Rare Earth Element Content and Distribution in Ash-Slag Mixes Deposited in the Gardawice Landfill

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DOI: 10.29227/IM-2017-01-18

Abstract

Raw materials policy plays an increasingly important role in the economies of countries all over the world. The development of new technologies grows the demand for resources. The list of critical resources accepted by the European Committee contains rare earth elements, commonly referred to as REEs. A prospective way of obtaining these elements is recovering them from power industry wastes originating from coal combustion. This publication presents the results of research aimed at evaluating the content as well as illustrating and interpreting the spatial distribution of rare earth elements in power industry wastes deposited in a chosen landfill. It also presents maps of horizontal variability in the content of REEs deposited in certain layers of the ash-slag mix.

Keywords: rare earth elements, fly ashes, landfill, recovery, raw materials

Introduction

Raw materials policy plays an increasingly important role in the economies of countries all over the world. The development of new technologies grows the demand for resources. Especially important is the issue of availability of critical resources, defined in 2008 by the Committee on Critical Mineral Impacts on US Economy. Critical resources are such resources which could run into a supply and distribution imbalance, which might have a significant impact on the entire economy. In 2010 the European Committee issued their first statement pertaining to 14 critical resources. The next statement was issued in 2014 and encompasses 20 critical resources. Remaining on the list are the so-called Rare Earth Elements (REE). They are a group of 15 lanthanides from lanthanum to lutetium, as well as scandium and yttrium, which exhibit similar chemical properties due to their similar outer electron shells and small difference in the overall atom and ion size. Due to their strong geochemical affinity, rare earth elements usually co-occur, with one of them in larger concentrations than the other.

Rare earth elements occur rather commonly in nature. According to some sources, the total content of rare earth elements in the Earth's crust is 146 ppm, which is higher than that of zinc or copper (Charewicz, 1990). Rare earth elements are usually found in the form of carbonates, oxides, phosphates and silicates. Although large quantities of rare earth elements can be found in hundreds of minerals, only a few of them are economically significant. They are (among others) bastnaesite, loparite, monazite, xenotime, fergusonite (Chakhmouradian, Wall 2012).

Rare earth elements have application in modern technologies, especially in the arms, glass (cerium), steel (cerium) and chemical industries, in the production of x-ray film and catalytic converters (lanthanum), electronics (gadolinium, erbium, europium), as well as in the production of renewable energy sources and in many other areas. Elements of highest significance in modern technologies are: lanthanum, europium, erbium and neodymium.

Natural deposits of rare earth elements in Poland are located in the Sudetes, near Szklarska Poręba and Markocice, as well as in north-eastern Poland, near Suwałki. These deposits are mostly connected with monazite ((Ce, La, Nd, Th, Y, Pr) PO_4), xenotime (YPO_4), apatite ($Ca_5[(F,Cl,OH)(PO_4)_3]$) and carbonatites with REE content ranging from 0.15 to 5.27%. Rare earth elements can also concentrate in waste phosphate gypsums in concentrations making them secondary deposits. For example, a waste dump containing such wastes in Wizów (Lower-silesian Voivodeship) with a documented volume of 2 mln Mg contains 8 thousand Mg of a mixture of REEs, including 200 Mg of yttrium and 30 Mg of europium. Other, smaller phosphate gypsum waste dumps which could become a source of REEs can be found in Gdańsk and Police.

A prospective use for power industry wastes left over after burning coal is recovering metals from them, including rare earth elements. As many as 81 metals have been found in power plant ashes (Hycnar, 1987).

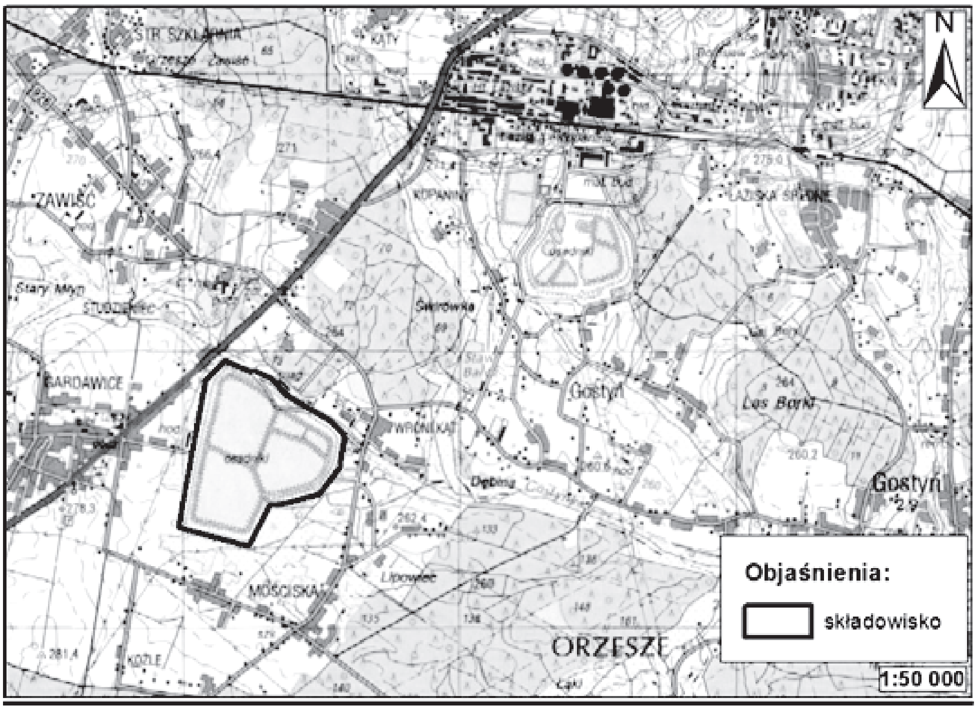

Fig. 1. The landfill "Gardawice" in Łaziska (Poland)

Rys. 1 Składowisko „Gardawice" w Łaziskach (Polska)

The concentrations of elements in ashes are a few to several dozen times higher when compared to coals. So far research on the concentration of rare earth elements in fly ashes left over from burning coal in Poland have been conducted by: Smółka-Danielowska (2007, 2010, 2013), Całus Moszko, Białecka (2012, 2013), Wdowin, Franus (2014), Całus Moszko et al. (2016). The ashes have been shown to contain rare earth phosphates, mainly cerium monazite, and trace amounts of zircon and xenotime. A correlation has been determined between the concentration of thorium and the cerium, lanthanum and neodymium contents. Worth noting is the high cerium (39-186 ppm) and lanthanum (16-86 ppm) content in all the power industry waste examined.

Aim and Scope of Research

The aim of the research was to evaluate the content as well as illustrate and interpret the spatial distribution of rare earth elements in power industry wastes (ash-slag mixes) deposited in the part of the "Gardawice" landfill used by the Łaziska Power Plant branch of TAURON Wytwarzanie S.A. The scope of the research encompassed:

- developing a research schedule and conducting field tests,
- carrying out laboratory tests on the ash-slag mix samples for REEs,
- research result analysis.

Testing Site

Tests were conducted at the power industry waste landfill No. 2 in Gardawice (commune of Orzesze). The landfill is located about 3 kilometres south-west of the Łaziska Power Plant branch of TAURON Wytwarzanie S.A. and east of the village of Gardawice (Figure 1). The landfill lies between the following roads: Katowice–Wisła (in the west), Orzesze-Mościska (in the south), Wroni Kąt-Mościska (in the east), and the river Gostynka in the north. The site is surrounded by wet meadows and farmlands from the south, south-east and west, and a forest from the north. In the vicinity of the heap there are residential buildings of the Gardawice, Mościska, Wroni Kąt and Zawiść villages.

The "Gardawice" waste heap takes up an area of 84 ha consisting of 3 quarters of 28 ha, 27 ha and 29 ha which can store waste in 5 layers, 4–5 m each. The installation at the "Gardawice" No. 2 landfill consists of:

- 3 quarters for gathering waste with a drainage system made with ceramic Ø150 drains located in the main walls,
- 4 Ø356 pipages piping in the ash-slag pulp or drainage water from the Slag Desiccation Installation into the excavation which is being refilled,
- a sludge supernatant drainage system,
- a return water pumping station,
- a drainage water pumping station.

The landfill was commissioned in 1978 as an embankment combustion waste heap situated on a layer of

Fig. 2. Field test area, quarter III of the “Gardawice” landfill

Rys. 2 Powierzchnia pola testowego, kwarta III składowiska „Gardawice”

Fig. 3. The location of boreholes and sampling spots in the “Gardawice” landfill

Rys. 3 Lokalizacja odwiertów i punktów poboru próbek na składowisku „Gardawice”

natural clays. The walls of stage 1 were made of local clay obturated with ash. The next two layers of the wall were made with coal shale, and the last with a mineral layer. A layer of concentrated ashes in form of emulsions was used for the foundation of the heap. Since 2006, when the Łaziska power plant launched its Slag Desiccation Installation, waste is only being directed to the heap in times of emergency, as a means of temporary waste deposition.

Deposited in the “Gardanice” landfill of the Łaziska Power Plant are wastes coded 10 01 80 – ash-slag mixes from wet combustion waste disposal. The mix comprises mainly slags from combustion chambers and ash from the second pass of all the boilers of the coal combustion installation, which go through deslaggers and crushers and are directed hydraulically to the ash slurry pump, where ashes from periodic electro-filter and boiler cleaning are also drained to.

Research Methodology and Result Interpretation

Sampling

Quarter III of the landfill was chosen as an optimal place for taking samples, where until 1997 ash-slag mixes were deposited in 4 layers with a total thickness of 20 m. The section was closed afterwards and grassed over (Figure 2).

Three boreholes (G-1, G-2, G-3) were made as part of the tests, outlining a triangle with a surface area of 19 750 m^2. In terms of surface, the test area should be treated as a sample containing about 7% of the overall surface of quarter 3.

Through the location of individual boreholes we attempted to capture the maximum possible variability

Fig. 4. The auger filled with an ash-slag mix

Rys. 4 Rdzeń wypełniony mieszanką popiołowo-żużlową

in the waste which could result from the way they had been deposited in the landfill. The boreholes were located in the following way:

- borehole G-1 – ner the middle of the quarter's northern wall,
- borehole G-2 – in the central area of the quarter,
- borehole G-3 – in the south-eastern corner of the quarter.

The location of the boreholes have been presented on the map shown in Figure 3.

A "dry" mechanical rotary drilling system was used to drill the boreholes using an H20SG drilling rig made by WAMET Sp. z o. o., with an auger with a diameter of 100 mm and a screw picker (Figure 4).

Samples were taken from each of the boreholes from the waste superstratum with a thickness of 10.0 m and a sampling density of 1 sample per linear metre of the borehole profile. 30 samples were taken in total with each weighing about 2 kg.

Laboratory Tests

Tests on the content of rare earth elements (scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium) in ash-slag mixes were conducted at the accredited Solid Waste Analysis Laboratory of the Faculty of Environmental Monitoring at GIG (Central Mining Institute). The tests were carried out using wavelength-dispersive fluorescent x-ray spectrometry with a sequential wavelength-dispersive fluorescent x-ray spectrometer, PRIMUS II made by RIGAKU.

Test Results and Interpretation

Test t, a tool of the STATISTICA® ver. 10 program, was used for the interpretation, including testing mean values against a constant reference value. Element concentration maps were created using the ArcGIS 10.3 for Desktop Advanced program by ERSI and the Spatial Analyst dedicated extension.

Statistical parameters which synthetically describe the set of results from tests on rare earth elements' content in ash-slag mixes from quarter 3 of the "Gardawice" landfill have been presented in Table 1.

From the 16 rare earth elements examined (including scandium and yttrium) the highest mean concentrations in the material tested were those of: cerium (~113 mg/kg), lanthanum (~60 mg/kg), neodymium (~48 mg/kg), scandium (~33 mg/kg) and yttrium (~31 mg/kg). The concentrations of the other elements are much lower with only praseodymium exceeding the 10 mg/kg threshold. It should be noted that the variability coefficient, the relative measure of variability, has the lowest values for elements with the highest concentrations. Therefore, the data sets on cerium, neodymium, scandium, lanthanum and praseodymium content should be considered the least variable. Among the elements with lower concentrations, erbium shows a relatively low variability coefficient (19%). The percentage content of all the rare earth elements in the ash-slag samples tested is 296 ppm to 366 ppm. The average concentration of REEs is 330 ppm and the low standard deviation value (0.0019%) shows that the data set is rather invariable.

Five elements from the so-called light rare earth elements (LREE), i.e. scandium, yttrium, lanthanum, cerium and neodymium, together make up 86% of the

Tab. 1. Statistical parameters of the data set on rare earth elements' content in ash-slag mixes deposited in the "Gardawice" landfill

Tab. 1 Parametry statystyczne zbioru danych dotyczących zawartości pierwiastków ziem rzadkich zdeponowanych na składowisku „Gardawice"

Rare earth elements	The average content in the earth's crust (Patnaik 2003)	Minimum	Maximum	Mediana	Avarage	Standard deviation	Variability coefficient
	mg/kg (ppm)						%
Sc	22	24,7	42,3	33,3	33,3	3,7	10
Y	33	16,7	39,2	34,1	31,1	6,8	23
La	30	43,8	73,6	61,0	59,8	6,8	13
Ce	66	100,5	125,9	113,0	112,6	6,7	7
Pr	8,2	7,4	15,4	11,6	11,6	2,1	21
Nd	24	39,5	56,9	48,1	47,7	4,2	9
Sm	7	3,1	10,0	7,3	7,5	1,5	24
Eu	2,1	0,7	1,9	1,4	1,4	0,3	19
Gd	6,2	0,1	9,9	6,2	6,1	1,8	39
Tb	1,2	0,05	1,4	1,2	1,2	0,3	16
Dy	5,2	6,3	16,1	8,4	9,1	2,7	28
Ho	1,3	0,2	2,9	1,6	1,7	0,6	40
Er	2,8	0,5	3,8	2,9	2,9	0,6	31
Tm	0,52	0,2	0,9	0,6	0,6	0,2	32
Yb	3,2	1,3	4	2,9	2,9	0,6	22
Lu	0,5	0,1	0,4	0,2	0,2	0,1	40
∑REE	213,2	245,2	404,6	333,8	329,7		

overall marked REE content. Figures 5–8 show example maps of horizontal variability in the content of these elements in certain layers of the ash-slag mix.

In the 0.0–1.0 m bgl depth range, the lowest scandium content was observed near the G-2 borehole, while the highest concentration occurred near the G-3 borehole (Figure 5a). At 3–4 m bgl the maximum concentrations of scandium occurred in the vicinity of the G-1 borehole (Figure 5b).

The map of yttrium content in ash-slag wastes in the surface layer (from 0.0 to 1.0 m bgl) indicates that the maximum concentrations of this element occur in the vicinity of the G-3 borehole (Figure 6a). However, the yttrium concentration variability map at depths of 2 to 3 m bgl gives a more representative image for the tested part of the landfill mass. In Figure 6b we can see a clear yttrium rich area near the G-1 and G-2 boreholes.

The lanthanum content in the surface layer (0.0–1.0 m bgl) is constant up to to about 6.0 m bgl (Figure 7a) while the map shown in Figure 7b is more representative for ash-slag mixes deposited below that level.

The map of cerium content in the 0.0–1.0 m bgl ash-slag mix layer is representative of the sampled landfill mass (Figure 8a). In the surface layer, the highest cerium content was observed in the G-3 borehole and the lowest in the G-1 borehole. Maxima and minima of the aforementioned element's concentration in ash-slag mixes deposited at various depths can be located in different boreholes.

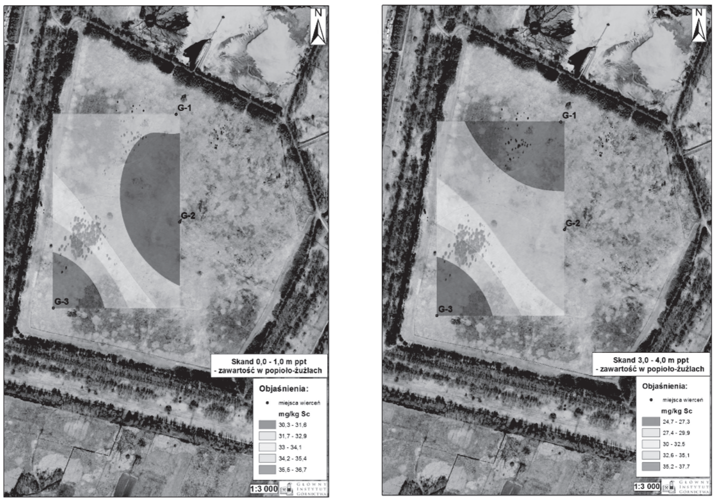

Fig. 5. Map of horizontal distribution of scandium content a) in the 0.0 to 1.0 m bgl layer, b) in the 3.0 to 4.0 m bgl layer

Rys. 5 Mapa rozkładu poziomego zawartości skandu: a) w warstwie od 0,0 do 1,0 m bgl, b) w warstwie od 3,0 do 4,0 m bgl

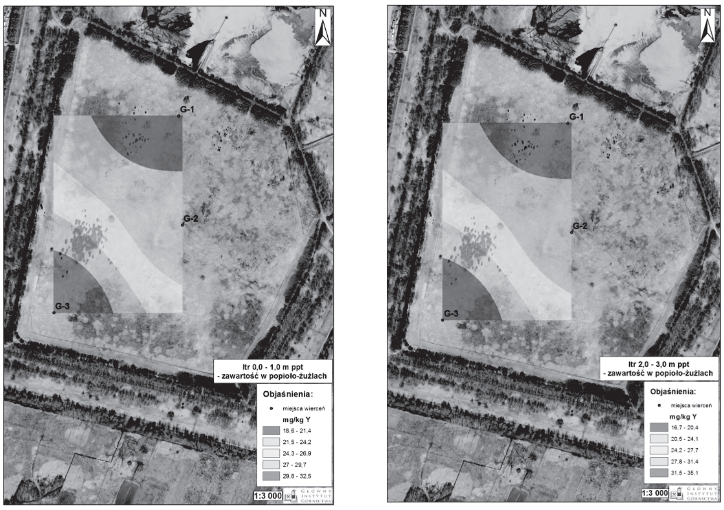

Fig. 6. Map of horizontal distribution of yttrium content a) in the 0.0 to 1.0 m bgl layer, b) in the 2.0 to 3.0 m bgl layer

Rys. 6 Mapa rozkładu poziomego zawartości itru: a) w warstwie od 0,0 do 1,0 m bgl, b) w warstwie od 2,0 do 3,0 m bgl

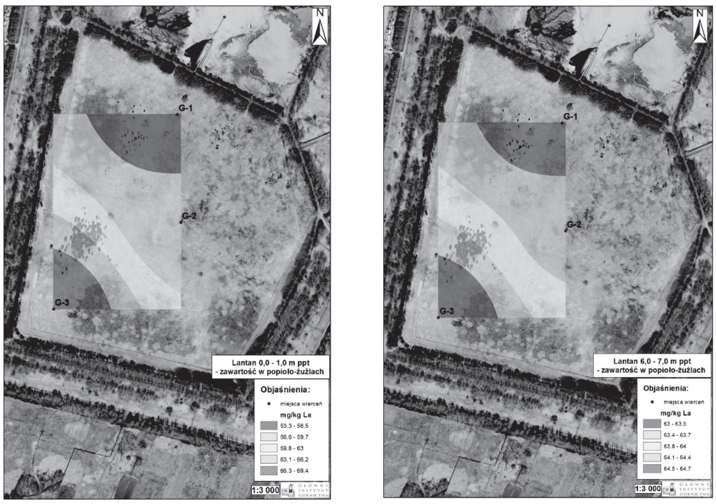

Fig. 7. Map of horizontal distribution of lanthanum content a) in the 0.0 to 1.0 m bgl layer, b) in the 6.0 to 7.0 m bgl layer

Rys. 7 Mapa rozkładu poziomego zawartości lantanu: a) w warstwie od 0,0 do 1,0 m bgl, b) w warstwie od 6,0 do 7,0 m bgl

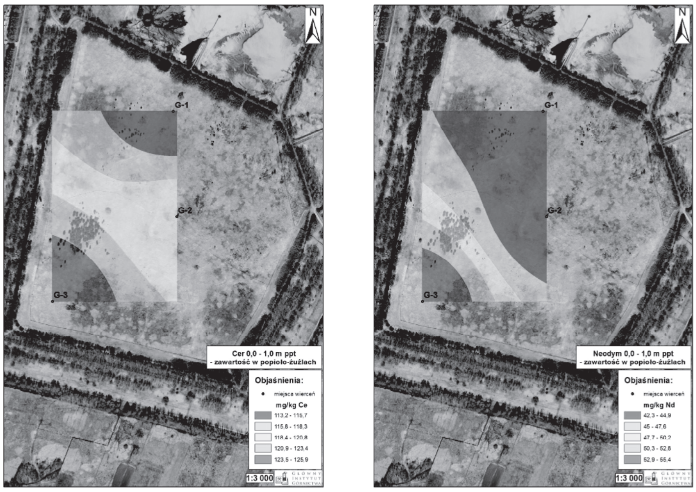

Fig. 8. Map of horizontal distribution a) of cerium content in the 0.0 to 1.0 m bgl layer, b) of neodymium content in the 0.0 to 1.0 m bgl layer

Rys. 8 Mapa rozkładu poziomego: a) zawartości ceru: w warstwie od 0,0 do 1,0 m, b) zawartości neodymu w warstwie od 0,0 do 1,0 m

At the same time the map of neodymium content in the ash-slag mix layer of 0.0 to 1.0 m bgl illustrates the variability in the element's content in the upper, 3-metre, most variable part of the profile (Figure 8b). the concentrations of neodymium in ash-slag mixes deposited further below the surface, up to 9 m bgl, are less varied.

Conclusions

The research conducted on the content and spatial distribution of rare earth elements in ash-slag mixes deposited in the "Gardawice" landfill allowed us to formulate the following conclusions:

1. The research has shown that 6 of the 16 elements tested show concentrations significantly higher than those average for the Earth's crust (with a statistical significance of α=0,05). Those elements are scandium, lanthanum, cerium, praseodymium, neodymium and dysprosium.

2. Elements with the highest average content in ash-slag mixes were: cerium (~113 mg/kg), lanthanum (~60 mg/kg), neodymium (~48 mg/kg), scandium (~33 mg/kg) and yttrium (~31 mg/kg). Concentrations of other elements are much lower with only praseodymium exceeding the 10 mg/kg threshold.

3. The percentage content of all the rare earth elements in the ash-slag mixes tested ranged from 296 ppm to 366 ppm (an average of 330 ppm). Five elements, i.e. scandium, yttrium, lanthanum, cerium and neodymium combined comprise 86% of the overall marked REE content. The combined concentration of praseodymium, samarium, gadolinium and dysprosium was 10% and the combined content of europium, terbium, holmium, erbium, thulium and lutetium was 4%.

4. The variability of the data set on the concentration of individual elements varies greatly. Variability coefficients are the lowest (from 6% to 18%) for elements with the highest concentrations, i.e. cerium, neodymium, scandium, lanthanum and praseodymium. The variability coefficients of the results for elements with lower concentrations can exceed 30%.

5. Among the elements with the highest concentration in ash-slag mixes scandium, lanthanum, cerium, praseodymium and neodymium do not exhibit pronounced change tendencies in the vertical profile while a clear tendency correlated with depth was found in case of yttrium and dysprosium.

The paper has been prepared in the frames of the project: "Assessment of possible recycling directions of heavy & rare metals recovered from combustion waste products" (ERA-MIN/RAREASH/01/201), funded by the National Centre for Research and Development under the ERA-NET ERA-MIN Programme.

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Zawartości pierwiastków ziem rzadkich i ich występowanie w mieszaninach popiołowo-żużlowych zdeponowanych na składowisku Gardawice

Gospodarka surowcami mineralnymi pełni coraz większą rolę w ekonomii krajów na całych świecie. Rozwój nowych technologii powoduje wzrost zapotrzebowania na zasoby. Lista surowców krytycznych zaakceptowana przez Komisję Europejską zawiera pierwiastki ziem rzadkich (REE). Jedną z możliwości pozyskania tych pierwiastków jest ich odzysk z odpadów energetycznych, pochodzących ze spalania węgla. W artykule przedstawiono wyniki badań, których celem była ocena zawartości i rozkładu przestrzennego pierwiastków ziem rzadkich w odpadach przemysłu energetycznego zlokalizowanych na wybranym składowisku. Ponadto, przedstawiono mapy poziomej zmienności zawartości pierwiastków REE zdeponowanych w określonych warstwach mieszanki popiołowo-żużlowej.

Słowa kluczowe: mieszanki popiołowo-żużlowe, pierwiastki ziem rzadkich (REE), spalanie węgla, przemysł energetyczny