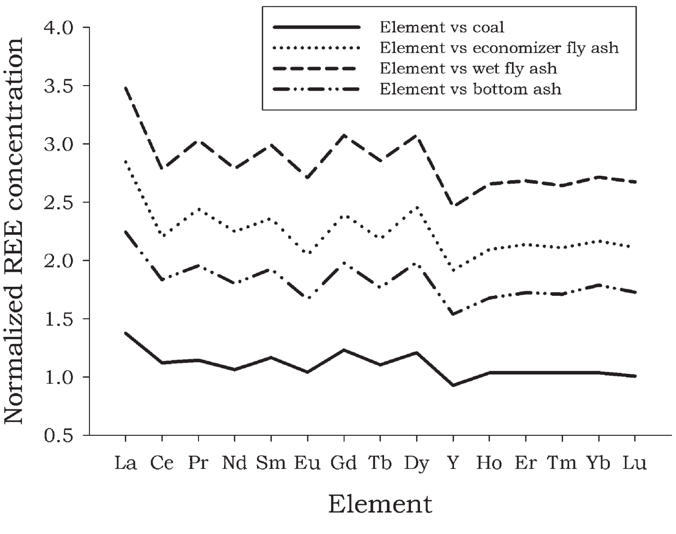

Fig. 2. The distribution patterns of rare earth elements in the Junger feed coal, economizer fly ash, wet fly ash, and bottom ash. REE plots are normalized by Upper Continental Crust (UCC) (Taylor and McLennan, 1985).

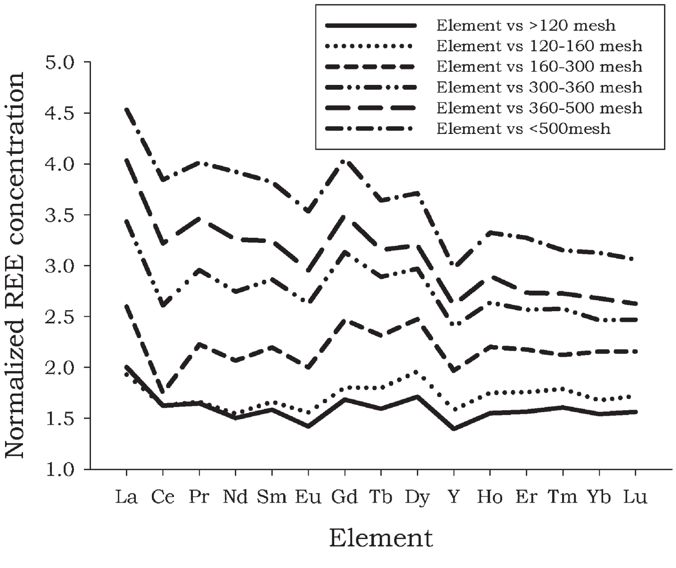

Fig. 3. The distribution patterns of REY in the different size-fractions of the Junger coal and ashes. REE plots are normalized by Upper Continental Crust (UCC) (Taylor and McLennan, 1985).

Considering the non-lanthanide elements, notable differences appear between the sets of ashes (Appendix A). The petroleum coke + coal-fired fly ash (sample 93469) has high concentrations of Ni, V, and Sn. The tdf + coal-fired fly ashes (plant P samples 93446–93448, representing three ESP rows) have high Zn and Cd, as expected for fly ashes with tdf in the blend because Zn (and the associated Cd) is a part of both the rubber and the steel belts in the tires (Hower et al., 2001, 2007). Arsenic, Pb, Sn, Sb, Tl, Ga, Ge, and Mo are also higher in tdf + coal-fired fly ashes than in the strictly coal-fired fly ashes. The Bulgarian Republika (93516–93518) and Bobov Dol (93520–93522) fly ashes, the products of the combustion

Table 5
REY concentrations (ppm, whole coal or whole ash) from the Republika and Bobov Dol power plants, Bulgaria; a Turkish power plant; and six Kentucky power plants

	Plant	Unit	Row	Sample	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Bulgaria	Republika		1	93516	32.7	37.7	82.4	9.3	35.3	7.2	1.7	7.3	1	5.4	1.1	3	0.4	2.8
Bulgaria	Republika		2	93517	34.8	40.2	87.1	9.8	37.1	7.6	1.8	7.7	1.1	5.8	1.1	3.2	0.5	3
Bulgaria	Republika		3	93518	35.1	39	87.6	9.6	36.7	7.6	1.8	7.7	1.1	5.8	1.2	3.3	0.5	3.1
Bulgaria	Bobov Dol		1	98520	30.9	39.1	85.6	9.4	35	7.1	1.6	7.3	1	5.4	1.1	2.9	0.4	2.8
Bulgaria	Bobov Dol		2	98521	30.7	39.1	86.2	9.4	34.8	7	1.6	7.2	1	5.4	1.1	3	0.4	2.8
Bulgaria	Bobov Dol		3	98522	31.3	38.4	84.2	9.3	34.7	7.1	1.6	7.3	1	5.4	1.1	3	0.4	2.9
Turkey					33	36	72	8.5	32	6.2	1.7	6.4	1.0	5.4	1.0	2.9	0.4	2.7
Turkey					40	38	85	9.4	38	7.2	1.8	7.3	1.1	6.5	1.3	3.8	0.5	3.4
Turkey					32	37	75	8.5	31	6.4	1.7	6.3	0.9	5.3	1.0	3.0	0.4	2.7
Turkey					26	41	80	9.0	34	6.1	1.6	5.7	0.8	4.4	0.9	2.5	0.4	2.3
Kentucky	F	2	1	93438	23.4	21.9	48.2	5.7	21.4	4.4	0.9	4.6	0.7	3.8	0.8	2.2	0.3	2.1
Kentucky	P	1	1	93446	40.1	36	83.2	9.2	34.5	6.9	1.4	7.2	1.1	6.2	1.3	3.7	0.5	3.5
Kentucky	P	1	2	93447	49.5	41.9	96.5	10.6	40.1	8.1	1.8	8.7	1.3	7.6	1.6	4.7	0.7	4.3
Kentucky	P	1	3	93448	53.4	43.4	100.9	11.1	42	8.6	1.9	9.2	1.4	8.2	1.7	5	0.7	4.7
Kentucky	S	1	3	93469	30.5	29.1	65.3	7.5	28.5	5.8	1.2	6.1	0.9	5	1	2.9	0.4	2.7
Kentucky	H	3	1	93295	88.2	86.1	188.5	20.7	80.7	16.8	4.0	19.9	2.9	15.2	3.0	8.7	1.2	7.9
Kentucky	H	3	2	93297	86.0	80.5	175.7	19.5	77.0	16.2	3.9	19.1	2.8	14.7	2.9	8.4	1.1	7.6
Kentucky	H	3	3	93299	70.6	61.9	131.8	15.1	60.1	12.9	3.1	15.3	2.3	12.1	2.4	6.8	0.9	6.2
Kentucky	H	3	4	93304	55.8	46.2	98.4	11.5	46.2	10.0	2.5	12.1	1.8	9.5	1.9	5.4	0.7	4.8
Kentucky	R	1	1	93307	47.1	49.8	105.3	12.0	47.6	9.6	2.2	11.5	1.6	8.2	1.6	4.8	0.7	4.7
Kentucky	R	1	2	93310	47.6	50.9	107.3	12.2	48.2	9.8	2.3	11.7	1.6	8.4	1.7	4.9	0.7	4.8
Kentucky	R	1	3	93312	46.6	50.8	108.5	12.2	48.0	9.7	2.3	11.6	1.6	8.1	1.6	4.8	0.7	4.7
Kentucky	R	1	4	93314	44.7	50.3	106.3	12.1	47.2	9.5	2.2	11.3	1.5	7.8	1.6	4.7	0.7	4.5
Kentucky	R	1	5	93316	44.1	49.7	104.6	12.0	46.8	9.3	2.2	11.3	1.5	7.6	1.5	4.5	0.6	4.4
Kentucky	I	2	1	93382	86.1	88.2	188.9	21.6	86.2	17.9	4.1	21.2	3.0	15.0	2.9	8.5	1.2	7.9
Kentucky	I	2	2	93385	95.2	87.1	186.1	21.6	86.9	18.3	4.3	22.2	3.2	16.3	3.2	9.3	1.3	8.6
Kentucky	I	2	3	93387	106.7	89.8	194.8	22.6	91.3	19.6	4.7	23.4	3.5	17.9	3.5	10.3	1.4	9.4

					Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
					Correction factor:													
	Plant	Unit	Row	Sample	0.212	0.319	0.82	0.121	0.615	0.2	0.0761	0.267	0.0493	0.33	0.0755	0.216	0.0329	0.221
Bulgaria	Republika		1	93516	154.2	118.1	100.5	76.6	57.4	36.2	22.1	27.5	20.6	16.3	14.2	14.0	13.3	12.8
Bulgaria	Republika		2	93517	164.2	126.1	106.3	81.0	60.3	38.0	23.2	29.0	21.8	17.4	15.1	14.8	14.0	13.7
Bulgaria	Republika		3	93518	165.6	122.3	106.9	79.5	59.6	37.8	23.4	28.8	21.9	17.7	15.3	15.2	14.2	13.8
Bulgaria	Bobov Dol		1	98520	145.8	122.6	104.4	77.8	56.9	35.5	21.4	27.5	20.3	16.3	13.9	13.6	12.9	12.6
Bulgaria	Bobov Dol		2	98521	144.8	122.5	105.2	77.6	56.6	35.2	21.6	27.1	20.5	16.2	14.0	13.7	13.0	12.8
Bulgaria	Bobov Dol		3	98522	147.6	120.4	102.7	76.6	56.4	35.3	21.4	27.5	20.6	16.4	14.2	14.0	13.1	12.9
Turkey					153.3	112.5	87.7	69.8	52.2	30.9	21.7	23.8	19.5	16.2	13.4	13.2	13.1	12.2
Turkey					187.3	117.9	103.7	77.9	61.0	35.8	24.2	27.1	22.1	19.5	16.7	17.6	15.2	15.2
Turkey					151.9	115.7	92.0	70.2	51.1	31.8	21.8	23.4	18.7	15.9	13.4	13.7	12.8	12.3
Turkey					120.8	127.0	97.0	74.4	55.0	30.7	20.4	21.2	16.6	13.4	11.3	11.3	10.6	10.5
Kentucky	F	2	1	93438	110.4	68.6	58.8	46.7	34.8	21.9	12.1	17.0	13.5	11.4	10.1	10.2	9.8	9.4
Kentucky	P	1	1	93446	189.2	112.8	101.5	76.2	56.1	34.3	18.8	27.1	21.6	18.7	17.0	17.4	16.4	16.0
Kentucky	P	1	2	93447	233.5	131.2	117.7	87.9	65.3	40.7	23.0	32.5	26.7	23.1	21.2	21.6	20.3	19.6
Kentucky	P	1	3	93448	251.9	136.2	123.1	92.1	68.3	42.9	24.3	34.3	28.6	25.0	22.9	23.1	21.8	21.1
Kentucky	S	1	3	93469	143.9	91.3	79.6	62.3	46.4	29.1	16.0	22.7	18.1	15.1	13.5	13.6	12.8	12.4
Kentucky	H	3	1	93295	416.1	269.9	229.9	170.8	131.2	84.2	52.4	74.4	58.7	46.1	39.6	40.1	35.7	35.6
Kentucky	H	3	2	93297	405.9	252.4	214.3	161.4	125.2	81.1	50.8	71.7	57.0	44.5	38.3	38.7	34.5	34.4
Kentucky	H	3	3	93299	332.9	194.0	160.7	125.0	97.7	64.7	41.2	57.4	46.6	36.6	31.4	31.3	27.9	27.9
Kentucky	H	3	4	93304	263.1	144.9	120.0	94.7	75.2	50.2	32.3	45.3	36.6	28.8	24.5	24.9	21.8	21.6
Kentucky	R	1	1	93307	222.4	156.1	128.4	99.4	77.4	48.0	29.2	42.9	32.5	24.9	21.6	22.3	20.6	21.1
Kentucky	R	1	2	93310	224.8	159.6	130.8	101.2	78.3	48.8	29.8	43.8	33.4	25.5	22.0	22.9	20.9	21.6
Kentucky	R	1	3	93312	219.8	159.2	132.3	101.1	78.0	48.3	29.9	43.4	32.4	24.7	21.5	22.3	20.7	21.1
Kentucky	R	1	4	93314	210.8	157.6	129.7	99.8	76.7	47.3	29.4	42.4	31.3	23.7	20.6	21.6	20.0	20.5
Kentucky	R	1	5	93316	207.8	155.8	127.5	98.9	76.0	46.4	28.5	42.2	30.5	23.0	20.1	20.8	19.3	20.0
Kentucky	I	2	1	93382	406.1	276.5	230.3	178.8	140.1	89.5	53.5	79.5	60.7	45.3	38.8	39.2	35.5	35.8
Kentucky	I	2	2	93385	448.8	273.2	227.0	178.8	141.2	91.7	56.7	83.3	64.4	49.3	42.5	43.0	38.6	38.8
Kentucky	I	2	3	93387	503.4	281.7	237.6	187.0	148.5	98.0	61.7	87.7	70.2	54.2	46.8	47.6	42.6	42.3

									Seredin (2010) classes							
	Plant	Unit	Row	Sample	LREE	HREE	Y+REE	LREE/ HREE	LREY	MREY	HREY	Critical	Uncritical	Excessive	La/Yb	$REY_{critical}$/ REY_{tota}
Bulgaria	Republika		1	93516	173.6	21.5	227.8	8.07	171.9	48.1	7.7	79.1	61.5	87.1	13.46	34.7
Bulgaria	Republika		2	93517	183.6	22.8	241.2	8.05	181.8	51.2	8.3	83.8	65.3	92.2	13.40	34.7
Bulgaria	Republika		3	93518	182.3	23.0	240.4	7.93	180.5	51.5	8.6	83.8	63.9	92.9	12.58	34.9
Bulgaria	Bobov Dol		1	98520	177.8	21.3	230.0	8.35	176.2	46.2	7.6	76.8	62.9	90.3	13.96	33.4

Table 5—Continued

									Seredin (2010) classes							
	Plant	Unit	Row	Sample	LREE	HREE	Y+REE	LREE/ HREE	LREY	MREY	HREY	Critical	Uncritical	Excessive	La/Yb	$REY_{critical}$/ REY_{tota}
Bulgaria	Bobov Dol		2	98521	178.1	21.3	230.1	8.36	176.5	45.9	7.7	76.5	62.7	90.9	13.96	33.2
Bulgaria	Bobov Dol		3	98522	175.3	21.6	228.2	8.12	173.7	46.6	7.8	77.0	62.1	89.0	13.24	33.7
Turkey					156.2	20.1	208.8	7.77	154.5	46.9	7.4	75.4	56.9	76.5	13.30	36.1
Turkey					178.5	24.2	242.5	7.37	176.7	56.3	9.4	90.4	61.5	90.6	11.22	37.3
Turkey					160.2	20.0	212.4	8.02	158.5	46.3	7.5	74.4	58.0	80.0	13.57	35.0
Turkey					170.5	17.2	213.3	9.89	168.9	38.1	6.3	68.7	61.3	83.4	17.53	32.2
Kentucky	F	2	1	93438	102.5	14.7	140.6	6.97	101.6	33.4	5.7	52.4	36.6	51.7	10.43	37.3
Kentucky	P	1	1	93446	171.2	24.1	235.4	7.10	169.8	56.0	9.5	87.0	59.3	89.0	10.29	37.0
Kentucky	P	1	2	93447	199	29.5	278.0	6.75	197.2	68.9	11.9	105.0	69.3	103.7	9.74	37.8
Kentucky	P	1	3	93448	207.9	31.6	292.9	6.58	206.0	74.1	12.8	111.9	72.3	108.7	9.23	38.2
Kentucky	S	1	3	93469	137.4	19.5	187.4	7.05	136.2	43.7	7.4	69.0	48.5	69.8	10.78	36.8
Kentucky	H	3	1	93295	396.8	59.8	544.8	6.63	392.8	130.2	21.9	199.7	143.5	201.7	10.93	36.6
Kentucky	H	3	2	93297	372.8	57.8	516.6	6.45	368.9	126.6	21.1	192.8	135.4	188.5	10.58	37.3
Kentucky	H	3	3	93299	285.0	46.8	402.4	6.08	281.8	103.4	17.1	155.0	105.3	142.1	10.03	38.5
Kentucky	H	3	4	93304	214.8	36.8	307.4	5.84	212.3	81.6	13.4	121.1	79.8	106.5	9.70	39.4
Kentucky	R	1	1	93307	226.5	33.8	307.4	6.71	224.3	70.7	12.5	111.6	82.9	113.0	10.69	36.3
Kentucky	R	1	2	93310	230.6	34.5	312.8	6.68	228.4	71.7	12.8	113.1	84.6	115.1	10.67	36.1
Kentucky	R	1	3	93312	231.4	33.8	311.8	6.85	229.1	70.2	12.5	111.4	84.2	116.1	10.90	35.7
Kentucky	R	1	4	93314	227.5	32.8	305.0	6.93	225.3	67.6	12.1	108.1	83.1	113.8	11.11	35.5
Kentucky	R	1	5	93316	224.4	32.1	300.6	7.00	222.3	66.6	11.7	106.6	82.2	111.8	11.27	35.5
Kentucky	I	2	1	93382	406.8	60.8	553.8	6.69	402.8	129.3	21.7	202.7	149.0	202.1	11.15	36.6
Kentucky	I	2	2	93385	404.4	65.3	564.9	6.19	400.1	141.1	23.6	215.1	149.4	200.5	10.17	38.1
Kentucky	I	2	3	93387	422.9	70.7	600.4	5.98	418.2	156.2	26.0	234.4	155.5	210.5	9.60	39.0

of relatively high ash coals, do not have strikingly high trace element contents.

With respect to the lanthanide elements, the two Bulgarian power plants have similar REY concentrations, both being significantly less than the anthracite-derived fly ashes (Table 2) and Mardon and Hower's (2004) tonstein-influenced fly ash (Table 1). As an example, the Republika and Kentucky plant H (burning an eastern Kentucky moderate-sulfur, high-volatile A bituminous blend) fly ash REY distributions are compared in Figure 4. The REY concentrations for the three Republika ESP rows are similar to each other and are lower than the plant H concentrations. Plant H REY shows a substantial decrease from the first through fourth ESP row, showing a range similar to the within-row variation in the Mardon and Hower (2004) fly ashes, but with a greater percent decrease. The LREE/HREE ratio for the Bulgarian ashes is similar to the Diandong fly ash, less than the ca. 9.00 LREE/HREE of the Anwen fly ash, and greater than the 6.76–7.42 LREE/HREE of the Mardon and Hower (2004) fly ash. Similar to the Mardon and Hower (2004) fly ash, the LREE/HREE for both Bulgarian power plants generally decreases with a lowering of flue gas temperature, although the magnitude of the decrease is not as great as in the Kentucky fly ash.

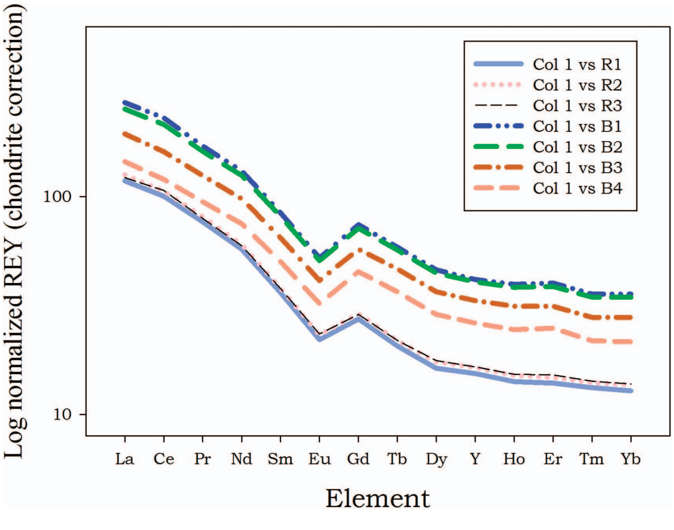

Fig. 4. Chondrite-normalized REY concentrations for Republika (Bulgaria) and plant H (Kentucky) fly ashes.

The plant P (93446–93448) samples represent the first through third rows of the ESP of a 100-MW cyclone-fired plant that burns a small amount of tires with the high-S coal (Silva et al., 2011). The REY is, overall, slightly higher than the totals for the Bulgarian plants, but as above, is lower than the concentrations in the Chinese anthracite and in the Mardon and Hower (2004) fly ashes. The LREE/HREE, on average lower than the ratio for the plant F fly ash and the lowest LREE/HREE of any fly ash derived strictly from coal, decreases from the first through the third ESP rows. Sample 93469, from the third ESP row of a plant burning 30% petroleum coke with coal, has a low REY, perhaps attributable in part to dilution of the coal by petroleum coke. The LREE/HREE is similar to plant F and plant P values.

The critical REY/total REY percentage increases from the first to the last ESP row in the Bulgarian power plants, although the difference is not significant, and in all of the Kentucky power plants with the exception of plant R. The caveat associated with this trend is that most of the fly ash is collected in the first two rows, perhaps on the order of 96% of the total, so a larger percentage of the critical REY in the third or fourth ESP row is of scientific interest but is not likely to represent a portion of the resource exploitable in isolation from the fly ash from the front rows. Additionally, we note that although plant H fourth row ESP fly ash has a nearly 3% higher critical REY/total REY percentage than the first ESP row, the fourth row fly ash has about 40% less REY than the first row fly ash.

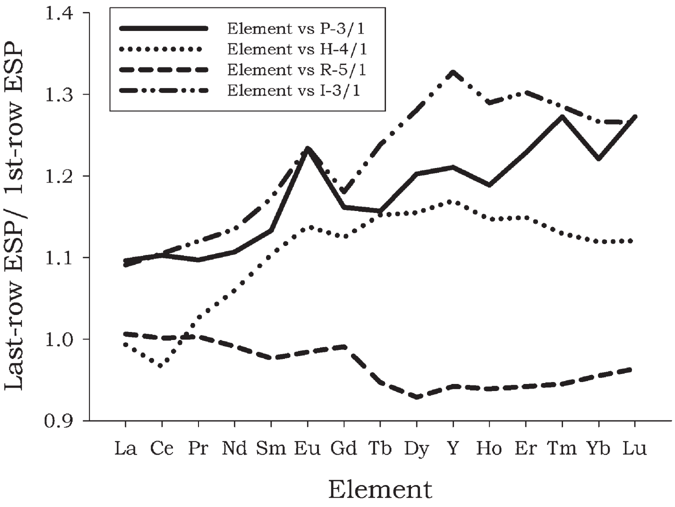

Fig. 5. The last row ESP (coolest fly ash) REY concentrations normalized to the first row ESP REY (hottest fly ash) concentrations for the four Kentucky power plants in Table 5. As with Figure 1, the cooler fly ash data are normalized to the hotter fly ash data.

4. Conclusions

The decrease in LREE/HREE from the hotter to the cooler ESP rows is an intriguing trend, first observed with the Mardon and Hower (2004) fly ash and confirmed here with a diverse collection of fly ashes from other power plants. Only plant R, burning a high-S Illinois Basin (western Kentucky) coal blend, does not follow the decreasing LREE/HREE trend (Table 5; Figure 5). Plant R does not follow the general trends expected of other elements, with the concentrations of volatile trace elements not partitioning toward the cooler ESP rows. Our experience with Kentucky power plants indicates that trace element concentrations can be higher in eastern Kentucky–source vs. western Kentucky–source feed coals, affecting the apparent partitioning of elements (Hower et al., 2005a, 2009).

With the limited data available to date, however, no single trend in LREE and HREE concentrations emerges. For the Mardon and Hower (2004) fly ashes, both the LREE and HREE vary in concentration through the ash collection system with the third ESP row, with both the coolest flue gas temperature and the finest fly ash, having neither the lowest LREE nor the highest HREE. In contrast, for tdf + coal fly ash, REY, LREE, and HREE all peak in the third ESP row, while LREE/HREE is at a minimum. Therefore, although it is possible to say that the LREE/HREE values do decrease with a decrease in the fly ash collection temperature, the element partitioning responsible for the LREE/HREE decrease is not fully understood. The nature of the REE associations within the fly ash will be investigated in future studies.

In many of the Kentucky power plants, the critical REY/total REY percentage increases from the first ESP row to the back rows of the ESP array. This percentage increase is tempered by the substantially smaller amount of fly ash collected in the back ESP rows and, in one case, the large decrease in total REY from the front to the back of the ESP array.

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