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RARE EARTH ELEMENTS OF ORZESKIE BEDS OF SOUTH-WEST PART UPPER SILESIAN COAL BASIN (POLAND)

PIERWIASTKI ZIEM RZADKICH Z POKŁADÓW WĘGLA WARSTW ORZESKICH POŁUDNIOWO-ZACHODNIEJ CZĘŚCI GZW (POLSKA)

The subject of the research concerned the coal samples from 360/1, 361 and 362/1 seams of the Orzesze beds in the "Pniówek" coal mine. The obtained samples were characterized by low ash content – 2.22-6.27% of the mass. The chemical composition of the ash indicates the presence of aluminosilicate minerals in the analyzed coal samples – most likely clay minerals, the presence of which has been confirmed in microscopic tests of the petrographic composition of channel samples of coal.

The content of rare earth elements (REE sum) in the ash of the tested coal seams ranged from 364 to 1429 ppm. Variation of the REE content has been observed within a single seam.

The fraction of REE indicates a relation with a mineral substance. No relation of the REE fraction and the presence of red beds has been found based on the tested samples.

The content of REE found in ash, normalized to chondrites, is characterized by LREE enrichment in relation to HREE. The Eu anomaly is most likely related to tuff and tonstein levels occurring in Orzesze beds, which accompany the coal seams in the Upper Silesian Coal Basin (i.a., south of the studied area).

The research has indicated that LREE in the tested samples are more related to the mineral substance, while HREE have a stronger affinity with organic substances.

Keywords: rare earth elements (REE), coal, Orzesze beds, USCB

Przedmiotem badań były próbki węgla z pokładów 360/1, 361 i 362/1 warstw orzeskich KWK Pniówek. Próbki te charakteryzują się niewielką zawartością popiołu 2,22-6,27% mas. Skład chemiczny popiołów wskazuje na obecność w analizowanych próbkach węgla minerałów z grupy glinokrzemianów najprawdopodobniej minerałów ilastych, których obecność była stwierdzona w badaniach mikroskopowych składu petrograficznego próbek bruzdowych węgla.

Zawartości pierwiastków ziem rzadkich (suma REE) w popiołach badanych pokładów węgla wahają się od 364 do 1429 ppm. Obserwuje się zróżnicowanie zawartości REE w obrębie jednego pokładu.

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158

Udział REE wykazuje związek z substancją mineralną. Nie stwierdzono związku udziału REE, w badanych próbkach, z obecnością utworów pstrych w stropie karbonu.

Zawartości REE oznaczone w popiołach, znormalizowane do chondrytów, charakteryzują się wzbogaceniem LREE wobec HREE. Anomalia Eu związana jest prawdopodobnie z występującymi w warstwach orzeskich (m.in. na północ od obszaru badań) Górnośląskiego Zagłębia Węglowego poziomami tufów i tonsteinów, które towarzyszą pokładom węgla.

Badania wykazały, że LREE w badanych próbkach związane są raczej z substancją mineralną, natomiast HREE posiadają silniejsze powinowactwo z substancją organiczną.

Słowa kluczowe: pierwiastki ziem rzadkich (REE), węgiel kamienny, warstwy orzeskie, GZW

1. Introduction

Rare earth elements (REE) include 17 elements, namely 15 lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) as well as Sc and Y. Two subgroups of lanthanides may be distinguished due to their properties: light rare earth elements (LREE) – La, Ce, Pr, Nd, Pm, Sm and Eu and heavy rare earth elements (HREE) – Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

In coal, REE constitute a group of elements bearing a special significance. Due to their chemical properties, REE are often studied as an entire group and rarely as single elements. REE in coal mostly occur in compounds with minerals (Lyons et al., 1989; Swaine, 1990). In hard coal, phosphate minerals, clay minerals and certain sulfides may act as potential REE carriers (Finkelman, 1982; Vassilev & Vasileva, 1996, 1997; Ward et al., 1999; Ward, 2002; Willet et al., 2000; Worrall & Pearson, 2001; Yang & Zhou, 2001; Zhang et al., 2002). However, other studies have indicated that REE in coal may form a compound both with the organic and non-organic substance (Finkelman, 1982; Palmer et al., 1990; Schatzel & Stewart, 2003; Fu et al., 2004). The research of rare earth elements in coal has also indicated that HREE are characterized by a higher affinity with the organic substance of coal that the LREE (Eskenazy, 1987a, b; Dai et al., 2008, 2012).

Rare earth elements in coal may provide information on the genesis and forming conditions of coal (Fu et al., 2004). The REE concentration in hard coal is variable and depends on its petrographic and mineral composition as well as the chemical properties (Smołka-Danielowska, 2010; Vassilev & Vassileva, 1996; Ward, 1999; Schatzel & Stewart, 2003; Pires & Querol, 2004; Zhang et al., 2004).

In the recent years, the research concerning the occurrence and concentration of trace elements, including REE, has been gaining importance (Diehl et al., 2004; Ren et al., 2004; Zhang et al., 2004; Dai et al., 2003; Finkelmann et al., 2002; Ward, 2002; Quick & Irons, 2002; Swaine, 2000; Karayigit et al., 2000; Spears & Zheng, 1999; Mastalerz & Padgett, 1999; Wang et al., 2006). The interest in these elements in coal is related mostly to ecological problems of coal mining, processing and combustion. Moreover, some of the rare earth elements are found on the Energy Critical Elements list, which includes elements that are strategic to the development of modern, advanced technologies in the EU. Due to the above, the aim of the research is to obtain the necessary data to develop and perfect the technology methods to recover some rare earth elements from coal and the side-products of its industrial use. In Poland, the research regarding trace elements (including REE) in coal has already been conducted for many years (Winnicki, 1973; Marczak, 1985; Parzentny, 1995; Różkowska & Ptak, 1995, 1995a; Smołka-Danielowska, 2010; Bielowicz, 2013; Nowak, 2013; Nowak et al., 2013).

Poland has rich deposits of hard coal, which constitutes one of the most important fuels for power production. Thus, it seems reasonable to take up systematical research aimed at the

specification of the content of these elements both in hard coal and in power-plant ash. The results of the study, besides scientific purposes, may result in future technologies for recovering REE from ash. The recovery of rare earth elements from ash from coal combustion could be an important trend in research as in the ash, as the concentration of rare earth elements is up to several dozen fold higher than the concentration in coal. This may constitute an important element of the Waste Framework Directive and clean coal technologies, allowing to protect natural resources and decrease the amount of wastes released to the environment.

The aim of this work was to determine the quality and quantity of rare earth elements occurring in KWK "Pniówek" seams of Orzesze beds, and to attempt to exhibit their relation with manifestations of thermal variations observed in coal seams in the area of red beds. No such detailed research has been conducted so far and the market demand as well as the number of possible applications in modern technologies is so large (Całusz Moszko & Białecka, 2012, 2013), that multidirectional research seems reasonable.

2. Geological setting of study area

The "Pniówek" coal mine is located in the southwestern part of the Upper Silesian Coal Basin, to the east of the Jastrzębie saddle, within the Zofiówka monocline (Fig. 1). The Pniówek coal mine is one of the five mining plants managed by the Jastrzębie Coal Company (JSW S.A.).

From the lithostratigraphic point of view, the overburden of the deposit in this part of the Upper Silesian Coal Basin consists of Quaternary formations (holocene, pleistocene), neogene (miocene). Their total thickness ranges from 220 m (in the northern part of the deposit) up to 1000 m (in the southern part of the deposit). The hard coal deposit is located in Upper Carboniferous formations (westphalian B i A and namurian C). The Carboniferous formations are represented by Orzesze beds, which are a part of the upper mudstone series, and Ruda beds, which are a part of the lower mudstone series (seams 401-406) and the lower part of the Upper Silesian sandstone series (seams 407-420) (Fig. 2).

The Orzesze beds run almost in the entire mining area of the "Pniówek" coal mine, except for the southern part, where their outcrops are located in the Carboniferous roof. The maximal thickness of the Orzesze beds is 600 m. In these strata, 19 coal seams have been documented, with numbers from 340/2 to 363. Claystones and mudstones prevail over sand formations in the lithological profile of the Orzesze beds. Coal seams most often occur among claystones and are characterized by high variability of thickness and quality. In the course of research, tuffs and tonsteins have been found to occur (i.a., north of the research area) in the area of the 325 seam (Staniszewski & Wagner, 1980; Łapot, 1992).

The Ruda beds occur at the entire mining area of the coal mine and their thickness, calculated starting from the 401 seam to the roof of the 501 seam, reaches the maximum of 700 m. The upper part of the Ruda beds has a form of claystone-mudstone facies in which seams 401 to 407 have been documented (the mudstone series). The lower part of the Ruda beds has a form of sandstone facies with intercalations of claystones and mudstones and many coal seams (the Upper Silesian sandstone series).

In the Jastrzębie region, including the region of the "Pniówek" coal mine operation, red beds, occurring in Carboniferous roof, have been found. Their presence has also been documented in the Czech part of the Upper Silesian Coal Basin, that is the region of Ostrava and Karvina

(Dopita, 1994; Klika & Kraussowva, 1993; Kowalski, 1977). The stratigraphic position of the red beds is not related to a specific stratigraphic link, as their genesis is most likely linked with:
- regional weathering, redeposition and sedimentation processes of the rock material (Dopita, 1994; Klika & Kraussowva, 1993; Kowalski, 1977), and
- zones of thermal and metasomatic activity of magmatic intrusions (Gabzdyl & Probierz, 1987; Probierz, 1989).

Research indicates that the following may be observed in areas of red formation occurrence:
- presence of new kinds of macerals, such as anisotropic semifusinite, low-reflectant fusinite and fluorescent bituminous substance (FBS) (Probierz, 1989; Komorek et al., 2010), and
- carbonification anomalies (Gabzdyl & Probierz, 1991; Probierz, 1986, 1989; Komorek et al., 2010).

The processes occurring in this part of the Upper Silesian Coal Basin, which result in the presence of red beds, have thus led to characteristic metamorphoses of the organic substance
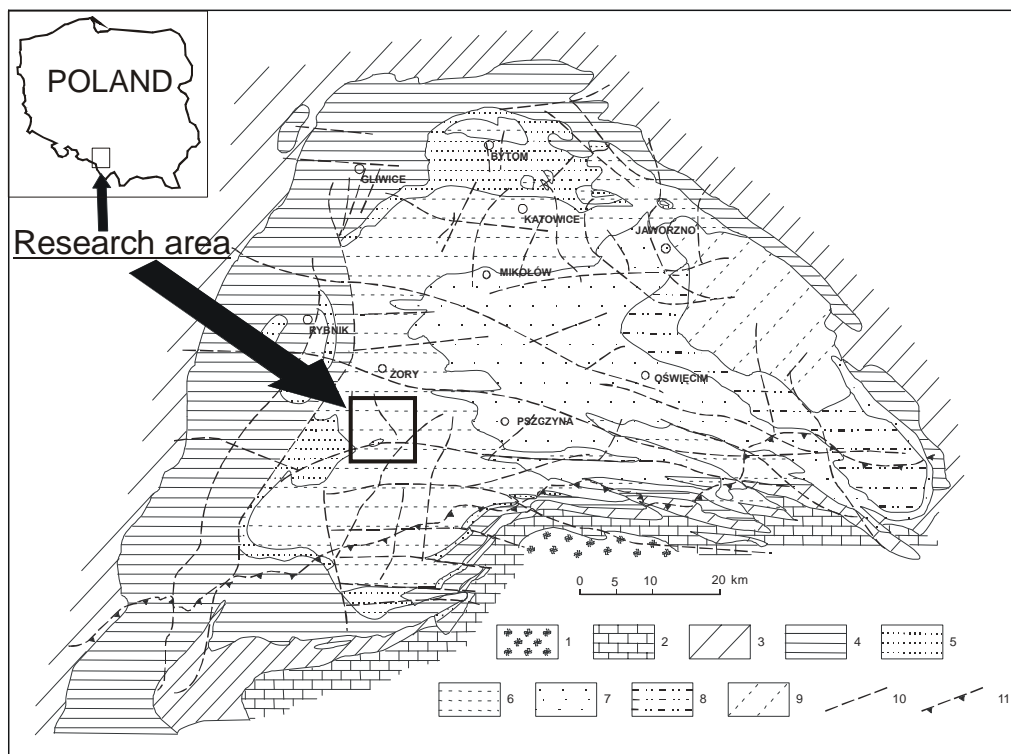

Fig. 1. Location of the area of study in the main geological zone in the Upper Silesian Coal Basin (Poland). Symbols: 1 – metamorphic rocks. DEVONIAN: 2 – carbonate and clastic marine sediments. CARBONIFEROUS: Namurian A – Upper Visean: 3 – diastrophic marine sediments. Namurian A: 4 – Paralic Series. Namurian B + C: 5 – Upper Silesian Sandstone Series. Westphalian A + B: 6 – Siltstone Series. Westphalian C + D: Cracow Sandstone Series: 7 – Łaziska layers, 8 – Libiąż layers. Stephanian: 9 – Kwaczała Arkose. 10 – main faults, 11 – Carpathian overthrust (according to Kotas A., 1982, modified)

(coal) and caused metamorphoses of the rocks accompanying the coal seams (Kowalski, 1977; Probierz, 1989; Adamczyk et al., 1994). The results of the study of accompanying rocks indicate that these metamorphoses led mostly to phase transitions between iron minerals, an increase in crystallinity of lithium and to silicification of rocks. As a result, the specific geochemical differentiation of many elements could have occurred both in coal and in accompanying rocks.
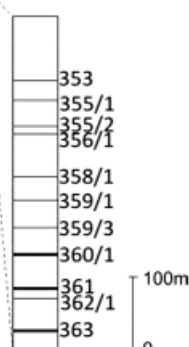

Fig. 2. Lithostratigraphic division of Carboniferous sediments in the Upper Silesian Coal Basin (after Jureczka et al. 2012) with profile and main coal seams of the study area

3. Materials and methods

3.1. Sampling

Channel samples obtained from the Orzesze bed seams of the "Pniówek" coal mine were used in the study. These seams were 360/1 (one sample), 361 (three samples) and 362/1 (two samples). The seams were available due to exploitation. The samples were obtained observing the PN-ISO 13909 standard.

The sampling of the seams was conducted in various tectonic blocks of the bed, with consideration to zones adjacent to red beds (Fig. 3). The sampling of the seams has been conducted in various headings – inclines, galleries, drifts and longwalls. The depth of the sampling locations ranged from (–598) to (–681) m below the sea level and the distance of that locations to the Carboniferous roof was 368÷691 m (Table 1). The samples were taken from seams in which changes caused by the vicinity of red beds were observed (Kralik, 1973; Kowalski, 1977; Dopita,1994; Probierz, 1989; Adamczyk et al., 2014).
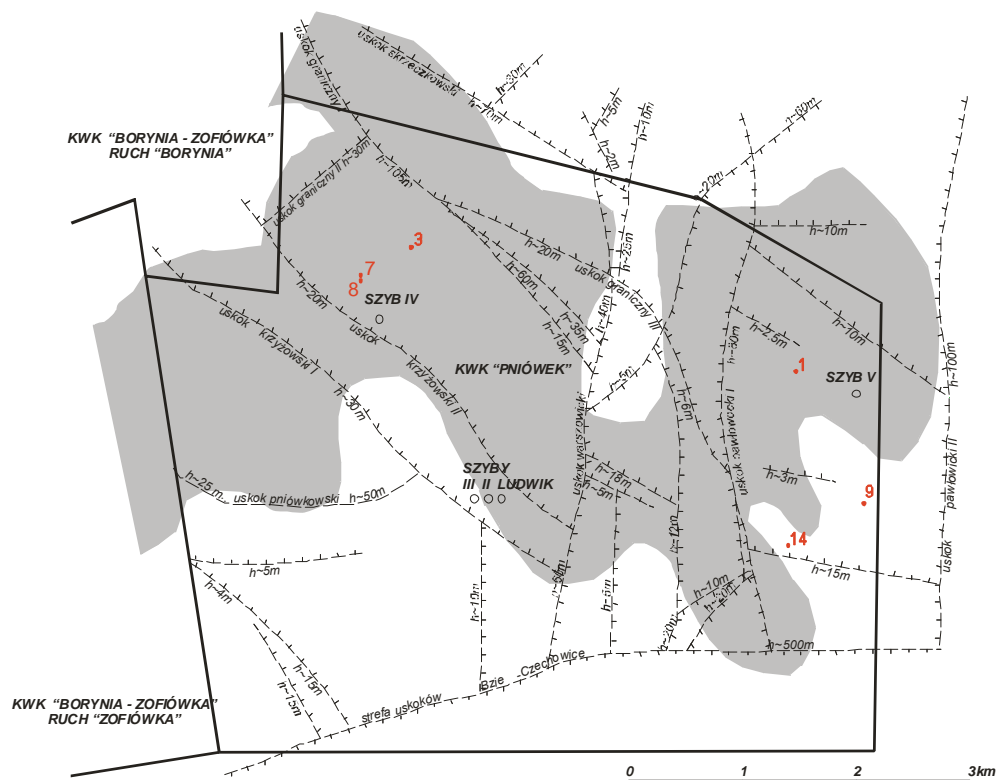
Fig. 3. Tectonic sketch of study area and samples localization (Geological Documentation of "Pniówek" coal mine). Explanations: •1 – localization and symbol of sample, ▢ – occurrences of red beds (according Dopita, 1994; Klika & Kraussowva, 1993; Kowalski, 1977)

TABLE 1

Samples localization in the geological profile of the Orzeskie beds in "Pniówek" coal mine

Sample	Coal seams symbol	Depth [m p.p.m.]	The distance of the ceiling Carbon [m]
9	360/1	−667	477
1	361	−681	691
3	361	−615	495
14	361	−598	368
7	362/1	−605	510
8	362/1	−605	510

3.2. Methods

The samples for testing were averaged, dried to air-dry state and grinded to the analytical grain size of $\varphi \leq 0.2$ mm. The samples prepared that way were then incinerated in a muffle furnace (815°C) and the content of ash was determined based on the PN-G-4512:1980/Az1:2002

standard. The coal ashes obtained from the samples constituted the research material used in the determination of oxide composition and the content of trace elements including rare earth metals. The determinations were conducted using the Fusion ICP/MS method with the application of Perkin Elmer SCIEX ELAN 6000 ICP-MS in Activation Laboratories Ltd. in Canada.

4. Results

4.1. Chemical composition

The coal samples were characterized by low ash content ranging from 2.22 to 6.27% of mass with a mean content of 4.61% of the mass (Table 2). The dominating chemical components of the ash was SiO_2, Al_2O_3 and $Fe_2O_{3(total)}$ (the total iron content converted into Fe_2O_3). The above components provided for 70% of the total ash mass. The sample from the 360/1 seam was an exception, as the sum of these components reached 60.60% of the mass. Sample No. 1 from the 361 seam was also significant, as the $Fe_2O_{3(total)}$ part in this sample was the highest among all the tested samples and it amounted to 49.74% of the mass, while in other samples it ranged from 14.18 to 22.24% of the mass.

TABLE 2

The chemical composition of the ash from coal seams of the Orzeskie beds in "Pniówek" coal mine
[in% masses]

Chemical components	Limit of detection	Coal seams, sample					
		360/1	361			362/1	
		9	1	3	14	7	8
SiO_2	0,01	23,81	18,31	32,19	24,46	31,32	35,00
Al_2O_3	0,01	22,61	17,60	27,49	27,33	29,18	33,41
$Fe_2O_{3(total)}$	0,01	14,18	49,74	22,24	20,19	17,39	18,93
MnO	0,001	0,21	0,38	0,22	0,32	0,22	0,11
MgO	0,01	4,09	4,75	3,62	6,19	2,83	2,33
CaO	0,01	19,11	4,88	5,27	14,04	8,15	3,34
Na_2O	0,01	2,04	1,17	3,25	2,70	2,75	4,80
K_2O	0,01	0,59	0,96	1,38	0,82	0,78	0,98
TiO_2	0,001	0,66	0,58	1,11	0,99	1,15	0,69
P_2O_5	0,01	12,71	1,61	3,25	2,96	6,23	0,41
Total	0,01	100,00	100,00	100,00	100,00	100,00	100,00
Ash content		5,45	5,06	5,94	2,73	6,27	2,22

Oxides were also significant chemical components that occured in the tested samples CaO, MgO, Na_2O i P_2O_5 their content usually reached several percent of the mass. The sample from the 360/1 seam called for particular attention, as it displayed the highest Cao and P_2O_5 concentrations – 19.11 and 12.71% of the mass, respectively. The phosphorus in coal is inorganic and it is related to the presence of apatite, crandallite, monazite and other phosphate minerals of syngenetic and/or volcanic origin (Morga, 2007). The phosphorus content in the seams of the "Pniówek" coal mine, analyzed by R. Morga (2005, 2007), ranged from 0.006 to 0.220% of the

mass, which constituted 0.013 to 0.504% of the mass when converted to P_2O_5 (Morga, 2005, 2007). The P_2O_5 content in the tested samples varied from 0.41 to 12.71% of the mass (with a mean value of 4.53%), which – when converted into the coal from the seams – constitutes 0.009 – 0.693% of the mass (mean of 0.241%) That percentage, in comparison to R. Morga's results, may be considered high.

Chemical differentiation may not only be observed among individual samples, but also among samples obtained from the same seam (coal seam 361 – samples 1, 3 and 14; coal seam 362/1 – samples 7 i 8). The highest variation within the 361 seam is displayed by the values of $Fe_2O_{3(total)}$ and CaO, while in the 362/1 seam CaO and P_2O_5 are characterized by the highest variability.

The remaining chemical components, that is MnO, K_2O and TiO_2 occur in lower concentrations and usually do not exceed 1% of the mass.

Coefficients of correlation between the fractions of the individual chemical components as well as between their content and the content of ash as well as the distance of the sample locations from the roof of the Carboniferous formations were specified for all the analyzed samples (Table 3). No correlation between the contents of individual chemical components and the content of ash was exhibited (the correlation coefficients did not exceed values above $|\pm0.55|$). On the other hand, high correlation coefficient values were observed between the contents of SiO_2 and Al_2O_3 and Na_2O as well as between Al_2O_3 and Na_2O (0.92, 0.91, 0.94, respectively for $p < 0.05$) in the tested ash samples. Such correlations may indicate the relation of these chemical components with a mineral substance in the analyzed samples (most likely the substances are clay minerals, the presence of which has been confirmed in the microscopic examination of the petrographic composition of the channel samples of coal which were used for the preparation of ashes for the purposes of this work – Adamczyk et al. 2014).

At the same time, what is exceptional is the high coefficient of correlation between the $Fe_2O_{3(total)}$ and the distance from the carboniferous roof (UP), which – in that region – is identified with the distance to the red beds (0.84 for $p < 0.05$).

TABLE 3

Coefficients of correlation among participations of chemical components in the ash and with chemical components of the ash in the coal (A) and the distance from the ceiling of the carboniferous period (red beds – UP)

	UP										
A	0.30	A									
SiO_2	−0.32	−0.13	SiO_2								
Al_2O_3	−0.51	−0.42	**0.92**	Al_2O_3							
$Fe_2O_{3(total)}$	**0.84**	0.08	−0.63	−0.70	$Fe_2O_{3(total)}$						
MnO	0.34	0.16	**−0.85**	−0.78	0.73	MnO					
MgO	−0.24	−0.18	−0.74	−0.53	0.30	0.79	MgO				
CaO	−0.62	0.08	−0.40	−0.26	−0.46	0.10	0.48	CaO			
Na_2O	−0.37	−0.52	**0.91**	**0.94**	−0.56	**−0.83**	−0.59	−0.38	Na_2O		
K_2O	0.25	0.07	0.38	0.18	0.26	−0.05	−0.17	−0.72	0.32	K_2O	
TiO2	−0.45	0.32	0.49	0.47	−0.44	−0.10	−0.05	−0.06	0.23	0.32	TiO_2
P_2O_5	−0.34	0.51	−0.21	−0.26	−0.47	−0.14	0.02	**0.82**	−0.37	−0.63	−0.03

4.2. Rare earth elements

The contents of rare earth elements in the examined ashes coming from the Orzesze coal bed seams of the "Pniówek" coal mine are diversified. The sum of the REE content in the examined ash samples varies from 364 to 1429 ppm (Table 4) – this value converted to coal reaches from 16.5 to 71.8 ppm. The mean REE content in coal deposits around the world is 60.2 ppm (Dai et al., 2010). Thus, the REE fraction in nearly all analyzed samples – converted to coal fraction – is much lower than the worldwide average (16.5-36.6 ppm). Sample 7 from the 361/1 seam is an exception where the REE sum (71.8 ppm) is higher than the worldwide average (60.2 ppm). It should be noted that over 80% of the REE sum is constituted by elements such as Sc, Y, La, Ce, Pr and Nd, which is a natural phenomenon resulting from the frequency of occurrence of these elements in the earth crust and the properties of lanthanides.

TABLE 4

The REE content in ashes from coal seams of the Orzeskie beds in "Pniówek" coal mine

Element	Limit of detection	Coal seams, sample					
		360/1	361			362/1	
		9	1	3	14	7	8
		[ppm]					
Sc	1	29	23	34	34	53	153
Y	2	97	48	84	75	162	368
La	0.1	73	57	94	104	162	131
Ce	0.1	139	119	202	208	371	297
Pr	0.5	16	13	23	22	43	40
Nd	0.1	64	56	98	89	186	177
Sm	0.1	15	12	21	18	43	46
Eu	0.05	3.40	2.48	4.53	3.86	9.63	11
Gd	0.1	18	10	19	16	39	50
Tb	0.1	3.08	1.65	2.84	2.37	6.11	8.92
Dy	0.1	17	9.20	15	14	32	56
Ho	0.1	3.19	1.76	2.84	2.71	5.90	12
Er	0.1	8.43	4.96	7.88	8.13	16	36
Tm	0.05	1.08	0.73	1.11	1.16	2.06	5.23
Yb	0.1	6.58	4.75	6.52	7.45	12	32
Lu	0.04	1.04	0.73	1.04	1.13	1.77	5.18
ΣREE		495 (27)	364 (18,4)	616 (36,6)	606 (16,5)	1145 (71,8)	1429 (31,7)
LREE		310	259	442	445	815	702
HREE		59	34	56	53	115	206
Average		776 (34)					

Explanations: In the parenthaties the sum of REE is given, based on the carbon organic matter.

Variation of the ΣREE content between the seams was observed, as the highest values (above 1000 ppm) were attributed to the ash from the 362/1 seam, while the lowest values (below 500 ppm) were characteristic of the ash from the 360/1 seam. This may suggest the increase of the fraction of these elements along with the stratigraphic position of the coal seam. This, however, should be confirmed with further research conducted for other coal seams.

Also the variation of the content of rare earth elements within the samples obtained from the same seam draws the attention. This especially concerns samples 1 (ΣREE = 364 ppm) i\and 3 (ΣREE = 616 ppm) from the 361 seam and samples 7 (ΣREE = 1145 ppm) and 8 (ΣREE = 1429 ppm) from the 362/1 seam.

The correlation between ΣREE, LREE, HREE and the chemical components of ashes, the ash content (A), the content of organic substance (OM) and the distance from the carboniferous roof (UP) has been analyzed (Table 5). High values of the correlation coefficient have been found in case of the correlation between ΣREE and SiO_2 and Al_2O_3 (for $p < 0.05$, $r = 0.82$ and $r = 0.86$, respectively). This indicates a relation between the REE content and the occurrence of aluminosilicates present in the clastic components in the samples (Schatzel & Stewart, 2003). As the study indicates (Cox et al., 1995), REE exhibit a tendency to concentrate in fine fractions of deposits. Moreover, the low coefficient of correlation in case of the relationship between the REE and $Fe_2O_{3(total)}$ contents may reflect the lack of relation between the REE fraction in the tested samples and the presence of red beds in the Carboniferous roof. This is additionally supported by the low coefficient of correlation between the sum of REE content and the distance from the Carboniferous roof. The values of the correlation coefficients calculated for the dependence of LREE and HREE from the content of the main chemical components in the tested ashes support the relation of LTEE and HREE with the minerals of the aluminosilicate group (Table 5).

No clear correlation has been found between the HREE and LREE contents and the fraction of the organic substance (OM). The higher value of the correlation coefficient for the HREE and (OM) than the LREE and (OM) ($r = 0.48$ and $r = 0.11$, respectively), however, indicates a slightly higher relation of organic substance with HREE than LREE. Such dependence is frequently observed for coals all over the world (Plamer, 1990; Querol et al.,1995; Eskenazy, 1987a, 1987b; Eskenazy, 1999).

TABLE 5

Coefficients of correlation among participations of the total REE and LREE and HREE and with chemical components of ash, ash (A), organic matter (OM) and the distance from the ceiling of the carboniferous period (red beds – UP)

	SiO_2	Al_2O_3	$Fe_2O_{3(t)}$	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	A	OM	UP
ΣREE	**0.82**	**0.86**	−0.50	−0.67	−0.71	−0.38	0.74	0.00	0.40	−0.23	−0.20	0.20	−0.18
LREE	0.80	**0.83**	−0.50	−0.60	−0.66	−0.35	0.68	0.00	0.51	−0.20	−0.11	0.11	−0.20
HREE	0.76	0.81	−0.41	**−0.80**	−0.76	−0.41	**0.85**	−0.01	−0.05	−0.30	−0.48	0.48	−0.07

The REE contents determined for the tested ashes have been normalized to chondrites. The REE contents in the ashes were characterized by typical enrichment of LREE in relation to HREE and relatively flat HREE curve (Fig. 4). Similar tendencies have been observed in *North American Shale Composite* (NASC) and *Post-Archean Australian Shale* (PAAS) which are a standard for comparative purposes in the appraisal of REE content (Schatzel & Stewart, 2003). Based on that, it may be determined that the primary source of REE in the Orzesze beds of the "Pniówek" coal mine was the clastic material.

In all the tested samples, an Eu anomaly may be observed which often occurs in magmatic rocks including tuffs accompanying coal deposits (Godarzi et al., 1990; Zhou et al., 2000; Gre-
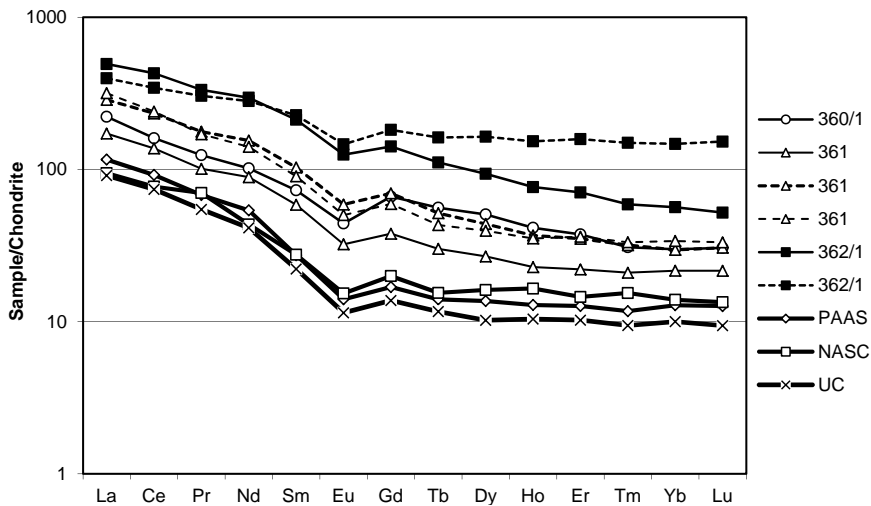
Fig. 4. Chondrite normalized rare earth REE diagram of coal ash from the Orzeskie Beds Upper Silesian
Coal Basin (Poland) and North American Shale Composite – NASC (Gromet et al., 1984)
and Post-Archean Australian Shale – PAAS, upper crust – UC (Taylor & McLennan, 1985)

venitz et al., 2003). Europium, indeed, may be reduced to Eu^{2+}, which is a result of its different geochemical behavior during the magmatic process in comparison with other lanthanides (Rard, 1985). Such reduction is possible in extremely reductive conditions (such as hydrothermal solutions), which do not occur in natural water systems. It may thus be assumed that this anomaly is related to the presence of pyroclastic rocks. Tuffs as well as tonsteins are found in Orzesze beds – these form barren intercalations in coal seams (Staniszewski & Wagner, 1980; Łapot, 1992; Adamczyk, 1998). Also a decrease in the Eu value in ash samples from stratigraphically younger seams has been observed.

A similar characteristic of the above diagram (Fig. 4) has been obtained for Carboniferous tonsteins from Spain (Botor, 2005), Triassic coals from China (Dai et al., 2010), and Fire Clay coal bed from Kentucky (Hower et al., 1999).

Research concerning rare earth elements has exhibited that the content of individual REE elements in coal is characterized by high correlation with the ash content. Their presence in coal is related to (mostly clay and phosphate) minerals (Chou, 1997; Dai et al., 2008; Finkelman, 1995). This is why this work includes calculations of correlation coefficients between the ash content and the content of individual rare earth elements in coal. In almost all analyzed REE (with the exception of Lu), positive insignificant correlations with the ash fraction in coal have been found (Fig. 5). The obtained results indicate that LREE are characterized by higher correlation with ash ($r \geq 0.50$) than HREE (Fig. 5), which may suggest that in the tested samples, LREE are more related to an organic substance.
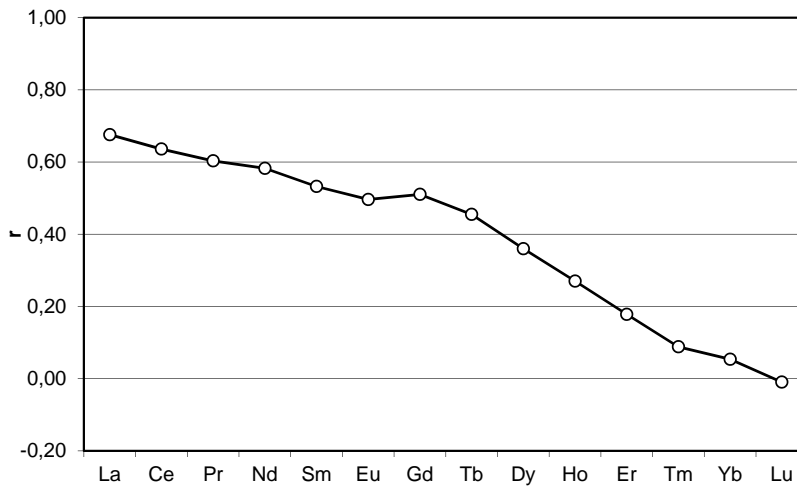
Fig. 5. The correlation coefficients for relationship between ash content and individual rare element content in coal

5. Conclusion

Based on the conducted study of ashes obtained from coal of the Orzesze beds in the "Pniówek" coal mine, the following conclusions have been drawn:

Coal samples are characterized by low content of ash ranging from 2.22 to 6.27% of the mass.

The ashes of the tested coal samples are characterized by diversified chemical composition both in case of different seams and when considering samples of a single seam. The chemical composition of ashes indicates the presence of aluminosilicate minerals – most probably clay minerals, the presence of which has been identified in microscopic examination of the petrographic composition of the channel coal samples.

The REE contents in ashes obtained from Orzesze bed seams in the "Pniówek" coal mine are diversified both within a single seam and between different seams.

The REE fraction exhibits a relation with a mineral substance. In the tested samples, no relation between the REE content and the presence of red beds in the Carboniferous roof have been found.

The REE contents determined for the ashes and normalized to chondrites are characterized by typical LREE enrichment in relation to HREE. The Eu anomaly is most likely related to tuff and tonstein levels occurring in the Orzesze beds of the Uppersilesian Coal Basin, which accompany the coal seams.

The study has indicated that LREE are more related to a mineral substance, while HREE have a higher affinity with an organic substance.

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