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The high temperature ashes (HTA) from bituminous coal combustion as a potential resource of rare earth elements

Introduction

REEs in coal constitute a group of elements of special importance. Due to their chemical properties they are usually studied as one group rather than individually.

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. There are several classifications of these elements that take into account geochemical and economic considerations (Seredin 2010; Seredin and Dai 2012). According to a geochemical classification, REE fall into three subgroups: light rare earth elements (LREE: La, Ce, Pr, Nd, Pm, Sm), medium rare earth elements (MREE: Eu, Gd, Tb, Dy) and heavy rare earth elements (HREE: Ho, Er, Tm, Yb and Lu). 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.

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Yttrium in nature is closely associated with the lanthanides, since its ionic radius is similar to that of Ho and its ionic charge is equal to that of Ho. For this reason yttrium is usually inserted on the REY distribution patterns between Dy and Ho (Bau 1996).

Rare earth elements, both in the form of metals as well as oxides, find use in modern technology. Rare earth metals are used, for instance, in the glass industry (cerium), steel industry (cerium), chemical industry in the manufacture of X-ray films and of catalysts for waste gas treatment (lanthanum), electronic industry (europium, gadolinium, erbium), high-energy magnetic materials industry (samarium and neodymium). They are also used in the automotive industry (batteries and catalysts), in the aircraft and rocket industry (engine parts) and in medical diagnostics, in the armaments industry (radars, lasers, etc.). The rarity of these metals is only apparent, as they occur almost everywhere, although their concentrations in nature are mostly low (Smakowski 2011).

The widespread shift from coal-fired power plants to wind/solar plants and from automobiles with internal combustion engines to electric cars can, within a few decades, cause even a 26-fold increase in demand for two rare earth elements: dysprosium and neodymium, which are produced almost exclusively in China (Chen 2011; Alonso et al. 2012; Całusz-Moszko and Białecka 2013; Du and Graedel 2013; Hoenderdal et al. 2013; Seredin et al. 2013).

REY deposits are found mainly outside Europe, with large potential resources, mostly unexplored, existing in many African countries. At present, China controls about 57% of evidenced rare earth resources and about 97% of the rare earth metal market (Smakowski 2011).

Rare earth minerals occur in Poland, but the content of rare earth elements is low and these minerals have no economic significance. REY occur predominantly in the form of carbonates, oxides, phosphates and silicates. In Poland, rare earth deposits are located in Lower Silesia in the vicinity of Szklarska Poręba (up to 0.5%) and Bogatynia (1.55%). They have the form of oxides, and are of mineralogical significance only, mainly because of low rare earth elements content, which adversely affects the economics of producing rare earth concentrates. The secondary sources are potentially economically important, i.e. waste phosphogypsum, apatite concentrates (0.8–1.0% REO) imported from the Khibiny Massif in Russia.

The phosphogypsum disposal site at the Wizów chemical plant in Lower Silesia is also well explored. The national demand for rare earth elements is met by imports, mainly from China, West European countries, USA, and from Estonia (2007–2008) (Radwanek-Bąk 2011; Całusz-Moszko and Białecka 2012; Blaschke et al. 2015; Jarosiński 2016).

The rare earth elements are raw materials of high economic importance and have been identified as 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 the 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 first data on the potential of lanthanides and yttrium (REY) recovery as by-products of coal mining emerged 25 years ago after the discovery of high REY content coal deposits (0.2-0.3% in ash) in one of the coal basins in the Russian Far East (Seredin and Dai 2012). During the next five years, several coal seams have been found with similar or even higher REY content, up to 1.0% in ash (Seredin 1996). Since that time REY-rich coals have been identified in many coal basins (Hower et al. 1999; Mardon and Hower 2004; Dai et al. 2008, 2011; Seredin and Dai 2012; Blissett et al. 2014; Hower et al. 2016). In order to evaluate the possibilities of extracting rare earth elements from any source (including coal ash), several parameters have to be taken into account, such as:

- ◆ the amount of resources of these metals and the feasibility of their use,
- ◆ simplicity and rate of hydrometallurgical recovery,
- ◆ environmental impact and effect on human health of recovery and processing of rare earth elements.

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

Based on experimental data on REY extraction from ashes from coals of the Russian Far East, it was found that REO content in ash greater than 1000 ppm (0.1%) allows for the successful recovery of these metals from low rank coal (Seredin and Dai 2012). The prices of rare earth metals systematically increased until 2012, but began to decrease as of 2013. However, according to predictions, the demand for REY will increase by 2030. This will cause their prices to rise again. The limit at which it will be profitable to recover REY from coal ashes will decline in the future (Seredin and Dai 2012; Zhou et al. 2017; Fernandez 2017). We now know that the limit could be lower, in the order of 800-900 ppm, and could be related to ashes from the combustion of any coals, not limited to low-rank coals (Seredin and Dai 2012).

The second 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 (Seredin 2010). This approach is not based on the traditional division into light REY and heavy REY, but on current market trends. In accordance with this division, 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).

Based on this approach, the ideal composition of the REY raw material (e.g. coal ash) should contain as many critical REY elements as possible, and as few excessive REY elements as possible. In view of these criteria, in order to evaluate coal ash as an alternative source of REYs, 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):

$$C_{outl} = \frac{Nd + Eu + Tb + Dy + Er + Y}{Ce + Ho + Tm + Yb + Lu} \quad (1)$$

The average content of REY of world coals, according to Ketriss and Yudovich 2009, is 68.5 ppm, which is 2.5 times lower than the REY content in the rocks of the upper continental crust (UCC) (168.4 ppm) (Taylor and McLennan 1985).

The average content of REYs in ashes from coals of world deposits is 404 ppm, which is about 3 times higher than in UCC. The content of the REY oxides (REO) is a common indicator of REY content in an ore. The REO content in ashes of coals from world deposits is 483 ppm. That value is close to the REO content in some REY-rich deposits.

Therefore, if the average REY content in coal ashes determined by the analysis of numerous samples is comparable to the fact that in some ores, coal-burning waste could and should be considered as a possible source of these elements (Seredin and Dai 2012).

The aim of this study was to evaluate high-temperature ashes (HTA) from the combustion of coal from the Ruda beds in the Pniówek coal mine as an alternative source of REY.

1. Samples and analytical procedures

The research was based on 13 samples of high-temperature ashes (HTA) from the combustion of metabituminous (B) coal collected from the Ruda coal seams in the Pniówek coal mine, namely: 401/1 – sample M4; 403/1 – samples M2, M11, M12; 404/1 – samples M10, M13 and 404/2 – samples M5, M6, A1-A5 (Adamczyk et al. 2014). Coal samples were taken in compliance with PN-ISO 13909, they were reduced, and grinded to the fraction $\phi < 0.2$ mm. Ash content (A^d) was determined in all samples according to PN-G-4512:1980/Az1:2002. HTA for testing were produced by coal combustion in a muffle oven at 815°C. HTA obtained in this manner from coal samples 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.

2. Chemical composition of the HTA samples

Nearly all of the coal samples from which HTA samples were produced featured low ash content ($A^d < 10\%$). For this reason all tested coal samples were classified as very low ash samples ($A^d < 5\%$) or as low ash samples ($5\% \leq A^d < 10\%$) (PN-ISO 11760:2007 (pl)). One exception was sample M12 from the 403/1 seam, where ash content was 11.24% which classified it as a medium ash sample ($10\% \leq A^d < 20\%$) (Table 1, Adamczyk et al. 2014).

The predominant chemical constituents of the ashes included SiO_2 and Al_2O_3 oxides, the combined content of which in almost all samples exceeded 49%. The exceptions were samples M6 and A4 obtained from the coal seam 404/2, where the total content of these constituents was much lower at 32.86% and 33.12%, respectively. Furthermore these samples featured the highest content of Fe_2O_3 among the tested ash samples: 45.25% and 42.07%,

respectively. The Fe_2O_3 content in the other samples was much lower, varying between 2.3% and 16.05% (Table 1). The high content of Fe_2O_3 is associated with the occurrence of siderite in coal samples (Adameczyk et al. 2016).

Other important chemical constituents of the tested samples included CaO and P_2O_5 oxides. The CaO content in the ash samples varied between 3.57% and 23.15%, whereas the P_2O_5 content varied between 0.87% and 17.10%. The high content of P_2O_5 and CaO is associated with the occurrence of apatite, calcite and dolomite in coal samples (Adameczyk et al. 2016).

The tested samples also contained significant amounts of MgO, Na_2O and SO_3 , the content of which was usually at a level of a few percent (Table 1).

Other chemical constituents, i.e. MnO, K_2O and TiO_2 , were present in lower amounts, usually below 2% (Table 1).

The studies have shown that the analyzed HTA obtained from coals from the Ruda bed seams differed in chemical composition despite the fact that these coals were characterized by a similar coal rank.

In accordance with the chemical classification of HTA introduced by Vassilev (Vassilev and Vassileva 1998) and based on the normalized content of the five main oxides, HTA obtained from the coal samples from the Ruda beds were assigned to the following types (Fig. 1): *sialic* – M4; *sialocalcic* – M2; *sialoferricalcic* – M12, M10; *calsialic* – M13; *ferricalcic* – M5, M6, A1-A5; *ferrisialic* – M11.

Among all of the examined samples, the *sialic* type ash demonstrated the highest content of SiO_2 and Al_2O_3 (sample M4) and the lowest content of CaO. This ash also showed the lowest ratio $(\text{MgO} + \text{CaO})/(\text{K}_2\text{O} + \text{Na}_2\text{O})$.

Among all of the tested samples, the *sialocalcic* type ash (sample M2) demonstrated the highest content of K_2O and TiO_2 . This ash also had the lowest content of Na_2O . The *sialocalcic* type ash was also characterized by the highest ratios $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ (Table 1).

Among all of the examined samples, the *calsialic* type ash was found to have the lowest content of Fe_2O_3 , MnO, MgO and SO_3 , and the highest content of CaO and P_2O_5 (sample M13). This ash was also characterized by the highest ratios $(\text{MgO} + \text{CaO})/(\text{K}_2\text{O} + \text{Na}_2\text{O})$ and CaO/MgO (Table 1).

It was found that HTA classified as *ferricalcic* type were obtained only from coal channel samples from the 404/2 seam. However, there is a high differentiation of chemical composition between ashes of this type. The *ferricalcic* samples, the M6 and A4 were found to have the highest Fe_2O_3 content and among of all analyzed samples simultaneously (Fig. 1). Moreover, these ashes had the highest content of the oxides MnO (0.49% and 0.40% in M6 and A4 samples, respectively).

Among all of the examined samples, the *ferrisialic* type ashes were found to have the highest content of the following oxides: MgO (sample M5), Na_2O (sample A5) and SO_3 (sample A2). The *ferrisialic* ash type samples were characterized by the content of Al_2O_3 (samples A4), SiO_2 , SiO_2 , P_2O_5 (sample M6) and TiO_2 (sample A2) oxides lower than in other samples, as well as by the lowest CaO/MgO (sample M6), $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ (sample A2) ratios (Table 1).

Table 1. The ash content (A^d) of coal samples and the chemical composition of HTA samples
 Tabela 1. Zawartość popiołu (A^d) w próbkach węgla i skład chemiczny popiołów HTA

Coal seam	Sample	A^d	(% wt.)														CaO MgO	K ₂ O Na ₂ O
			SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	SO ₃	SiO ₂ Al ₂ O ₃	MgO + CaO K ₂ O + Na ₂ O			
401/1	M4	9.1	46.83	35.55	3.40	0.05	1.40	3.57	2.30	1.97	1.19	2.65	1.10	1.32	1.16	2.56	0.86	
403/1	M2	4.9	42.23	27.46	4.55	0.08	2.02	10.37	1.18	2.06	1.36	5.61	3.08	1.54	3.82	5.13	1.75	
403/1	M11	9.7	34.63	33.68	12.43	0.04	1.84	5.95	2.04	1.99	0.69	4.28	2.43	1.03	1.93	3.24	0.98	
403/1	M12	11.2	40.01	34.44	7.03	0.04	1.11	5.82	2.22	2.05	0.97	5.84	0.48	1.16	1.62	5.24	0.93	
404/1	M10	6.8	40.00	33.25	7.72	0.08	1.45	6.58	1.25	1.46	0.74	6.56	0.90	1.20	2.97	4.53	1.17	
404/1	M13	8.8	28.44	24.77	2.30	0.03	0.85	23.15	1.50	0.95	0.58	17.1	0.35	1.15	9.83	27.17	0.63	
404/2	M5	2.6	29.22	25.86	12.12	0.19	6.42	11.63	2.67	0.87	0.60	2.10	8.33	1.13	5.10	1.81	0.32	
404/2	M6	4.6	17.50	15.33	45.25	0.49	4.83	7.31	2.45	0.46	0.35	0.87	5.15	1.14	4.17	1.51	0.19	
404/2	A1	1.9	24.16	26.24	16.05	0.26	4.61	13.77	2.54	0.80	0.41	2.05	9.13	0.92	5.51	2.99	0.31	
404/2	A2	1.6	23.20	26.09	11.60	0.23	5.09	17.24	2.89	0.50	0.24	1.49	11.43	0.89	6.58	3.39	0.17	
404/2	A3	5.1	31.90	31.15	13.84	0.11	1.48	9.78	1.75	1.06	0.56	7.73	0.64	1.02	4.01	6.61	0.61	
404/2	A4	3.8	17.90	15.22	42.07	0.40	5.57	8.58	2.48	0.64	0.37	1.40	5.38	1.18	4.54	1.54	0.26	
404/2	A5	4.6	33.08	30.09	13.73	0.15	2.47	8.89	3.14	1.39	0.86	4.18	2.02	1.10	2.51	3.59	0.44	

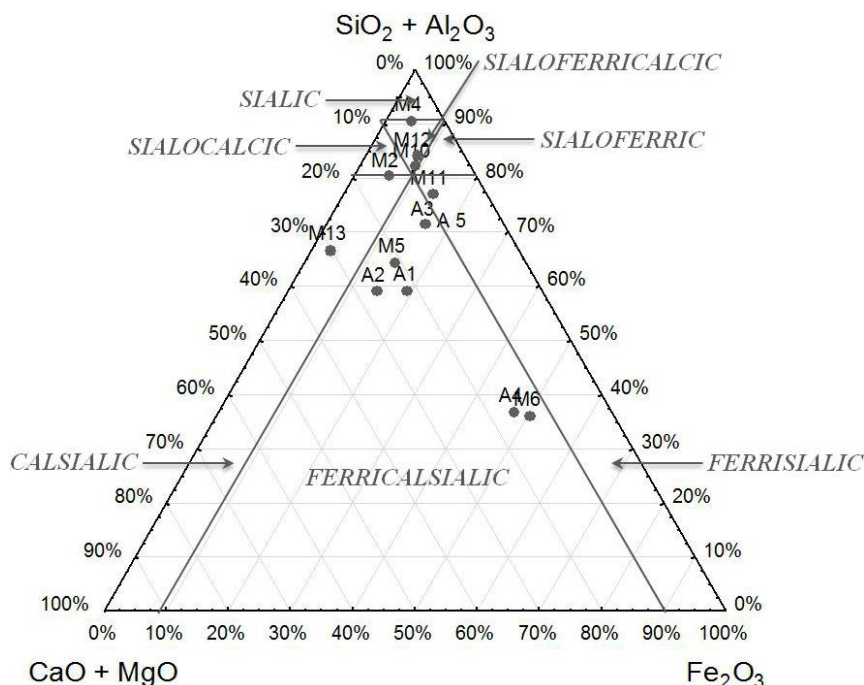


Fig. 1. The chemical classification system of HTA samples (Vassilev and Vassileva 1998)

Rys. 1. Chemiczna klasyfikacja popiołów HTA

The *ferrisialic* samples M6 and A4 paid special attention because they had the smallest SiO_2 and Al_2O_3 contents and the highest Fe_2O_3 from all analyzed samples. Therefore the chemical composition of these samples significantly differed from that of the other analyzed ashes.

3. Rare earth elements and yttrium (REY) in HTA samples

The content of REY in the analyzed samples of HTA varied between 380.80 and 1886.50 ppm and it was characterized by high variability ($V = 49\%$). The average REY content in the analyzed ashes was 1038.67 ppm and it was 2.5 times higher than the world average (404 ppm).

The data presented showed that in seven ash samples from coals from the 404/1 and 404/2 seams the REY content was higher than 800 ppm, i.e. it exceeded the limit at which REY recovery from coal ashes is profitable.

The REO content in all HTA samples was, on average, 1230.10 ppm (oxide basis) and was 2.5 times higher than the average for the coal ashes of world deposits (483 ppm).

Table. 2. The REY content in the examined HTA samples

Tabela 2. Zawartość REY w badanych próbkach HTA

Coal seam	Sample	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		Detection limit (ppm)														
	2	0.1	0.1	0.1	0.05	0.1	0.1	0.05	0.1	0.1	0.1	0.1	0.1	0.05	0.1	0.04
401/1	M4	77.00	101.00	195.00	23.50	95.50	20.50	4.29	17.50	2.70	14.20	2.70	7.40	1.00	6.30	0.98
403/1	M2	78.00	87.20	171.00	18.10	72.00	14.80	3.42	14.70	2.40	13.30	2.60	7.70	1.08	7.10	1.12
403/1	M11	110.00	110.00	271.00	31.90	140.00	30.50	6.69	27.30	4.10	22.50	4.30	11.50	1.54	9.40	1.39
403/1	M12	101.00	104.00	212.00	25.80	105.00	24.00	5.32	20.70	3.50	19.30	3.60	10.30	1.44	8.70	1.38
404/1	M10	223.00	193.00	434.00	55.00	237.00	55.40	12.60	50.90	8.00	42.60	7.80	20.80	2.69	15.90	2.36
404/1	M13	234.00	159.00	366.00	46.60	200.00	48.70	11.50	48.20	8.10	44.30	8.20	21.90	2.78	16.00	2.30
404/2	M5	145.00	163.00	371.00	43.30	185.00	37.50	8.21	34.70	5.30	27.90	5.10	13.90	1.95	12.10	1.85
404/2	M6	87.00	48.60	108.00	13.10	55.70	13.60	3.27	15.00	2.40	13.70	2.80	8.00	1.16	7.30	1.17
404/2	A1	326.00	208.00	567.00	70.90	300.00	71.40	17.10	72.10	10.90	64.50	12.30	33.50	4.39	27.70	4.07
404/2	A2	348.00	229.00	612.00	73.60	301.00	72.00	17.50	73.70	11.10	65.70	12.60	33.90	4.51	27.90	3.99
404/2	A3	302.00	198.00	507.00	60.80	262.00	62.80	15.30	61.50	9.60	55.20	10.20	27.30	3.49	21.30	3.17
404/2	A4	105.00	84.40	203.00	25.30	103.00	24.30	5.77	23.90	3.70	21.20	4.00	10.80	1.43	9.20	1.35
404/2	A5	184.00	155.00	356.00	44.30	175.00	42.00	9.81	40.40	6.20	36.20	6.70	18.10	2.32	14.70	2.15
S		178.46	141.55	336.38	40.94	171.63	39.81	9.29	38.51	6.00	33.89	6.38	17.32	2.29	14.12	2.10
min		77.00	48.60	108.00	13.10	55.70	13.60	3.27	14.70	2.40	13.30	2.60	7.40	1.00	6.30	0.98
max		348.00	229.00	612.00	73.60	301.00	72.00	17.50	73.70	11.10	65.70	12.60	33.90	4.51	27.90	4.07
ds		98.67	56.09	160.02	19.92	84.64	20.73	5.10	21.17	3.21	19.04	3.58	9.51	1.22	7.47	1.06
V		55.29	39.62	47.57	48.66	49.31	52.08	54.92	54.98	53.55	56.18	56.13	54.92	53.05	52.90	50.42

Table 2. cont.

Tabela 2. cd.

Coal seam	Sample	REY			MREY			HREY			MREY (%)			HREY (%)			critical	uncritical	excessive	Coutl	REO (ppm)
		REY	LREY	MREY	LREY	MREY	HREY	LREY	MREY	HREY	MREY (%)	LREY	MREY	HREY	critical	uncritical					
401/1	M4	569.57	435.50	115.69	18.38	76.46	20.31	3.23	201.09	162.50	205.98	35.31	28.53	36.16	0.98	672.86					
403/1	M2	494.52	363.10	111.82	19.60	73.42	22.61	3.96	176.82	134.80	182.90	35.76	27.26	36.99	0.97	585.26					
403/1	M11	782.12	583.40	170.59	28.13	74.59	21.81	3.60	294.79	199.70	287.63	37.69	25.53	36.78	1.02	924.04					
403/1	M12	646.04	470.80	149.82	25.42	72.87	23.19	3.93	244.42	174.50	227.12	37.83	27.01	35.16	1.08	764.29					
404/1	M10	1361.05	974.40	337.10	49.55	71.59	24.77	3.64	544.00	354.30	462.75	39.97	26.03	34.00	1.18	1610.94					
404/1	M13	1217.58	820.30	346.10	51.18	67.37	28.43	4.20	519.80	302.50	395.28	42.69	24.84	32.46	1.32	1444.15					
404/2	M5	1055.81	799.80	221.11	34.90	75.75	20.94	3.31	385.31	278.50	392.00	36.49	26.38	37.13	0.98	1247.33					
404/2	M6	380.80	239.00	121.37	20.43	62.76	31.87	5.37	170.07	90.30	120.43	44.66	23.71	31.63	1.41	452.95					
404/2	A1	1789.86	1217.30	490.60	81.96	68.01	27.41	4.58	752.00	422.40	615.46	42.01	23.60	34.39	1.22	2120.90					
404/2	A2	1886.50	1287.60	516.00	82.90	68.25	27.35	4.39	777.20	448.30	661.00	41.20	23.76	35.04	1.18	2236.18					
404/2	A3	1599.66	1090.60	443.60	65.46	68.18	27.73	4.09	671.40	383.10	545.16	41.97	23.95	34.08	1.23	1896.97					
404/2	A4	626.35	440.00	159.57	26.78	70.25	25.48	4.28	249.47	157.90	218.98	39.83	25.21	34.96	1.14	741.45					
404/2	A5	1092.88	772.30	276.61	43.97	70.67	25.31	4.02	429.31	281.70	381.87	39.28	25.78	34.94	1.12	1293.96					
S		1038.67	730.32	266.15	42.20	70.78	25.17	4.05	416.59	260.81	361.27	39.59	25.51	34.90	1.14	1230.10					
min		380.80	239.00	111.82	18.38	62.76	20.31	3.23	170.07	90.30	120.43	35.31	23.60	31.63	0.97	452.95					
max		1886.50	1287.60	516.00	82.90	76.46	31.87	5.37	777.20	448.30	661.00	44.66	28.53	37.13	1.41	2236.18					
ds		506.29	340.12	147.00	22.80	3.88	3.36	0.56	218.44	116.85	172.89	2.87	1.54	1.66	0.14	600.37					
V		48.74	46.57	55.23	54.03	5.48	13.34	13.96	52.44	44.80	47.86	7.26	6.03	4.75	11.91	48.81					

S – average content; min, max – minimum and maximum content, ds – standard deviation of mean S; V – coefficient of variation.

Light elements (LREY), the average content of which was 730.32 ppm, had the highest share (above 70%) in the rare earth elements content. Heavy elements (HREY) had the lowest share (ca. 4%), their average content being 42.20 ppm.

The content of critical elements in the HTA samples varied between 170.07 ppm and 777.20 ppm, the average being 416.59 ppm, which constitutes 40% of the total REY content. The content of critical elements in the analyzed ashes is characterized by high variability ($V = 52\%$) (Table 2).

The content of uncritical elements in HTA samples varied between 90.30 ppm and 448.30 ppm, the average being 260.81 ppm, which constituted 25% of the total REY content. The content of uncritical elements in samples was also characterized by high variability ($V = 45\%$) (Table 2).

The content of excessive elements in the tested samples varied between 120.43 ppm and 661.00 ppm, the average being 361.27 ppm, which constituted 35% of the total REY content. The content of excessive elements in samples, as well as the share of critical and uncritical elements, was also characterized by high variability ($V = 48\%$) (Table 2).

In order to evaluate the tested samples of ash as an alternative 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 2, Fig. 2).

The value of the outlook coefficient C_{outl} for HTA samples varied between 0.97 and 1.41, with the mean value being 1.14. This value for HTA samples was characterized by low variability ($V = 12\%$). It allowed all of the analyzed ash samples to be regarded as promising REY raw materials (Table 2; Fig. 2).

In order to determine the degree of enrichment of the samples with rare earth elements in relation to their content in UCC, the REY content determined in the samples was 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 ($La_N/Lu_N < 1$) where N means the REY content normalized against its content in UCC.

The distribution pattern of each type may have a positive or negative anomaly of different amplitudes for different elements because their behavior 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 for the HTA samples were of a similar shape and they were M-H type. The distribution pattern had a shape characteristic of the M-L type only in one case (sample M4). All the distribution patterns were, within their entire range, positioned above the reference level. They featured a distinctive bulge, mainly within the range between Nd and Y. The content of some individual rare earth elements in the tested samples was up to almost 20 times higher than in UCC (Fig. 3).

Most of the distribution patterns had a maximum (positive anomaly) at a position corresponding to Eu. Positive anomalies were also observed in these curves for Dy (samples M2, M4, M5, M10–M13, A1–A5). A positive anomaly for Ho was observed in samples M11 and A4. The normalized curve of sample M2 also had a positive anomaly for Er. Note that almost all the distribution patterns had a slight negative anomaly for Y (samples M4, M5, M10–M13, A1, A2, A4, A5) and for Pr and Ce (samples M2 and M4).

Tests have shown that the distribution pattern of sample M6 had a form different from that the other analyzed HTA curves and that it had two positive extremes corresponding to Gd and Y.

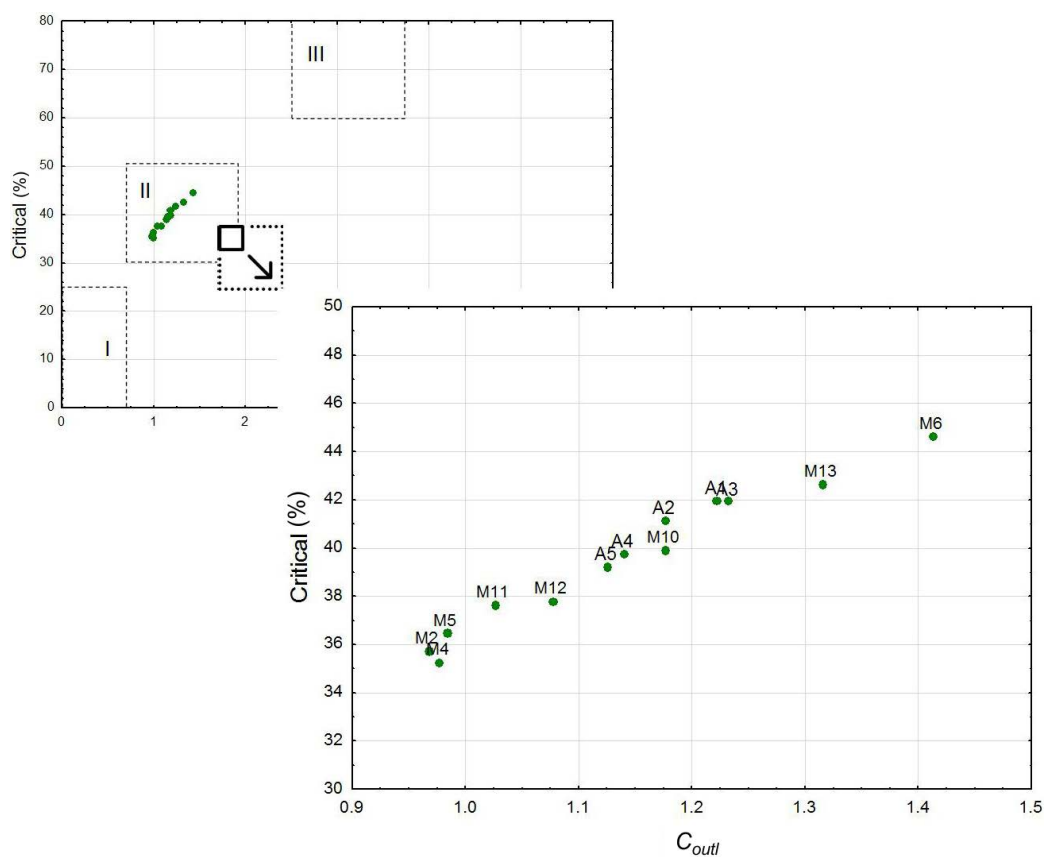


Fig. 2. The relationship between critical REY content and outlook coefficient C_{outl} on the REY enriched coal ashes classification (Seredin and Dai 2012).

REY source: I – unpromising; II – promising; III – highly promising

Rys. 2. Zależność procentowego udziału pierwiastków krytycznych w badanych próbkach od współczynnika perspektywnego C_{outl} na tle klasyfikacji popiołów węglowych wzbogaconych w REE.

Źródło REY: I – nie perspektywiczne; II – perspektywiczne; III – źródło REY wysoko perspektywiczne

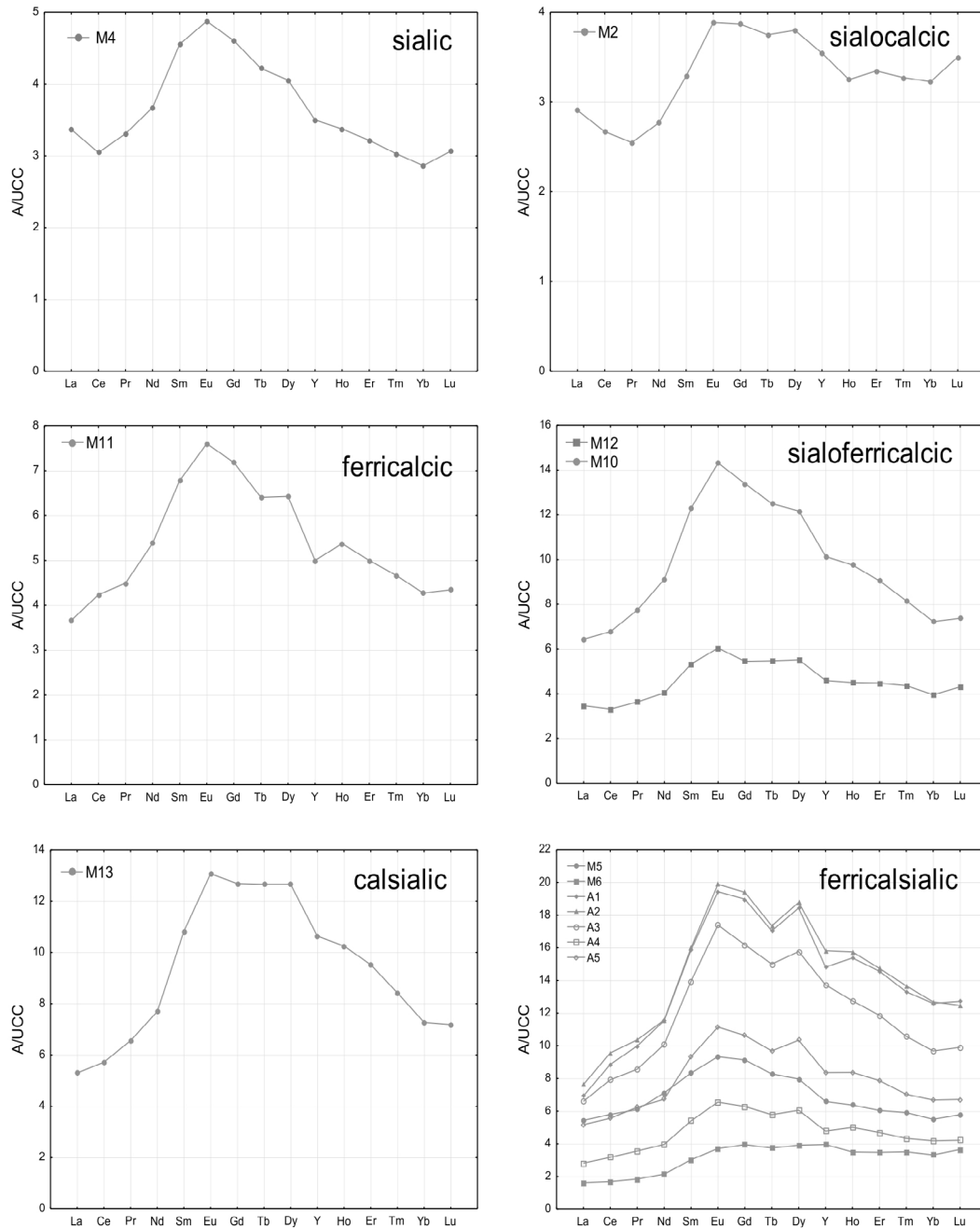


Fig. 3. Distribution patterns of REY in HTA samples (A) normalized by the Upper Continental Crust (UCC) (Taylor and McLennan 1985)

Rys. 3. Rozkład zawartości REY w próbkach HTA (A) znormalizowany do ich zawartości w górnej skorupie kontynentalnej (UCC)

Conclusions

The studies have shown that the analyzed HTA samples obtained from coals from the Ruda bed seams differed in chemical composition despite the fact that these coals were characterized by a similar coal rank.

In accordance with the chemical classification of HTA, the analyzed HTA samples were classified as belonging to the following types: *sialic*, *sialocalcic*, *sialoferricalcic*, *calsialic*, *fericalcic*, *ferisialic*.

The studies have shown that the REY content in the analyzed samples of HTA was characterized by high variability ($V = 49\%$) and ranged from 380.80 ppm to 1886.50 ppm. Whereas the average REY content in the ashes analyzed was 1038.67 ppm and it was 2.5 times higher than the world average (404 ppm).

Among rare earth elements, the light elements (LREY) had the highest share (above 70%) in the total rare earth elements content. Heavy elements (HREY) had the lowest share (ca. 4%). The content of critical rare earth elements in the ash samples was characterized by high variability ($V = 52\%$) between 170.07 ppm and 777.20 ppm.

It was found that the content of the individual rare earth elements in the examined HTA samples was up to almost 20 times higher than in UCC. The distribution patterns plotted for all the samples within their entire range were positioned above the reference level. For almost all of the samples these curves were of the M-H type. Only in the case of one sample (M4) the distribution had a shape characteristic of the M-L type.

The value of the outlook coefficient C_{outl} for the examined HTA samples varied between 0.97 and 1.41, and its variability was low ($V = 12\%$). The values of the outlook coefficient allowed all of the analyzed ash samples to be regarded as promising REY raw materials.

Considering the obtained values of C_{outl} and the fact that in 7 out of 13 analyzed ash samples the REY content was higher than 800 ppm, REY recovery from these ashes may prove economic.

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THE HIGH TEMPERATURE ASHES (HTA) FROM BITUMINOUS COAL COMBUSTION AS A POTENTIAL RESOURCE OF RARE EARTH ELEMENTS

Abstract

Potential sources of rare earth elements are sought after in the world by many researchers. Coal ash obtained at high temperatures (HTA) is considered among these sources.

The aim of the study was an evaluation of the suitability of the high temperature ash (HTA) formed during the combustion of bituminous coal from the Ruda beds of the Pniówek coal mine as a potential resource of REY. The 13 samples of HTA obtained from the combustion of metabituminous (B) coal were analyzed.

The analyses showed that the examined HTA samples varied in their chemical composition. In accordance with the chemical classification of HTA, the analyzed ash samples were classified as belonging to the following types: *sialic*, *sialocalcic*, *sialoferricalcic*, *calsialic*, *fericalcialsialic*, *ferisialic*.

The research has shown that the rare earth elements content (REY) in examined HTA samples are characterized by high variability. The average REY content in the analyzed ashes was 2.5 times higher than the world average (404 ppm).

Among rare earth elements, the light elements (LREY) were the most abundant. Heavy elements (HREY) had the lowest share.

A comparison of the content of the individual rare earth elements in HTA samples and in UCC showed that it was almost 20 times higher than in UCC.

The distribution patterns of REY plotted for all samples within their entire range were positioned above the reference level and these curves were of the M-H or M-L type.

The data presented indicate, that the analyzed ash samples should be regarded as promising REY raw materials. Considering the fact that in 7 out of 13 analyzed ash samples the REY content was higher than 800 ppm, REY recovery from these ashes may prove to be economic.

Key words: rare earth elements and yttrium (REY), high-temperature ash (HTA), critical raw materials

WYSOKOTEMPERATUROWE POPIOŁY (HTA) ZE SPALANIA WĘGLA KAMIENNEGO JAKO POTENCJALNE ŹRÓDŁO PIERWIĄTKÓW ZIEM RZADKICH

Streszczenie

Potencjalne źródła pierwiastków ziem rzadkich są poszukiwane w świecie przez wielu badaczy. Wśród tych źródeł rozpatrywany jest popiół z węgla uzyskiwany w wysokich temperaturach (HTA). Celem artykułu była ocena wysokotemperaturowych popiołów (HTA) pochodzących ze spalania węgla kamiennego warstw rudzkich z KWK Pniówek, pod kątem ich wykorzystania jako alternatywnego źródła REY. Badaniom poddano 13 próbek popiołów HTA uzyskanych ze spalania węgla o średnim stopniu uwęglenia B.

Zgodnie z klasyfikacją chemiczną popiołów HTA, badane próbki popiołów zaklasyfikowano do następujących typów: krzemianowo-glinowych, krzemianowo-glinowo-wapniowych, krzemianowo-glinowo-żelazowo-wapniowych, wapniowo-krzemianowo-glinowych, żelazowo-wapniowokrzemianowo-glinowych, żelazowo-krzemianowo-glinowych.

Badania wykazały, że zawartość pierwiastków ziem rzadkich REY w badanych próbkach popiołów HTA charakteryzuje się dużą zmiennością. Średni udział REY w analizowanych popiołach jest 2,5 razy większy od średniej dla złóż światowych (404 ppm). Wśród pierwiastków ziem rzadkich największy udział mają pierwiastki lekkie LREY. Najmniejszym udziałem charakteryzują się pierwiastki ciężkie HREY.

Porównanie zawartości poszczególnych pierwiastków ziem rzadkich w próbkach popiołów HTA i w UCC wykazało, że jest ona prawie do 20 razy większa niż w UCC.

Krzywe normalizacyjne wyznaczone dla wszystkich próbek w całym swoim zakresie znajdują się powyżej poziomu odniesienia i są to krzywe typu M-H lub typu M-L.

Przedstawione dane wskazują, że analizowane próbki popiołów należy uznać za obiecujące surowce REY. Uwzględniając fakt, że w 7 z 13 analizowanych próbek popiołu zawartość REY jest wyższa niż 800 ppm, odzysk REY z tych popiołów może okazać się ekonomiczny.

Słowa kluczowe: pierwiastki ziem rzadkich i itr (REY),
wysokotemperaturowy popiół węglowy (HTA), surowce krytyczne