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CHANGES IN THE CONCENTRATION OF SOME RARE EARTH ELEMENTS IN COAL WASTE

ZMIANY KONCENTRACJI WYBRANYCH PIERWIASTKÓW ZIEM RZADKICH (REEs) W ODPADACH WĘGLOWYCH

Coal waste is formed during coal mining and processing operations. That waste comprises mainly sedimentary rocks that occur in roofs and floors of underground workings and in partings in coal seams. It contains numerous trace elements, including rare earth elements (REEs). Hypergenic processes that take place in coal waste piles may lead to endogenous fires. Thermal transformations of waste have an effect on changes in its phase and chemical composition, including the concentration of trace elements.

The paper presents changes in the content of selected rare earth elements (Sc, Y, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu) in wastes of varying degree of thermal transformation. The results of REE content determination in lump samples were subjected to statistical analysis and coefficients of correlation between the studied rare earth elements and the main chemical constituents were determined.

The primary carriers of REEs in coal waste are clay minerals. Phase transformations that take place at high temperatures (including dehydroxylation of clay minerals and formation of minerals characteristic of contact metamorphism) cause changes in the concentration of rare earth elements.

Keywords: Rare Earth Elements (REEs), post mining waste, coal wastes, thermal transformations

Odpady powęglowe powstają w wyniku eksploatacji oraz przeróbki węgla kamiennego. Są to głównie skały osadowe występujące w stropach i spągach oraz przerostach pokładów węgla. Odpady te zawierają liczne pierwiastki śladowe, w tym pierwiastki ziem rzadkich (REEs). Procesy hipergeniczne zachodzące na zwałowiskach odpadów powęglowych mogą prowadzić do powstawania pożarów endogenicznych. Przeobrażenia termiczne odpadów wpływają na zmiany ich składu fazowego i chemicznego, w tym koncentracji pierwiastków śladowych.

W artykule przedstawiono zmiany zawartości wybranych pierwiastków ziem rzadkich (Sc, Y, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu) w odpadach o różnym stopniu termicznego przeobrażenia. Wyniki oznaczeń zawartości REEs w próbkach kawałkowych poddano analizie statystycznej i wyznaczono współczynniki korelacji pomiędzy badanymi pierwiastkami ziem rzadkich a głównymi składnikami chemicznymi.

Pierwotnym nośnikiem REEs w odpadach powęglowych są minerały ilaste. Przeobrażenia fazowe zachodzące pod wpływem wysokiej temperatury (w tym dehydroksylacja minerałów ilastych i tworzenia

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się minerałów charakterystycznych dla metamorfizmu kontaktowego) powodują zmiany koncentracji pierwiastków ziem rzadkich.

Słowa kluczowe: pierwiastki ziem rzadkich (REEs), odpady górnicze, odpady powęglowe, przeobrażenia termiczne

1. Introduction

Due to their properties, rare earth elements play an important role in advanced technologies, and have therefore become a strategic resource (Castor & Hedrick, 2006; Kato et al., 2011; Alonso et al., 2012; Mayfield & Lewis, 2013; Haque et al., 2014). Growth in demand for REEs, as well as reduced supplies from China, the main producer, makes the search for new sources of these materials a priority.

There is an intense research conducted across the world on the occurrence of rare earth elements not only in ores, but also in coals and rocks that accompany coal (Brik & White, 1991; Ekskenazy, 1999; Ward et al., 1999; Xu et al., 2004; Zheng et al., 2007; Ketris & Yudovich, 2009; Dai et al., 2012; Yang et al., 2012; Całus-Moszko & Białecka, 2013; Adamczyk et al., 2015). The purpose of these studies is to find REE sources that would constitute an alternative for natural deposits. One of the important issues that determine the feasibility of obtaining these elements is how these elements are bound in minerals.

The coal industry generates substantial amounts of mineral waste, both during mining as well as during processing. In lithological terms, claystones are the prevailing constituents of coal waste. Due to the sorption capacity of clay minerals, such waste can be a carrier of a number of trace elements, including rare earth elements (Hanak et al., 2011; Całus-Moszko & Białecka, 2013; Nowak & Kokowska-Pawłowska, 2013; Kokowska-Pawłowska et al., 2013).

Hypergenic processes that take place in coal waste piles may lead to endogenous fires. These fires are particularly frequent in old, uncompacted piles, where no fire prevention measures are applied, as well as in coal outcrops and in open pit mines (Mółka, 1999; Trenczek, 2008; Panigrahi et al., 2013).

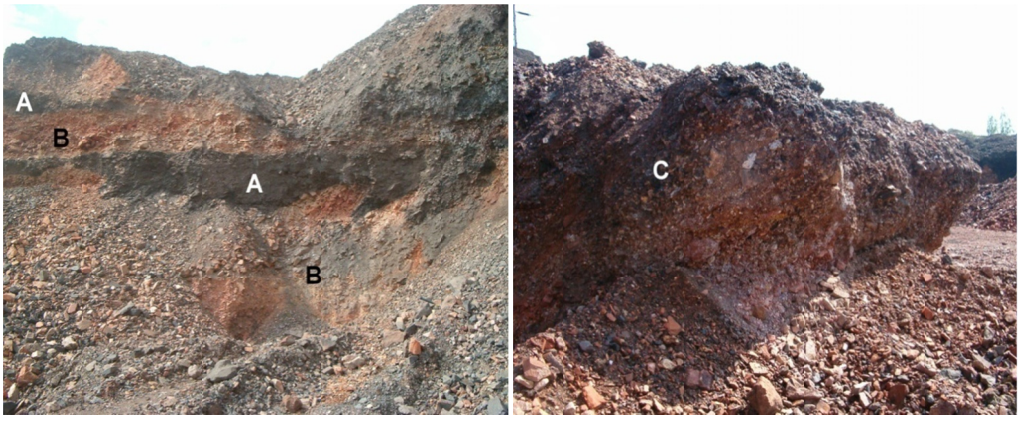

Fig. 1. A coal waste pile. A – thermally untransformed zones, B – moderately thermally transformed zones, C – intensively thermally transformed zones

Organic matter (coal) is the most susceptible to transformation at elevated temperatures (Hanak & Nowak, 2010). However, during fires of coal waste piles the temperatures may exceed a thousand degrees Celsius. At these temperatures the thermal processes in the waste pile affect not only the organic matter, but also the mineral matter. This leads to substantial changes in mineral composition, petrographic character (structure and texture) and chemical composition, including the content of trace elements (Nowak, 2011, 2013, 2014).

The studies conducted by the authors enabled to distinguish three zones of varying degree of thermal transformation of waste within the thermally active waste piles. These comprise thermally untransformed zones, moderately thermally transformed zones and intensively thermally transformed zones (Fig. 1) (Jonczy et al., 2012; Nowak, 2014).

The paper presents the results of determination of selected rare earth elements in wastes differing in the extent of thermal transformation.

2. Waste pile characteristics and sampling

The samples used for the study were taken from a now non-existent Waste Pile No. 4 at the Nowy Wirek Coal Mine. That waste pile was located in the region of Upper Silesia, city of Ruda Śląska, near its administrative border with the city of Chorzów (Fig. 2).

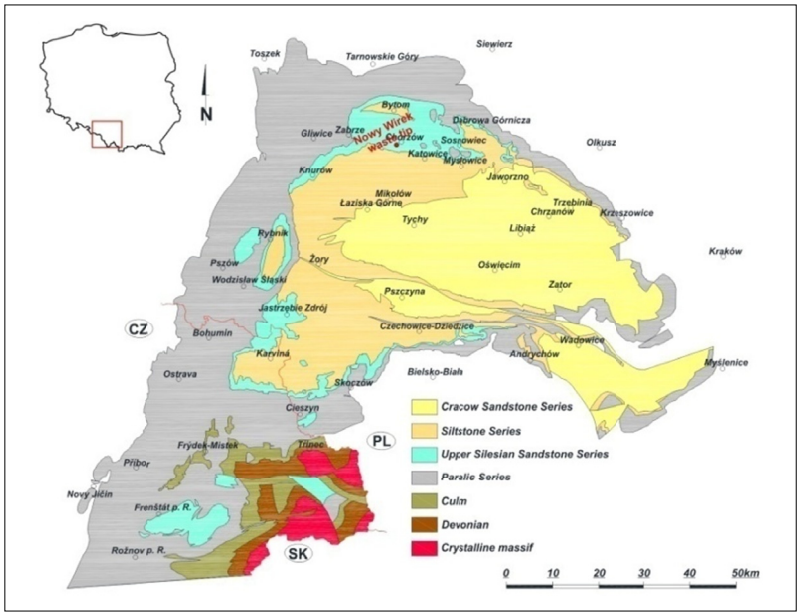

Fig. 2. Location of the waste pile from which samples were taken.

Waste was dumped there during the years 1973-1986. The coal waste deposited in the piles was derived from the mining of coal seams of the Namurian B and Namurian C series. The first endogenous fires were observed in 1976, afterwards they occurred with a varying intensity until

the pile was reclaimed in 1986, or even later. These fires led to the formation of zones within the pile, differing in the degree of thermal transformation of the waste. At the beginning of the 21st century excavations of the material deposited in the pile were started to produce construction aggregate. This enabled taking samples from the various zones of the pile (Założenia..., 1980).

33 lump samples of rocks of various petrographic character and various degree of thermal transformation were taken. These included: 10 samples from the thermally untransformed zone, 16 samples from the moderately thermally transformed zone, and 7 samples from the intensively thermally transformed zone.

Channel samples of the coal waste were also taken, weighing 10 to 15 kg each, and representing the various zones of the waste pile. Samples were taken in 4 sections. 5 samples were taken from the thermally untransformed zones, 6 samples from the moderately thermally transformed zones, and 3 samples from the intensively thermally transformed zones.

3. Research methodology

A macroscopic description of the lump samples was made, microscopic studies were carried out and phase detection was conducted using the X-ray diffraction method. The channel samples were also studied (Nowak, 2009).

Chemical composition of the samples was determined (SiO_2, Al_2O_3, Fe_2O_3, Na_2O, K_2O, TiO_2, P_2O_5, CaO, MgO, MnO). These tests were conducted using inductively coupled plasma mass spectrometry (ICP-MS). The content of some rare earth elements (Sc, Y, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu) was also determined using Instrumental Neutron Activation Analysis (INAA). Loss on ignition (LOI) was measured gravimetrically. These tests were carried out at Activation Laboratories Ltd. (ACTLABS) in Canada.

The results of REE content determination in lump samples were subjected to statistical analysis and coefficients of correlation (r) between the studied rare earth elements and the main chemical constituents were determined. Correlation analysis was performed using the Pearson correlation coefficient (r) and applying the limiting confidence coefficient of 0.05 in order to prove the significance of correlation (Cohen, 1988; Buda & Jarynowski, 2010).

The lump samples were grouped into 3 populations: samples from the thermally untransformed zone, samples from the moderately thermally transformed zone and samples from the intensively thermally transformed zone. The channel samples, due to small population size, were not analysed statistically.

4. Results

The results of the determination of selected rare earth elements are given in Tables 1 and 2. Correlations between REEs and selected chemical constituents are given in Tables 3 to 5 and in graphs (Fig. 3).

Scandium (Sc) may in minerals replace, by diadochy, iron, magnesium and, to a lesser extent, aluminium, manganese, other lanthanides, zirconium, uranium, and thorium. In sedimentary rocks it occurs mainly in clay minerals. High scandium concentrations (up to 600 ppm) is also observed in the ashes of some hard coals. As a result of hypergenic processes it forms accumulations with phosphorus (Polański & Smulikowski, 1969).

TABLE 1

Content of selected rare earth elements in lump samples of coal waste of varying degree of thermal transformation [ppm]

Element	Examples of content in the samples							Average	Min	Max	Standard deviation
Samples from the thermally untransformed zone											
Sc	3.8	6.4	11.4	18	19.5	11.6	17.5	**14.4**	**3.8**	**20.7**	**5.8**
Y	31	32	42	31	41	256	35	**34.0**	**25.0**	**45.0**	**6.8**
La	13.2	20.4	47.5	33.3	42.5	24.3	42.6	**34.7**	**13.2**	**55.0**	**12.8**
Ce	25	43	81	67	88	42	81	**67.3**	**25.0**	**113.0**	**25.8**
Nd	10	16	25	27	38	25	36	**27.1**	**10.0**	**45.0**	**10.4**
Sm	1.6	2.5	6.6	5.1	6.4	4	5.9	**4.9**	**1.6**	**7.8**	**1.9**
Eu	0.5	0.6	1.7	1.3	1.6	1.0	1.5	**1.3**	**0.5**	**2.1**	**0.5**
Tb	0	0	0	0.8	0.8	0.6	0	**0.4**	**0.0**	**1.3**	**0.5**
Yb	1.7	2.3	3.1	3.0	4.2	1.9	3.8	**3.0**	**1.7**	**4.6**	**1.0**
Lu	0.25	0.28	0.47	0.49	0.51	0.28	0.45	**0.4**	**0.3**	**0.6**	**0.1**
Sum REEs	87	123	219	187	243	136	224	**187.5**	**87.1**	**295.1**	**61.8**
Samples from the moderately thermally transformed zone											
Sc	20.6	7.2	9.0	16.4	22.0	19.6	7.1	**15.8**	**7.1**	**22.0**	**5.3**
Y	50	31	39	31	35	45	23	**36.9**	**20.0**	58.0	9.7
La	31.1	15.4	44.3	32.8	33.0	37.8	18.7	**33.4**	**15.4**	**48.7**	**9.3**
Ce	59	29	82	63	60	73	38	**62.7**	**29.0**	**91.0**	**17.1**
Nd	27	10	32	27	25	29	16	**25.7**	**10.0**	**34.0**	**6.8**
Sm	4.7	2.0	5.7	4.6	4.6	5.3	2.3	**4.6**	**2.0**	**6.7**	**1.3**
Eu	1.4	0.7	1.4	1.0	1.1	1.4	0.7	**1.1**	**0.7**	**1.5**	**0.3**
Tb	0.8	0	0.6	0.6	0.6	1.2	0.5	**0.6**	**0.0**	**1.2**	**0.3**
Yb	3.1	1.6	3.0	2.5	2.8	3.1	2.1	**2.9**	**1.5**	**4.2**	**0.7**
Lu	0.50	0.26	0.46	0.36	0.41	0.42	0.28	**0.4**	**0.2**	**0.6**	**0.1**
Sum REEs	198	97	217	179	184	216	109	**184.0**	**96.1**	**264.0**	**46.1**
Samples from the intensively thermally transformed zone											
Sc	12.3	26	19.7	17.0	10.5	18.1	18.3	**17.4**	**10.5**	**26.0**	**5.1**
Y	71	58	50	37	67	50	56	**55.6**	**37.0**	**71.0**	**11.4**
La	39.7	42.0	45.2	32.6	46.5	46.3	28.3	**40.1**	**28.3**	**46.5**	**7.1**
Ce	65	67	73	48	75	91	55	**67.7**	**48.0**	**91.0**	**14.0**
Nd	34	34	38	23	41	35	25	**32.9**	**23.0**	**41.0**	**6.6**
Sm	5.8	6.4	6.7	3.9	6.4	6.3	4.8	**5.8**	**3.9**	**6.7**	**1.0**
Eu	1.2	1.4	1.6	0.8	1.2	1.6	1.4	**1.3**	**0.8**	**1.6**	**0.3**
Tb	0.6	0.9	1.0	0	0.7	0	1.1	**0.6**	**0.0**	**1.1**	**0.5**
Yb	3.5	4.6	3.8	2.8	3.5	3.9	4.0	**3.7**	**2.8**	**4.6**	**0.6**
Lu	0.50	0.07	0.57	0.41	0.52	0.51	0.53	**0.5**	**0.4**	**0.7**	**0.1**
Sum REEs	234	241	240	165	252	253	194	**225.6**	**165.5**	**252.7**	**33.0**

In the coal waste studied scandium concentration ranged from 4 to 26 ppm and it was quite varied (Table 1). Scandium content in lump samples from thermally untransformed zones showed

highly negative correlation with SiO_2 (–0.95), and at the same time positive correlation with Al_2O_3 (0.73), TiO_2 (0.73) and with loss on ignition (LOI) (0.83) (Table 3). Similar relationships were observed between scandium content in lump samples from the moderately thermally transformed zone (Table 4) and SiO_2 (–0.97) on the one hand and Al_2O_3 (0.85) and TiO_2 (0.87) on the other. There was no correlation between that element and loss on ignition (–0.17). In samples from the intensively thermally transformed zone the highly negative correlation with SiO_2 (–0.83) was retained, whereas the other relationships disappeared or were very low (Table 5).

Scandium content in averaged samples was found to be less differentiated than in lump samples. A slight increase in scandium content in samples from the moderately and intensively thermally transformed zones was observed in comparison to samples from the thermally untransformed zones (Table 2).

The content of yttrium (Y) in lump samples is distinctly differentiated. In samples from the thermally untransformed zones it varied from 25 to 45 ppm (34 ppm on the average), in samples from the moderately thermally transformed zones it varied from 20 to 58 ppm (37 ppm on the average) and from 37 to 71 ppm in sinters (56 ppm on the average) (Table 1).

Yttrium content in lump samples from the thermally untransformed zones showed no correlation with any of the main chemical constituents (Table 3). Correlation between yttrium content and P_2O_5 content (0.65) was found in samples from the moderately thermally transformed zones (Table 4). Such relationship was also observed in samples from the intensively thermally transformed zone. Additionally, in those samples there was also a negative correlation with Al_2O_3 (–0.78) (Table 5).

The content of lanthanum (La) in lump samples varied from 13 to 55 ppm (Table 1) and, according to literature data, it fell within the range of content of this element in sedimentary rocks (Polański, 1988). Similar content of this element was found in channel samples (Table 2).

TABLE 2

Content of selected rare earth elements in channel samples of coal waste [ppm]

Component / Sample	Sc	Y	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
	ppm									
B3/1	14.9	29	34.1	64	29	4.5	1.1	< 0.5	3.0	0.43
B3/2	14.3	24	34.9	61	23	4.5	1.3	< 0.5	2.2	0.35
B3/3	22.5	42	50.7	102	39	6.9	1.7	1.1	4.8	0.64
B3/4	15.0	29	35.6	72	30	5.0	1.3	0.9	3.2	0.40
B4/1	16.8	29	35.1	67	21	4.8	1.3	< 0.5	3.2	0.43
B4/2	20.2	33	45.2	88	40	6.4	1.8	0.7	4.0	0.55
B4/3	18.0	30	40.3	77	33	5.4	1.3	0.8	3.4	0.41
B6/1	19.5	51	52.2	105	43	7.3	1.7	0.9	4.6	0.64
B6/2	20.9	45	47.1	95	39	6.7	1.8	1.1	3.7	0.53
B6/3	18.4	40	44	87	34	6.1	1.5	<0.5	3.4	0.47
B6/4	16.5	35	39.2	73	33	5.3	1.4	0.8	3.8	0.50
B8/1	19.3	29	37.9	74	32	5.2	1.3	<0.5	3.4	0.44
B8/2	15.3	30	36.2	72	25	5.0	1.4	<0.5	3.2	0.43
B8/3	19.9	36	41.4	85	32	5.9	1.5	0.9	4.1	0.50

■ – thermally untransformed zone, □ – moderately thermally transformed zone, ■ – intensively thermally transformed the zone

Based on the results obtained, no distinct trends were observed in lanthanum concentration changes caused by high temperatures, although the channel samples of sinters showed slightly higher content of lanthanum than thermally untransformed samples.

Lanthanum content in lump samples from the thermally untransformed zones showed no high correlation with any of the main chemical constituents (Table 3). A negative correlation between lanthanum content and SiO_2 content (–0.60) and positive correlation with Al_2O_3 (0.65) was found in samples from the moderately thermally transformed zones (Table 4). These correlations disappeared in lump samples from the intensively thermally transformed zones, whereas there have appeared correlations with Na_2O (0.79) and K_2O (0.82) (Table 5).

TABLE 3

Correlations between chemical composition and REE content in samples from the thermally untransformed zone

	Sc	**Y**	**La**	**Ce**	**Nd**	**Sm**	**Eu**	**Tb**	**Yb**	**Lu**
SiO_2	**–0,95**	–0,08	–0,59	**–0,64**	**–0,75**	**–0,66**	**–0,62**	**–0,62**	**–0,62**	**–0,69**
Al_2O_3	**0,73**	–0,12	0,50	0,49	0,53	0,52	0,50	0,38	0,35	0,46
Fe_2O_3	0,65	0,14	0,35	0,39	0,50	0,44	0,38	0,37	0,48	0,52
MnO	0,33	0,36	0,21	0,28	0,36	0,28	0,23	0,29	0,43	0,33
MgO	0,71	0,20	0,40	0,47	0,62	0,50	0,45	0,48	0,57	0,55
CaO	0,24	0,34	0,14	0,22	0,31	0,20	0,16	0,23	0,38	0,24
Na_2O	–0,27	–0,55	–0,53	–0,55	–0,25	–0,42	–0,46	–0,16	–0,46	–0,49
K_2O	0,55	–0,28	0,33	0,30	0,35	0,35	0,30	0,11	0,19	0,23
TiO_2	**0,73**	–0,08	0,56	0,51	0,59	0,59	0,56	0,34	0,38	0,48
P_2O_5	0,41	–0,26	0,12	0,09	0,19	0,22	0,18	0,19	0,05	0,25
S	0,57	0,13	0,29	0,36	0,43	0,33	0,27	0,32	0,44	0,42
LOI	**0,83**	0,19	0,47	**0,60**	**0,69**	0,52	0,50	**0,76**	**0,63**	**0,66**

Distinguished correlation with a confidence level of above 0.05

TABLE 4

Correlations between chemical composition and REE content in samples from the moderately thermally transformed zone

	Sc	**Y**	**La**	**Ce**	**Nd**	**Sm**	**Eu**	**Tb**	**Yb**	**Lu**
SiO_2	**–0,97**	–0,44	–0,60	**–0,57**	**–0,68**	**–0,66**	**–0,59**	**–0,71**	**–0,65**	**–0,65**
Al_2O_3	**0,85**	0,28	0,65	**0,58**	**0,67**	**0,57**	0,42	**0,54**	**0,56**	**0,65**
Fe_2O_3	0,49	0,43	0,10	0,13	0,19	0,27	0,41	0,41	0,26	0,20
MnO	0,25	0,43	0,05	0,09	0,11	0,20	0,32	0,29	0,17	0,11
MgO	0,57	0,25	0,11	0,11	0,18	0,25	0,41	0,41	0,22	0,19
CaO	0,11	0,31	–0,24	–0,22	–0,17	–0,08	0,14	0,07	–0,05	–0,06
Na_2O	0,06	0,18	0,08	0,10	–0,01	0,14	0,01	0,05	0,15	0,05
K_2O	0,65	0,43	0,51	0,48	0,46	**0,53**	0,44	**0,60**	**0,71**	**0,62**
TiO_2	**0,87**	0,56	**0,77**	0,74	0,79	0,76	0,60	0,73	0,72	0,73
P_2O_5	0,18	**0,65**	0,39	0,45	0,35	**0,54**	**0,51**	0,48	**0,50**	0,35
S	0,10	0,07	0,00	–0,02	0,11	0,06	–0,05	0,26	0,28	0,10
LOI	–0,17	–0,47	–0,15	–0,17	–0,11	–0,15	–0,25	–0,17	–0,21	–0,25

Distinguished correlation with a confidence level of above 0.05

The main cerium (Ce) containing mineral is monazite. This mineral, being resistant to weathering, is carried over to sedimentary rocks forming there the main source of cerium. Apart from cerium there are other rare earth elements (La, Th, Nd, Y) in monazite (Polański, 1988).

Cerium concentration in samples of rock and of their transformation products varied from 25 to 113 ppm, and in channel samples it varied from 61 to 105 ppm (Tables 1 and 2). Cerium concentration was particularly differentiated in samples from the thermally untransformed zones, whereas samples from the moderately thermally transformed zones and from the intensively thermally transformed zones showed less differentiation in the content of this element. Cerium concentrations were lower than those determined in claystones from variegated formations at the Marcel Coal Mine (186-409 ppm) (Lipiarski & Muszyński, 2001). Interpretation of the results obtained is impeded because no determinations have been made so far of this element in rocks that accompany coal in the Upper Silesian Coal Basin. Cerium content in channel samples showed a growing tendency in burnt waste and in sinters. Average cerium content in channel samples from the thermally untransformed zones was 70 ppm, 81 ppm in samples from the moderately thermally transformed zones, and 96 ppm in samples from the intensively thermally transformed zones (Tables 1 and 2).

Cerium content in lump samples from thermally untransformed zones showed negative correlation with SiO_2 content (–0.64), and positive correlation with loss on ignition (LOI) (0.60) (Table 3). In samples from the moderately thermally transformed zones there was still a negative correlation with SiO_2 (–0.57), while correlation with loss on ignition (LOI) disappeared. In those samples there was also a correlation with Al_2O_3 (0.58) and with TiO_2 (0.74) (Table 4). In samples from the intensively thermally transformed zones there were correlations with Na_2O (0.66) and K_2O (0.57) (Table 5).

Concentration of neodymium (Nd) in the tested samples of coal waste varied from 10 to 45 ppm (Table 1). Neodymium content in samples from thermally untransformed zones showed negative correlation with SiO_2 content (–0.75), and positive correlation with loss on ignition (LOI) (0.69) (Table 3). In samples from the moderately thermally transformed zones correlation with

TABLE 5

Correlations between chemical composition and REE content in samples from the intensively thermally transformed zone

	Sc	Y	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
SiO_2	**–0.83**	0.28	0.29	0.02	0.32	–0.02	**–0.54**	–0.37	**–0.74**	**–0.57**
Al_2O_3	0.56	**–0.78**	0.06	–0.13	–0.25	–0.17	–0.17	–0.44	–0.16	0.00
Fe_2O_3	0.59	0.05	–0.42	–0.16	–0.28	–0.01	0.46	0.64	0.74	0.57
MnO	0.75	0.10	–0.22	–0.08	–0.13	0.15	0.42	0.60	**0.87**	**0.80**
MgO	0.46	–0.03	–0.17	0.22	–0.09	0.16	0.71	0.44	0.70	0.43
CaO	–0.10	0.10	–0.14	0.31	–0.05	0.01	0.43	0.10	0.30	–0.03
Na_2O	–0.57	0.61	**0.79**	**0.66**	**0.92**	**0.73**	0.29	0.12	0.00	0.07
K_2O	0.30	0.24	**0.82**	**0.57**	**0.71**	**0.75**	0.29	–0.03	0.43	0.63
TiO_2	0.21	–0.55	0.41	0.10	0.12	0.05	–0.27	–0.55	–0.33	–0.09
P_2O_5	0.08	**0.74**	0.26	0.21	0.56	**0.66**	0.56	**0.89**	0.66	0.71
S	0.33	0.01	–0.64	–0.30	–0.48	–0.28	0.25	0.49	0.47	0.24
LOI	0.18	–0.23	–0.01	0.48	–0.16	0.01	0.50	–0.35	0.28	–0.08

Distinguished correlation with a confidence level of above 0.05

loss on ignition (LOI) disappeared, while there was a negative correlation with SiO_2 (–0.68), and positive correlation with Al_2O3 (0.67) and TiO_2 (0.79) (Table 4). These correlations disappeared in samples from the intensively thermally transformed zones, whereas there have appeared high correlations between neodymium content and Na_2O (0.92) and K_2O (0.71) (Table 5).

Analysis of neodymium content in channel samples has shown that it was usually higher in waste from the intensively thermally transformed zone (39 ppm on the average) and from the moderately thermally transformed zone (34 ppm on the average) than in waste from thermally untransformed zones (26 ppm on the average) (Table 2).

The content of samarium (Sm) in lump samples varied from 1.6 to 7.8 ppm and it was highly differentiated. Similar observations were made in the case of channel samples (Tables 1 and 2). There was only a slight increasing tendency in concentration in samples from the intensively thermally transformed zones.

In lump samples from the thermally untransformed zones there was only a negative correlation with SiO_2 (–0.66) (Table 3). Moreover, a positive correlation with Al_2O_3 (0.57) and with P_2O_5 (0.54), K_2O (0.53), TiO_2 (0.76) was found in samples from the moderately thermally transformed zones (Table 4). In samples from the intensively thermally transformed zones the strongest correlations were observed for Na_2O (0.73), K_2O (0.75) and P_2O_5 (0.66) (Table 5).

The content of europium (Eu) in lump samples varied from 0.5 to 2.1 ppm and it was differentiated (Table 1). Similarly, in channel samples there was also no distinct tendency to change with increasing degree of thermal transformation (Table 2).

No distinct correlation between europium concentration and the main chemical constituents was observed in lump samples from thermally untransformed zones (Table 3). In samples from the moderately thermally transformed zones a negative correlation occurred between europium content and SiO_2 content (–0.59), and a positive correlation occurred between europium content and TiO_2 content (0.60) and P_2O_5 content (0.51) (Table 4). These correlations disappeared in samples from the intensively thermally transformed zones (Table 5).

In eight lump samples the concentration of terbium (Tb) has not exceeded the detection limit (0.5 ppm), in other samples it reached 1.3 ppm. No distinct effect of the degree of thermal transformation on terbium content in waste samples has been observed (Tables 1 and 2).

Terbium content in lump samples from thermally untransformed zones showed correlation with loss on ignition (LOI) (0.76) (Table 3). This correlation disappeared in samples from the moderately thermally transformed zones. On the other hand, positive correlations have appeared between the content of this element and Al_2O_3 (0.54), K_2O (0.60), TiO_2 (0.73), and a negative correlation with SiO_2 (–0.71) (Table 4). In samples from the intensively thermally transformed zones there was only a strong correlation with P_2O_5 (0.89) (Table 5).

Ytterbium (Yb) content varied from 1.5 to 4.6 ppm in lump samples and from 2.2 to 4.8 in channel samples (Tables 1 and 2). The lowest ytterbium concentrations were found in channel samples from the thermally untransformed zones.

In the case of lump samples from thermally untransformed zones a correlation between ytterbium content and loss on ignition (LOI) (0.63) was observed (Table 3). This correlation disappeared in samples from the moderately thermally transformed zone, while there have appeared correlations with the content of Al_2O_3 (0.56), K_2O (0.71), TiO_2 (0.72) and P_2O_5 (0.50).

A negative correlation with SiO_2 (-0.65) was also found (Table 4). In samples from the intensively thermally transformed zones there was only a high correlation between ytterbium content and MnO (0.87) (Table 5).

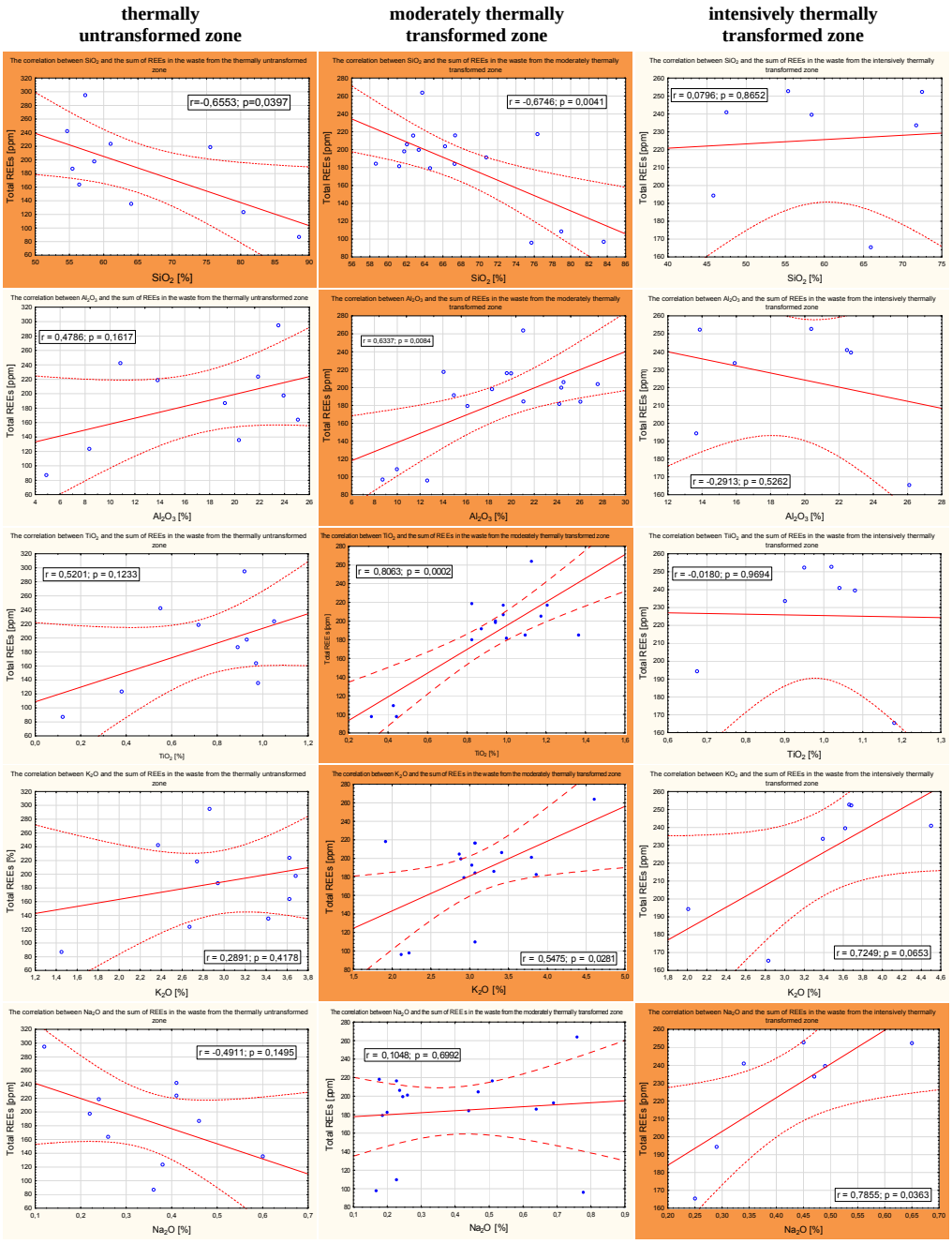

Fig. 3. Comparison of correlations between total REE content and concentration of selected chemical constituents in waste from zones of various degree of thermal transformation. Distinguished charts with a significant correlation ($p < 0,05$)

The content of lutetium (Lu) in lump samples varied from 0.2 to 0.70 ppm (Table 1). In channel samples that content varied from 0.35 to 0.64 ppm. (Table 2). A slight increase in lutetium content in samples from the moderately and intensively thermally transformed zones was observed in comparison to samples from the thermally untransformed zones. Lutetium content in lump samples from thermally untransformed zones showed negative correlation with SiO_2 content (–0.69), and correlation with loss on ignition (LOI) (0.66) (Table 3). In samples from the moderately thermally transformed zones a negative correlation still occurred between lutetium content and SiO_2 content (–0.65), and a correlation occurred with Al_2O_3 (0.65), K_2O (0.62) and TiO_2 (0.73) content (Table 4). In lump samples from the intensively thermally transformed zones there was only a correlation between lutetium content and MnO (0.80) (Table 5).

The effect of the degree of thermal transformation of waste on the total content of rare earth elements (REEs) in the tested lump samples was also noted (Table 1). Also the correlations between the total content of rare earth elements and the main chemical constituents varied with the degree of thermal transformation of the waste (Fig. 3).

SiO_2 showed significant negative correlation with total REE content in the thermally untransformed zone (–0.65 at $p = 0.04$) and in the moderately thermally transformed zone (–0.67 at $p = 0.004$). This correlation disappeared in samples from the intensively thermally transformed zone (Fig. 3).

Al_2O_3, TiO_2 and K_2O showed a significant correlation with total REE content only in the case of samples from the moderately thermally transformed zone. For Al_2O_3 the correlation was 0.63 at $p = 0.008$, for TiO_2 it was 0.81 at $p = 0.0002$, and for K_2O it was 0.55 at $p = 0.03$ (Fig 3).

Only samples from the intensively thermally transformed zone showed a significant correlation between Na_2O and total REE content (0.78 at $p = 0.04$) (Fig. 3).

5. Summary and conclusions

The content of rare earth elements in coal waste changes with the degree of thermal transformation. Burning of organic matter and dehydroxylation of clay minerals leads to weight loss, which causes a relative increase in the content of the other constituents, including REEs.

The primary carriers of REEs in coal waste are clay minerals. This is evidenced by the frequently observed negative correlation between REE content and SiO_2 and positive correlation with LOI and Al_2O_3 (Fig. 3). High content of quartz, the main SiO_2 carrier, affects the content of clay minerals and of REEs associated therewith.

Waste from the moderately thermally transformed zone has undergone burning out of organic matter, dehydration, dehydroxylation and decomposition of carbonate minerals (Nowak, 2014). The effect was the disappearance of correlation with LOI with a more distinct correlation with Al_2O_3, K_2O, TiO_2 (Fig. 3). Similar relationships were observed in the case of thermally untransformed rocks rich in clay minerals (Çimen et al., 2013). In the case of yttrium, samarium, europium and ytterbium a correlation with P_2O_5 was also found. In nature REEs are often associated with phosphate minerals, therefore this correlation may indicate the formation of new mineral phases that contain phosphorus and some REEs. To confirm this further detailed research is required.

Waste from the intensively thermally transformed zone has undergone partial or complete melting and partial homogenization of the melt. Correlations observed in waste from the thermally untransformed zone and from the moderately thermally transformed zone have disappeared in

waste from the intensively thermally transformed zone. On the other hand, correlations between total REE content and Na_2O and K_2O content were found (Fig. 3). This may indicate that REEs migrate to glaze, the important constituents of which are sodium (Na) and potassium (K).

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