ZDZISŁAW ADAMCZYK[1], JOANNA KOMOREK[1], MAŁGORZATA LEWANDOWSKA[1],
JACEK NOWAK[2], BARBARA BIAŁECKA[2], JOANNA CAŁUSZ-MOSZKO[2],
AGNIESZKA KLUPA[2]

Ashes from bituminous coal burning in fluidized bed boilers as a potential source of rare earth elements

Introduction

The Polish power industry is based on the processing of fossil fuels, in particular hard coal and lignite, which in the power generating process leads to the formation of large amounts of waste, which should be re-used (Szponder and Trybalski 2009).

The waste formed during coal combustion in a power plant is coal ash, i.e. fly ash and bottom ash. Fly ash comprises more than half of the waste from coal combustion. Fly ash is a material that can be subjected to recycling. In most cases it is used as a component in concrete manufacture. Bottom ash constitutes about 10% of the total waste from coal combustion. It is deposited on the bottom of the power boiler. This ash is not as widely used as fly ash. Bottom ash used as a road construction material it may prove toxic for the environment, as it may contain, for instance, heavy metals (Palmer 2015). Bottom ash and fly ash are used extensively in underground mines as a component of hydraulic filling material (Iwanek et al. 2008).

[1] Silesian University of Technology, Gliwice, Poland; e-mail: zdzislaw.adamczyk@polsl.pl;
　joanna.komorek@polsl.pl; malgorzata.lewandowska@polsl.pl; jacek.nowak@polsl.pl
[2] Central Mining Institut, Katowice, Poland; e-mail: bbialecka@gig.eu; jmoszko@gig.eu; aklupa@gig.eu

Selection of the appropriate method of ash disposal is very difficult and requires a thorough knowledge of physical properties and chemical composition of the ashes (Szponder and Trybalski 2009).

Since the 1930s hard coal is burned in power plants in both conventional boilers as well as fluidized bed boilers. Fluidized bed combustion is a clean combustion technology where the emission of all major pollutants is reduced directly in the furnace. The waste formed during coal combustion in fluidized beds consists of fluidized bed fly ash and fluidized bed bottom ash. The amount of this waste is systematically increasing, in Poland 2 million Mg/year is currently produced (Łaskawiec et al. 2010). These ashes contain various trace elements, some of them toxic, and also rare earth elements (REE).

REE constitute a group of elements of special importance. Rare earth elements (REE) include 17 elements, i.e. 15 lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and Sc, Y (Seredin 2010; Seredin and Dai 2012). According to a geochemical classification REE fall into three subgroups: light rare elements (LREE), medium rare elements (MREE) and heavy rare elements (HREE). If yttrium is included in the lanthanides, the following three subgroups are formed: light elements (LREY: La, Ce, Pr, Nd, Sm), medium elements (MREY: Eu, Gd, Tb, Dy, Y) and heavy elements (HREY: Ho, Er, Tm, Yb, Lu). The above classification is very convenient for describing the distribution of rare earth elements specifically lanthanides and yttrium (REY) in coal as well as in coal ash and in ores (Bau 1996; Seredin 2010; Seredin and Dai 2012).

Rare earth elements, both in the form of metals as well as oxides, are used in modern technology. Rare earth elements are raw materials of high economic importance. These elements have been identified as most critical for the European Union economy. These raw materials, apart from the small potential of obtaining them from secondary sources, will remain critical for the economies of EU countries. They are characterized by the high risk of their shortage resulting from limited resources (Radwanek-Bąk 2011; Smakowski 2011; Mayfield and Lewis 2013; Franus et al. 2015; Jarosiński 2016).

The discovery of REY-rich coal seams (up to 1% REY content) in a number of coal basins has drawn attention to the possibility of the recovery of lanthanides and yttrium as a by-product from coal deposits (Seredin 1996; Hower et al. 1999; Mardon and Hower 2004; Dai et al. 2008; 2011; Seredin and Dai 2012; Blissett et al. 2014).

For the initial estimation of the recovery potential of REYs from coal ashes, above all the REY content in ash and their individual composition should be taken into account.

Experimental data on REY extraction from ashes from coal combustion confirm that the content of rare earth elements calculated as oxides (REO) in ash greater than 1000 ppm (0.1%) allows for successful recovery of these metals from low-rank coals (Seredin and Dai 2012). The prices of rare earth metals are steadily rising, which suggests that in the future the limit at which REY recovery from coal ashes becomes economically justified will be lowered and that this will apply to ashes from the combustion of every type of coal (not limited to low-rank coals).

Another criterion that can be applied to determine the suitability of ash as a rare earth resource is the share of individual metals in the total REY content with account taken of the forecasts concerning the relationship between demand and REY supply in recent years (Seredin 2010). Based on that, REY were grouped as critical (Nd, Eu, Tb, Dy, Y, Er), uncritical (La, Pr, Sm, Gd) and excessive (Ce, Ho, Tm, Yb, Lu) (Seredin 2010).

The ideal composition of the REY raw material (e.g. coal ash) should contain as many critical REY elements as possible, and as little excessive REY elements as possible. Therefore, in order to evaluate coal ash as a potential source of REY, an outlook coefficient (C_{outl}) is calculated as the ratio of the total amount of critical REY elements to the total amount of excessive REY elements using the following formula (Seredin and Dai 2012):

$$C_{outl} = \frac{Nd + Eu + Tb + Dy + Er + Y}{Ce + Ho + Tm + Yb + Lu}$$

The average content of REY in ashes from coals of global deposits is 404 ppm, which is about 3 times higher than that in upper continental crust (UCC) – 168.4 ppm (Taylor and McLennan 1985). The content of the oxides of rare earth elements (REO), a common indicator of REY content in an ore, in ashes of coals from global deposits is 483 ppm and is similar to the REO content in some REY-rich deposits. If the average REY content in coal ashes determined by analysis of numerous samples is comparable to that in some ores, coal-burning waste could and should be considered as a possible source of these metals (Seredin and Dai 2012).

In the future, due to the high demand for critical elements, the lower limit of REY content currently considered to be prospective may be even lowered. Ashes can become an attractive resource of obtaining these elements.

The aim of this study was to evaluate ashes from the burning of coal in fluidized bed boilers as a potential source of REY.

1. Sampling and methods

Research was based on 12 samples of ashes from the burning of coal in fluidized bed boilers, comprising fluidized bed fly ash samples (L4, L5, L10, L14, L15, L19) and fluidized bed bottom ash samples (D3, D11, D13, D25, D26, D27). Samples were taken from various Polish power plants, a detailed list is given in Table 1.

The ashes obtained constituted a test material for determining the oxide composition and rare earth elements content. Analysis was carried out using the ICP-MS (inductively coupled plasma mass spectrometry) method on a Perkin Elmer SCIEX ELAN 6000 ICP-MS spectrometer at Activation Laboratories Ltd. in Canada.

Table 1.   The list of examined ash samples

Tabela 1.   Zestawienie próbek do badań

Power plant	Sample type (type of waste)	Sample
Łagisza	Fluidized bottom ash	D3
	Fluidized fly ash	L4
	Fluidized fly ash	L5
Jaworzno II	Fluidized fly ash	L10
	Fluidized bottom ash	D11
Siersza	Fluidized bottom ash	D13
	Fluidized fly ash	L14
	Fluidized fly ash	L15
Łaziska	Fluidized fly ash	L19
Czechowice	Fluidized bottom ash	D25
Stalowa Wola	Fluidized bottom ash	D26
	Fluidized bottom ash	D27

2. Chemical composition of the ashes

The predominant chemical constituents of the fluidized bed ashes included the oxides SiO_2 and Al_2O_3, the combined content of which in all samples exceeded 50%. Another major chemical constituent present in the analyzed samples was CaO. Calcium oxide content in the ash samples varied between 9.63% and 22.15%. The tested samples also contained significant amounts of SO_3, Fe_2O_3, MgO, K_2O and Na_2O, the content of which was usually at a level of up to a few percent (Table 2). Other chemical constituents, i.e. P_2O_5, TiO_2 and MnO, were present in lower amounts, usually below 1% (Table 2). The analyzed samples of fluidized bed ashes were characterized by varying values of loss on ignition (LOI), ranging between 2.83% and 9.88%.

In accordance with the chemical classification of fly ashes introduced by Vassilev (Vassilev and Vassileva 2007) and based on the normalized content of the main oxides, all of the fluidized bed fly ashes were assigned to the *calsialic*, low acid type (CS-LA) (Fig. 1):

Chemical analysis has shown that the predominant chemical constituents of the bottom fluidized bed ashes include the oxides SiO_2, CaO and Al_2O_3, the combined content of which in most samples exceeded 70%. The exceptions were samples D26 and D27 obtained from the burning of hard coal at the Stalowa Wola power plant, where the total content

Table 2.   Chemical composition of examined ash samples

Tabela 2.   Skład chemiczny badanych próbek

| Sample	SiO₂	TiO₂	Al₂O₃	Fe₂O₃	MnO	MgO	CaO	Na₂O	K₂O	P₂O₅	SO₃	LOI	$\frac{SiO_2}{Al_2O_3}$	$\frac{MgO+CaO}{K_2O+Na_2O}$	$\frac{CaO}{MgO}$	$\frac{K_2O}{Na_2O}$
						(% wt.)										
L4	32.27	0.77	18.60	6.69	0.06	2.60	19.08	1.95	1.98	0.35	8.69	6.96	1.73	5.52	7.34	1.02
L5	32.99	0.72	18.06	7.46	0.06	2.08	21.14	1.25	1.77	0.24	11.39	2.83	1.83	7.69	10.16	1.42
L10	35.22	0.71	17.34	5.84	0.05	1.74	22.15	1.38	1.82	0.14	7.90	5.70	2.03	7.47	12.73	1.32
L14	41.22	0.90	21.96	6.33	0.08	2.20	10.68	2.70	2.30	0.19	5.28	6.17	1.88	2.58	4.85	0.85
L15	41.88	0.93	22.65	6.44	0.09	2.30	9.63	2.60	2.34	0.21	4.39	6.54	1.85	2.41	4.19	0.90
L19	33.50	0.75	18.88	5.25	0.06	2.11	17.67	0.98	2.11	0.34	8.46	9.88	1.77	6.40	8.37	2.15
D3	41.45	0.78	16.31	4.42	0.05	1.64	19.44	1.00	1.87	0.12	10.70	2.23	2.54	7.34	11.85	1.87
D11	32.91	0.58	13.23	2.94	0.04	1.40	31.76	1.15	1.45	0.07	9.74	4.73	2.49	12.75	22.69	1.26
D13	42.66	0.64	15.42	2.77	0.07	1.74	19.52	1.06	1.86	0.08	11.66	2.52	2.77	7.28	11.22	1.75
D25	37.99	0.61	14.14	3.22	0.08	1.92	22.55	0.94	2.64	0.34	14.06	1.51	2.69	6.84	11.74	2.81
D26	30.98	0.70	4.89	1.70	0.44	5.03	22.37	0.55	12.35	2.93	8.36	9.71	6.34	2.12	4.45	22.45
D27	19.87	0.39	3.49	1.33	0.39	4.00	19.03	0.67	23.30	2.43	15.49	9.61	5.69	0.96	4.76	34.78
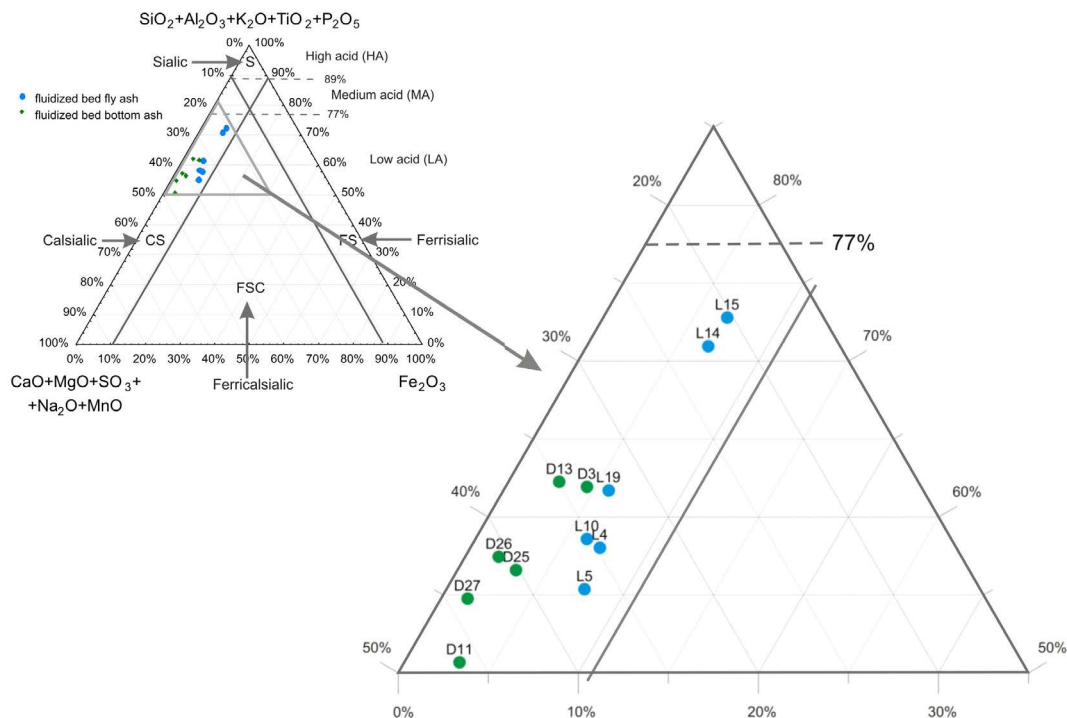
Fig. 1. Distribution of examined fly and bottom ash samples on the chemical classification system of fly ash
(Vassilev and Vassileva 2007)

Rys. 1. Analizowane próbki popiołów lotnych i dennych na tle chemicznej klasyfikacji popiołów lotnych
(Vassilev i Vassileva 2007)

of these constituents was much lower at 58.24% and 42.38%, respectively. These samples also had the lowest content of Al_2O_3 at no more than 5%, whereas in the other samples that content exceeded 10%. These samples were also found to have the lowest SiO_2 content (Table 2).

Other important chemical constituents of the examined samples included the oxides SO_3 and K_2O. The content of SO_3 in the ash samples varied between 8.36% and 15.49%. Whereas the content of K_2O varied between 1.45% and 23,30%. It should, however, be pointed out that in most of the bottom ash samples the content of K_2O was not higher than 3%, except for ash samples D26 and D27 from the Stalowa Wola power plant, where that content was much higher at 12.35% and 23.30%, respectively. It is related to the combustion of coal and biomass.

The tested samples also contained significant amounts of Fe_2O_3, MgO, and Na_2O, the content of which was usually at a level of up to 1% (Table 2). Special attention must be drawn to ash samples D26 and D27 from the Stalowa Wola power plant, which contained much less Fe_2O_3 and Na_2O and more MgO than the other analyzed bottom ashes.

Other chemical constituents, i.e. TiO_2, P_2O_5 and MnO, were present in lower amounts, usually below 1% (Table 2). It should, however, be pointed out that in the ash samples D26 and D27 from the Stalowa Wola power plant the content of P_2O_5 and MnO is much higher than in the other samples (Table 2).

The analyzed samples of fluidized bed bottom ashes were characterized by varying values of loss on ignition (LOI), ranging between 1.51% and 9.71%. The highest loss on ignition was observed in bottom ashes D26 and D27 from the Stalowa Wola power plant.

Chemical composition of the bottom ashes is presented in relation to the chemical classification of fly ashes of Vassilev (Vassilev and Vassileva 2007). Based on that, the analyzed fluidized bed bottom ashes were classified as the *calsialic*, low acid type (*CS-LA*) (Fig. 1).

The determined values of the SiO_2/Al_2O_3 ratio for fluidized bed fly ashes varied between 1.73 and 2.03 and were lower than the corresponding values for fluidized bed bottom ashes. The SiO_2/Al_2O_3 ratio for the bottom ashes ranged from 2.49 to 6.34. The highest ratio was observed in bottom ash samples D26 and D27 from the Stalowa Wola power plant.

The K_2O/Na_2O ratio was less than 3 for almost all of the analyzed samples. Exceptions included bottom ash samples D26 and D27 from the Stalowa Wola power plant, where that ratio was much higher at 22.45 and 34.78, respectively (Table 2).

The $(MgO + CaO)/(K_2O + Na_2O)$ ratio for most of the analyzed ashes ranged from 2.12 to 7.69. Samples D11 and D27 were an exception, where the ratio was equal to 12.75 and 0.96, respectively (Table 2).

The CaO/MgO ratio for all analyzed ash samples varied in a wide range from 4.19 to 22.69 (Table 2).

3. Rare earth elements and yttrium (REY) in ashes

REY content in the analyzed samples of fluidized bed fly ash varied between 146.63 and 249.94 ppm. REY content in samples was characterized by low variability (V = 20%). The average REY content in the ashes analyzed was 206.43 ppm and it was 2 times lower than the world average for coal ash.

REO content in all fluidized bed fly ash samples was, on the average, 243.99 ppm (oxide basis) and was about two times lower than the world average for coal ash. Light rare elements (LREY), the average content of which was 155.40 ppm, had the highest share (75%) in the total rare earth elements content. Heavy rare elements (HREY) had the lowest share (4% of the total REY content), their average content being 43.27 ppm (Table 3).

The content of critical elements in fluidized bed fly ashes varied between 55.70 ppm and 90.80 ppm, the average being 72.33ppm, which constituted 35% of the total REY content. The content of critical elements in the analyzed ashes was characterized by low variability (V = 18%) (Table 3).

Table. 3.   The REY content in examined fly ash samples

Tabela 3.   Zawartość REY w badanych próbkach popiołów lotnych

Sample	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
								(ppm)							
L4	30.10	41.70	86.48	9.50	38.00	7.60	1.90	6.50	0.90	5.60	1.00	3.10	0.50	2.70	0.40
L5	28.30	37.90	76.53	8.90	30.30	6.60	1.60	6.10	0.90	5.10	0.90	2.90	0.30	2.50	0.40
L10	29.50	42.70	84.75	9.60	37.30	7.10	1.60	5.50	1.00	5.30	1.00	3.00	0.40	2.80	0.30
L14	24.20	21.00	49.73	5.90	22.60	4.90	1.10	5.30	0.80	4.60	0.80	2.40	0.40	2.50	0.40
L15	24.40	25.10	57.56	6.80	26.60	5.30	1.40	4.80	0.90	5.10	1.00	2.70	0.40	2.50	0.40
L19	39.20	41.10	86.44	10.00	37.10	7.30	1.70	7.60	1.20	7.40	1.40	4.20	0.70	4.00	0.60
AM	29.28	34.92	73.58	8.45	31.98	6.47	1.55	5.97	0.95	5.52	1.02	3.05	0.45	2.83	0.42
min	24.20	21.00	49.73	5.90	22.60	4.90	1.10	4.80	0.80	4.60	0.80	2.40	0.30	2.50	0.30
max	39.20	42.70	86.48	10.00	38.00	7.60	1.90	7.60	1.20	7.40	1.40	4.20	0.70	4.00	0.60
sd	5.47	9.42	16.07	1.69	6.49	1.11	0.27	1.00	0.14	0.98	0.20	0.62	0.14	0.59	0.10
CV	19	27	22	20	20	17	18	17	15	18	20	20	31	21	24

Sample	REY	LREY	MREY	HREY	LREY	MREY	HREY	critical	uncritical	excessive	critical	uncritical	excessive	Coutl	REO
		(ppm)			(%)			(ppm)			(%)				(ppm)
L4	235.98	183.28	45.00	7.70	78	19	3	79.60	65.30	91.08	34	28	39	0.87	278.64
L5	209.23	160.23	42.00	7.00	77	20	3	69.10	59.50	80.63	33	28	39	0.86	247.21
L10	231.85	181.45	42.90	7.50	78	19	3	77.70	64.90	89.25	34	28	38	0.87	273.78
L14	146.63	104.13	36.00	6.50	71	25	4	55.70	37.10	53.83	38	25	37	1.03	173.57
L15	164.96	121.36	36.60	7.00	74	22	4	61.10	42.00	61.86	37	25	38	0.99	195.02
L19	249.94	181.94	57.10	10.90	73	23	4	90.80	66.00	93.14	36	26	37	0.97	295.73
AM	206.43	155.40	43.27	7.77	75	21	4	72.33	55.80	78.30	35	27	38	0.93	243.99
min	146.63	104.13	36.00	6.50	71	19	3	55.70	37.10	53.83	33	25	37	0.86	173.57
max	249.94	183.28	57.10	10.90	78	25	4	90.80	66.00	93.14	38	28	39	1.03	295.73
sd	41.75	34.56	7.66	1.59	3	2	1	12.93	12.89	16.60	2	1	1	0.08	49.26
CV	20	22	18	20	4	11	15	18	23	21	6	5	2	8	20

AM – average content, min, max – minimum and maximum content, sd – standard deviation of mean S, CV – coefficient of variation.

The content of uncritical elements in the analyzed fluidized bed fly ashes varied between 37.10 ppm and 66.00 ppm, the average being 55.80 ppm, which on the average constituted 27% of the total REY content. The content of uncritical elements in samples was characterized by modest variability ($V = 23\%$) (Table 3).

The content of excessive elements in the tested samples varied between 53.83 ppm and 93.14 ppm, the average being 78.30 ppm, which constituted 38% of the total REY content. The content of excessive elements in samples, as was the case of uncritical elements, was also characterized by mediocre variability ($V = 21\%$) (Table 3).

In order to evaluate the tested samples of fluidized bed fly ash as a potential REY source, the outlook coefficient (C_{outl}) was calculated, with the content of critical and excessive elements taken into account. In addition, in order to determine the potential industrial value of the ashes, a graph showing the relationship between the percentage of critical elements and C_{outl} was plotted (Seredin and Dai 2012; Dai et al. 2016) (Table 3, Fig. 2).
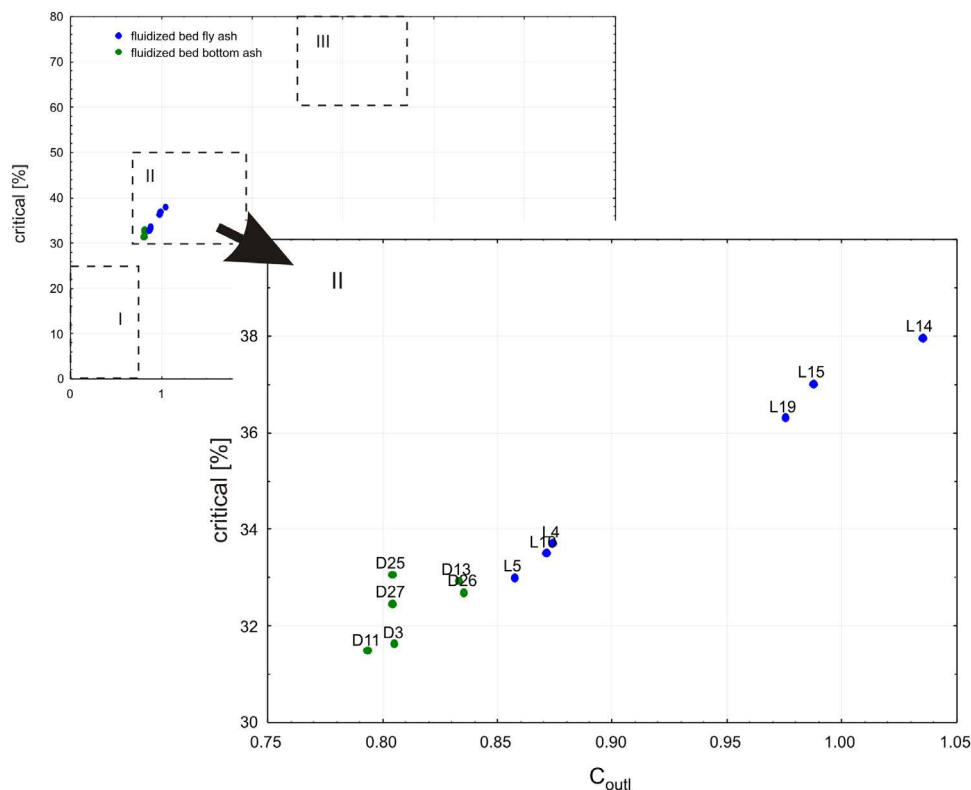
Fig. 2. The relationship between critical REY content and outlook coefficient C_{outl} on the REY enriched coal ashes classification (Seredin and Dai 2012)
REY source: I – unpromising; II – promising; III – highly promising

Rys. 2. Zależność procentowego udziału pierwiastków krytycznych w badanych próbkach od współczynnika perspektywicznego C_{outl} na tle klasyfikacji popiołów węglowych wzbogaconych w REY (Seredin i Dai 2012).
Źródło REY: I – nie perspektywiczne; II – perspektywiczne; III – źródło REY wysoko perspektywiczne

The value of the outlook coefficient C_{outl} for fluidized bed fly ash samples varied between 0.86 and 1.03, with the mean value being 0.93. This value for the analyzed samples was characterized by low variability (V = 8%). It allows all of the analyzed fluidized bed fly ash samples to be regarded as promising REY raw materials (Table 3; Fig. 2).

In order to determine the degree of enrichment of the samples with rare earths elements in relation to their content in UCC, the REY content in the samples is normalized against its content in UCC. With regard to the distribution of REY content in comparison to UCC, the samples may be classified into the following groups: enriched with LREY – L type ($La_N/Lu_N > 1$), enriched with MREY – M type ($La_N/Sm_N < 1$ and $Gd_N/Lu_N > 1$), and enriched with HREY – H type ($La_N/Lu_N < 1$). The normalized pattern of each type may have a positive or negative anomaly of different amplitudes for different elements because their behaviour in the environment may differ from that of other REYs. Subtypes and intermediate types can be distinguished due to the anomalies (Seredin and Dai 2012; Hower et al. 2013).

The distribution patterns determined for fly ash samples were classified as L-M and H-M type. These curves were, within almost all of their entire range, positioned above the reference level. The content of the individual rare earth elements in these samples was even twice as high as in UCC (Fig. 3). Samples L4, L5 and L10 were enriched primarily with LREY
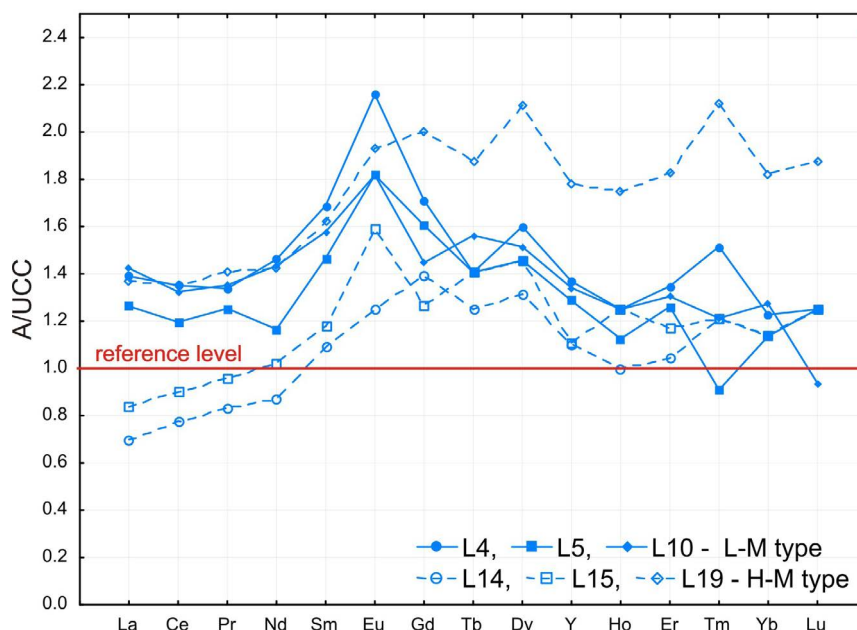
Fig. 3. Distribution patterns of REY in fly ash samples. REY are normalized by Upper Continental Crust (UCC)
(Taylor and McLennan 1985)

Rys. 3. Rozkład zawartości REY w próbkach popiołów lotnych.
Udział REY znormalizowano do ich zawartości w górnej skorupie kontynentalnej (UCC)
(Taylor i McLennan 1985)

and MREY. The normalized curves for these samples were characterized by a distinct positive anomaly for Eu (L-M type). Samples L14, L15 and L19 were enriched with LREY and MREY. The normalized curves for these samples were characterized by weak positive anomalies for Eu, Dy and Tm and a bulge in the Nd to Y range (H-M type).

REY content in the analyzed samples of fluidized bed bottom ash varied between 39.10 and 167.77 ppm. REY content in samples was highly variable (V = 47%). The average REY content in the ashes analyzed was 109.92 ppm and it was about 4 times lower than the world average for coal ash.

REO content in all fluidized bed bottom ash samples was, on the average, 129.82 ppm (oxide basis) and was about 4 times lower than the world average for coal ash. Light elements (LREY), the average content of which was 86.02 ppm, had the highest share (78%) in the total rare earth elements content. Heavy elements (HREY) had the lowest share (3% of the total REY content), their average content being 3.45 ppm (Table 4).

The content of critical elements in fluidized bed bottom ashes varied between 12.70 ppm and 53.10 ppm, the average being 35.47 ppm, which constituted 32% of the total REY content. The content of critical elements in the analyzed ashes was characterized by high variability (V = 46%) (Table 4).

The content of uncritical elements in the analyzed fluidized bed bottom ashes varied between 10.60 ppm and 48.70 ppm, the average being 30.68 ppm, which on the average constituted 28% of the total REY content. The content of uncritical elements in samples was characterized by high variability (V = 49%) (Table 4).

The content of excessive elements in the tested samples varied between 15.80 ppm and 65.97 ppm, the average being 43.70 ppm, which constituted 40% of the total REY content. The content of excessive elements in samples, as was the case of critical and uncritical elements, was also characterized by high variability (V = 46%) (Table 4).

As was the case with fluidized bed fly ashes, in order to evaluate the tested samples of fluidized bed bottom ash as a potential REY source, the outlook coefficient (C_{outl}) was calculated. In order to determine the potential industrial value of these ashes, a graph showing the relationship between the percentage of critical elements and C_{outl} was plotted (Seredin and Dai 2012; Dai et al. 2016) (Table 4, Fig. 2).

The value of the outlook coefficient C_{outl} for the fluidized bed bottom ash samples varied between 0.79 and 0.84, and its variability was low (V = 2%), with the average value being 0.81. These values for bottom ash samples are lower than for fly ashes. Nevertheless all these tested bottom ashes can still be classified as promising REY raw materials (Table 4; Fig. 2).

REY content values determined for the tested fluidized bed bottom ash samples were normalized with regard to UCC. These curves were classified as L type (samples D11, D26), L-M type (samples D3, D25) and H type (samples D13, D27). They were positioned on or below the reference level, meaning that the content of the individual rare earth elements in these samples was the same or up to about 4 times lower than in UCC (Fig. 4). Bottom ash samples were therefore characterized by the lowest REY content among the analyzed samples. A slight positive anomaly for Eu was observed on most of the curves.

Table. 4.   The REY content in examined bottom ash samples

Tabela 4.   Zawartość REY w badanych próbkach popiołów dennych

Sample	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	(ppm)														
D3	19.30	32.00	62.97	7.30	26.50	4.90	1.20	4.50	0.60	3.60	0.70	1.90	0.30	1.70	0.30
D11	18.20	28.90	56.34	6.20	22.10	4.10	1.00	3.80	0.60	3.40	0.60	1.70	0.30	1.70	0.30
D13	18.40	23.30	49.81	5.40	19.30	4.40	1.00	3.40	0.50	3.10	0.60	1.50	0.30	1.60	0.30
D25	15.90	18.70	43.95	4.20	15.90	3.50	0.80	2.50	0.50	2.60	0.50	1.40	0.20	1.30	0.20
D26	7.50	11.00	21.77	2.50	9.00	1.40	0.30	1.50	0.20	1.30	0.20	0.80	0.10	0.70	0.10
D27	5.10	6.80	14.90	1.60	6.20	1.20	0.20	1.00	0.10	0.60	0.20	0.50	0.10	0.50	0.10
AM	14.07	20.12	41.62	4.53	16.50	3.25	0.75	2.78	0.42	2.43	0.47	1.30	0.22	1.25	0.22
min	5.10	6.80	14.90	1.60	6.20	1.20	0.20	1.00	0.10	0.60	0.20	0.50	0.10	0.50	0.10
max	19.30	32.00	62.97	7.30	26.50	4.90	1.20	4.50	0.60	3.60	0.70	1.90	0.30	1.70	0.30
sd	6.17	9.91	19.25	2.19	7.77	1.58	0.41	1.36	0.21	1.22	0.22	0.54	0.10	0.53	0.10
CV	44	49	46	48	47	49	54	49	51	50	46	42	45	42	45

Sample	REY	LREY	MREY	HREY	LREY	MREY	HREY	critical	uncritical	excessive	critical	uncritical	excessive	Coutl	REO
	(ppm)				(%)			(ppm)			(%)				(ppm)
D3	167.77	133.67	29.20	4.90	80	17	3	53.10	48.70	65.97	32	29	39	0.80	197.93
D11	149.24	117.64	27.00	4.60	79	18	3	47.00	43.00	59.24	31	29	40	0.79	176.17
D13	132.91	102.21	26.40	4.30	63	31	6	43.80	36.50	52.61	33	24	33	0.83	157.09
D25	112.15	86.25	22.30	3.60	77	20	3	37.10	28.90	46.15	33	27	40	0.80	132.60
D26	58.37	45.67	10.80	1.90	77	20	3	19.10	16.40	22.87	33	26	41	0.84	68.94
D27	39.10	30.70	7.00	1.40	79	18	4	12.70	10.60	15.80	32	27	40	0.80	46.19
AM	109.92	86.02	20.45	3.45	78	19	3	35.47	30.68	43.77	32	28	40	0.81	129.82
min	39.10	30.70	7.00	1.40	77	17	3	12.70	10.60	15.80	31	26	39	0.79	46.19
max	167.77	133.67	29.20	4.90	80	20	4	53.10	48.70	65.97	33	29	41	0.84	197.93
sd	51.18	40.55	9.30	1.47	1	1	0	16.14	14.97	20.17	1	1	1	0.02	60.40
CV	47	47	45	43	1	6	7	46	49	46	2	4	2	2	47

AM – average content, min, max – minimum and maximum content, sd – standard deviation of mean S, CV – coefficient of variation.
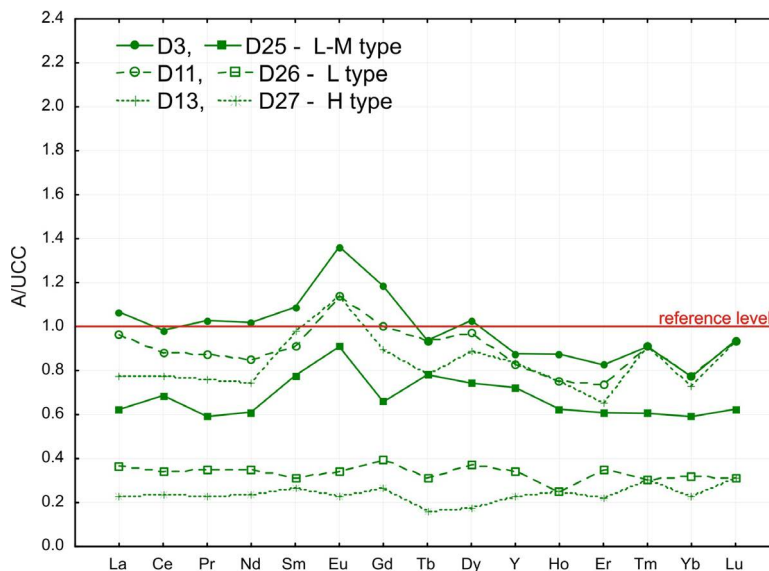
Fig. 4. Distribution patterns of REY in bottom ash samples. REY are normalized by Upper Continental Crust (UCC) (Taylor and McLennan 1985)

Rys. 4. Rozkład zawartości REY w próbkach popiołów dennych. Udział REY znormalizowano do ich zawartości w górnej skorupie kontynentalnej (UCC) (Taylor i McLennan 1985)

Summary and conclusions

Comparison between chemical composition of fluidized bed fly ashes and that of fluidized bed bottom ashes shows that the bottom ashes always have a lower Fe_2O_3 content than the fly ashes. Moreover, when referring to the total content of oxides (CaO + MgO + + SO_3 + Na_2O + MnO), the tested ash samples can be classified into three groups. The first group includes samples L14 and L15 which have the lowest total content of these oxides (<25%). The second group is represented by fly ash and bottom ash samples with (CaO + MgO + SO_3 + Na_2O + MnO) content in the range of about 32% to 37% (samples L4, L5, L10, L19, D3, D13). The third group includes bottom ash samples D11, D25, D26 and D27, which have the highest total oxide content (>40%).

Tests have shown that despite some differences in chemical composition the analyzed fly ash and bottom ash from fluidized beds could be classified as the *calsialic*, low acid type.

Comparison of REY content in the analyzed fluidized bed ashes shows that fly ashes contain more REY than the bottom ashes. However, in both cases the REY content is 2 and 4, respectively, times lower than the world average for coal ash.

Tests showed that among rare earth elements, the light elements (LREY) had the highest share (above 70%) in the total rare earth elements content in both fly ash and bottom ash. Heavy elements (HREY) had the lowest share (ca. 3–4%).

It was found that the content of critical elements and of excessive elements in fly ash and bottom ash differs, which has an effect on the value of the outlook coefficient C_{outl}, and which is always higher in the case of fly ash than in the case of bottom ash. The critical REY content all tested samples was over 30%. The computed values of the outlook coefficient $C_{outl} > 0.7$ allow both fly ash and bottom ash from fluidized beds to be regarded as promising REY raw materials. However, to obtain these elements economically justified, their total content, the form of occurrence of elements in waste and the technological possibilities of their separation should be taken into consideration. Therefore the possible recovery of rare earth elements from coal and its combustion products is an interesting new research area.

REFERENCES

Bau, M. 1996. Controls of the fractionation of isovalent trace elements in magmatic and aqueous systems: evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. *Contributions to Mineralogy and Petrology* 123, pp. 323–333.

Blissett et al. 2014 – Blissett, R. S., Smalley, N. and Rowson, N. A. 2014. An investigation into six coal fly ashes from the United Kingdom and Poland to evaluate rare earth element content. *Fuel* 119, pp. 236–239.

Dai et al. 2008 – Dai, S., Li, D., Chou, C.-L., Zhao, L., Zhang, Y., Ren, D., Ma, Y. and Sun, Y. 2008. Mineralogy and geochemistry of boehmite-rich coals: new insights from the Haerwusu Surface Mine, Jungar Coalfield, Inner Mongolia, China. *International Journal of Coal Geology* 74, pp. 185–202.

Dai et al. 2011 – Dai, S., Wang, X., Zhou, Y., Hower, J.C., Li, D., Chen, W. Zhu, X. and Zou, J. 2011. Chemical and mineralogical compositions of silicic, mafic, and alkali tonsteins in the late Permian coals from the Songzao Coalfield, Chongqing, Southwest China. *Chemical Geology* 282(1–2), pp. 29–44.

Dai et al. 2016 – Dai, S., Liu, J., Ward, C. R., Hower, J. C., French, D., Jia, S., Hood, M. M. and Garrison, T.M. 2016. Mineralogical and geochemical compositions of Late Permian coals and host rocks from the Guxu Coalfield, Sichuan Province, China, with emphasis on enrichment of rare metals. *International Journal of Coal Geology* 166, pp. 71–95.

Franus et al. 2015 – Franus, W., Wiatros-Motyka, M.M. and Wdowin, M. 2015. Coal fly ash as a resource for rare earth elements. *Environmental Science and Pollution Research* 22(12), pp. 9464–9474.

Hower et al. 1999 – Hower, J.C., Ruppert, L.F., and Eble, C.F. 1999. Lanthanide, yttrium, and zirconium anomalies in the Fire Clay coal bed, Eastern Kentucky. *International Journal of Coal Geology* 39, pp. 141–153.

Hower et al. 2013 – Hower, J.C., Dai, S., Seredin, V.V., Zhao, L., Kostova, I.J., Silva, L.F.O., Mardon, S.M. and Gurdal, G. 2013. A Note on the Occurrence of Yttrium and Rare Earth Elements in Coal Combustion Products. *Coal Combustion and Gasification Products* 5, pp. 39–47.

Iwanek et al. 2008 – Iwanek, P., Jelonek, I. and Mirkowski, Z. 2008. Preliminary research on fly ash from the fluidal boiler in the context of its development *(Wstępne badania popiołów z kotła fluidalnego w aspekcie ich zagospodarowania). Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 24 (4/4), pp. 91–104 *(in Polish)*.

Jarosiński, A. 2016. The possibilities of the acquisition of rare-earth metals under national conditions *(Możliwości pozyskiwania metali ziem rzadkich w Polsce). Zeszyty Naukowe Instytutu Gospodarki Surowcami Mineralnymi i Energią Polskiej Akademii Nauk* No 92, pp. 75–88 *(in Polish)*.

Łaskawiec et al. 2010 – Łaskawiec, K., Michalik, A., Małolepszy, J. and Zapotoczna-Sytek, G. 2010. Research on using fluidized ashes for the production of autoclaved aerated concrete *(Badania nad zastosowaniem popiołów lotnych ze spalania węgli w kotłach fluidalnych do wytwarzania autoklawizowanego betonu komórkowego). Prace Instytutu Ceramiki i Materiałów Budowlanych* 3(6), pp. 123–140 *(in Polish)*.

Mardon, S.M. and Hower, J.C. 2004. Impact of coal properties on coal combustion by product quality: examples from a Kentucky power plant. *International Journal of Coal Geology* 59, pp. 153–169.

Mayfield, D.B. and Lewis, A.S. 2013. Environmental review of coal ash as a resource for rare earth and strategic elements. *Word of Coal Ash Conference (WOCA)* – April 22–25 2013 Lexington, KY. [Online] Available: at http://www.flyash.info/ [Accessed: 20 July 2017].

Palmer, B. 2015. *Coal Ash, Fly Ash, Bottom Ash, and Boiler Slag*. [Online] Available at: https://www.nrdc.org/onearth/coal-ash-fly-ash-bottom-ash-and-boiler-slag [Accessed: 20 July 2017].

Radwanek-Bąk, B. 2011. Mineral Resources of Poland in the Aspect of the Assessment of Critical Minerals to the European Union Economy *(Zasoby kopalin Polski w aspekcie oceny surowców krytycznych Unii Europejskiej)*. *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 27(1), pp. 5–19.

Seredin, V.V. 1996. Rare earth element-bearing coals from the Russian Far East deposits. *International Journal of Coal Geology* 30, pp. 101–129.

Seredin, V.V. 2010. A new method for primary evaluation of the outlook for rare earth element ores. *Geology of Ore Deposits* 52, pp. 428–433.

Seredin, V.V. and Dai, S. 2012. Coal deposits as potential alternative sources for lanthanides and yttrium. *International Journal of Coal Geology* 94, pp. 67–93.

Smakowski, T. 2011. Critical or deficit mineral commodities for EU and Poland economy *(Surowce mineralne – krytyczne czy deficytowe dla gospodarki UE i Polski)*. *Zeszyty Naukowe Instytutu Gospodarki Surowcami Mineralnymi i Energią PAN* 81, pp. 59–68 *(in Polish)*.

Szponder, D.K. and Trybalski, K. 2009. Determination of fly ashes properties with use of different research methods and measuring devices *(Określanie właściwości popiołów lotnych przy użyciu różnych metod i urządzeń badawczych)*. *Górnictwo i Geoinżynieria* 33(4), pp. 287–298 *(in Polish)*.

Taylor, S.R. and McLennan, S.H. 1985. *The Continental Crust: its Composition and Evolution. Blackwell*, Oxford, 312 pp.

Vassilev, S.V. and Vassileva, C.G. 2007. A new approach for the classification of coal fly ashes based on their origin, composition, properties, and behavior. *Fuel* 86, p. 1490–1512.

**ASHES FROM BITUMINOUS COAL BURNING IN FLUIDIZED BED BOILERS
AS A POTENTIAL SOURCE OF RARE EARTH ELEMENTS**

Abstract

Rare earth elements are characterized by the high risk of their shortage resulting from limited resources. From this reason REE constitute a group of elements of special importance for the European Union.

The aim of this study was to evaluate ashes from the burning of coal in fluidized bed boilers as an potential source of REY. Twelve samples of fly ash and bottom ash taken from power plants in Poland were analyzed. Tests have shown that despite some differences in chemical composition, the fly ash and bottom ash from fluidized beds could be classified as the calsialic, low acid type. It was found that fly ashes contained more REY than bottom ashes. Among REY, the light elements (LREY) had the highest share in the total REY content in both fly ashes and bottom ashes. Heavy elements (HREY) had the lowest content.

The normalized curves plotted for fly ash samples within almost all of their entire range were positioned above the reference level and these curves were of the L-M or H-M type. The content of the individual REY in these samples was even twice as high as in UCC. The normalized curves plotted for bottom ash samples were classified as of L, L-M or H type. They were positioned on the reference level or above it. The content of the individual REY in these samples was the same or up to about 4 times lower than in UCC.

It was found that the content of critical elements and of excessive elements in fly ash and bottom ash differs, which has an effect on the value of the outlook coefficient C_{outl}, and which is always higher in the case of fly ash than in the case of bottom ash. Nevertheless, the computed values of the outlook coefficient C_{outl} allow both fly ash and bottom ash from fluidized beds to be regarded as promising REY raw materials.

K e y w o r d s : rare earth elements and yttrium (REY), fluidized bed fly ash,
fluidized bed bottom ash, critical raw materials

POPIOŁY ZE SPALANIA WĘGLA KAMIENNEGO W KOTŁACH FLUIDALNYCH, JAKO POTENCJALNE ŹRÓDŁO PIERWIASTKÓW ZIEM RZADKICH

S t r e s z c z e n i e

Pierwiastki ziem rzadkich charakteryzują się wysokim ryzykiem niedoboru, wynikającym z ograniczonej ilości źródeł ich pozyskiwania. Z tego powodu stanowią grupę pierwiastków o specjalnym znaczeniu w Unii Europejskiej. Celem pracy była ocena popiołów ze spalania węgla kamiennego w kotłach fluidalnych, pod kątem ich wykorzystania, jako potencjalnego źródła REY.

Badaniom poddano 12 próbek popiołów lotnych i dennych fluidalnych pobranych z elektrowni w Polsce.

Badania wykazały, że mimo różnic w składzie chemicznym badane popioły lotne i denne fluidalne zostały zaklasyfikowane do typu *calsialic* – słabo kwaśnych. Stwierdzono, że popioły lotne charakteryzują się większą zawartością REY niż denne. Zarówno w popiołach lotnych, jak i dennych największy udział wśród REY mają pierwiastki lekkie LREY. Natomiast najmniejszym udziałem charakteryzują się pierwiastki ciężkie HREY.

Krzywe normalizacyjne wyznaczone dla próbek popiołów lotnych w prawie całym swoim zakresie znajdują się powyżej poziomu odniesienia, są to krzywe typu L-M lub H-M. Zawartości poszczególnych REY w tych próbkach są nawet dwukrotnie większe niż w UCC. Krzywe normalizacyjne wyznaczone dla próbek popiołów dennych zaliczono do typów L, L-M i H. Znajdują się one, na lub poniżej poziomu odniesienia. Zawartość poszczególnych REY w tych próbkach jest taka sama lub do około 4 razy mniejsza niż w UCC.

Stwierdzono, że udział pierwiastków krytycznych i nadmiarowych w popiołach lotnych i dennych różni się, co ma wpływ na wartość współczynnika perspektywicznego C_{outl}, który dla popiołów lotnych przyjmuje zawsze wyższe wartości niż dla dennych. Pomimo to, uzyskane wartości współczynnika perspektywicznego C_{outl} pozwalają zaliczyć, zarówno analizowane popioły lotne jak i denne fluidalne do surowców perspektywicznych REY.

S ł o w a   k l u c z o w e : pierwiastki ziem rzadkich i itr (REY), surowce krytyczne,
popiół lotny fluidalny, popiół denny fluidalny