DOI: 10.32056/KOMAG2020.4.3

Determination of rare earth elements in power plant wastes

Published online: 29-12-2020

Rafał BARON

KOMAG Institute of Mining Technology, Pszczyńska 37, 44-100 Gliwice, Poland

e-mail: rbaron@komag.eu

Keywords: rare earth elements (REE), power industry, power plant wastes, fly ashes, furnace slags

Słowa kluczowe: pierwiastki ziem rzadkich (REE), energetyka, odpady energetyczne, popioły lotne, żużle paleniskowe

Abstract:

The results of laboratory analyzes determining the share of rare earth elements (REE) in power plant wastes (fly ashes and furnace slag) are presented. The waste material was acquired from power plants located in the Upper Silesian Industrial District. Ashes and slags were analysed in the laboratory using the inductively coupled plasma mass spectrometry method (ICP-MS), aimed at determining the quantitative share of REE in power plant wastes. The results of measurement of rare earth elements content in fly ashes and furnace slags were compared with the literature data, showing some discrepancies in the intensity of valuable elements. On the basis of laboratory analyzes, the economic justification for recovering the valuable elements from the selected material was formulated.

Streszczenie:

Artykuł zawiera wyniki analiz laboratoryjnych, określających udział pierwiastków ziem rzadkich (REE) w odpadach energetycznych (popioły lotne i żużle paleniskowe). Materiał odpadowy pozyskany został z elektrowni znajdujących się na terenie Górnośląskiego Okręgu Przemysłowego. Analizy laboratoryjne popiołów oraz żużli przeprowadzono metodą spektrometrii mas z jonizacją w plazmie indukcyjnie sprzężonej (ICP-MS), mające na celu określenie ilościowego udziału REE w odpadach energetycznych. Wyniki pomiarów zawartości pierwiastków ziem rzadkich w popiołach lotnych i żużlach paleniskowych porównano z danymi literaturowymi, wykazując pewne rozbieżności w intensywności ich występowania. Na podstawie analiz laboratoryjnych sformułowano ekonomiczne uzasadnienie odzyskiwania cennych pierwiastków z wybranego materiału.

1. Introduction

Rare earth elements (REE), due to their high strategic importance in development of advanced technologies, have been classified by the European Union among the group of 20 critical mineral resources. It has been forecasted that the demand for rare earth elements will double by 2060, reporting systematic increases in the coming years [2]. In the countries of the European Community, the resources of fossil minerals containing valuable elements are gradually decreasing, therefore the institutions of the European Union launched numerous research projects to identify new prospective sources of rare earth elements and to develop innovative technologies for their recovery. Some actions are taken to maintain the continuity of raw material supplies, also through the recovery of a useful elements from waste [1].

The current projects on determination of rare earth elements content show the presence of these valuable elements in fly ashes and furnace slags. The content of REE in power plant combustion wastes exceeds the concentration of these elements in hard coal to be burned [2, 3].

Rare earth elements make a group of 17 elements which, due to their specific physicochemical properties, are used in state-of-the-art technologies. The term "rare earth elements" is imprecise because they are present in the earth's crust in a relatively large amount, but their concentration in the extracted ore is low, and therefore, their recovery often remains economically unjustified.

Publisher: KOMAG Institute of Mining Technology, Poland

Examples of the economic application of each element are as follows [2, 4, 5, 6, 7, 8]:

- scandium (Sc) – aviation industry, aircraft construction and radiotherapy,
- lanthanum (La) – optical products, hybrid vehicles,
- yttrium (Y) – ceramics, metal alloys,
- cerium (Ce) –metallurgy, chine dye, analytical chemistry,
- praseodymium (Pr) – a dye for glass and stones,
- neodymium (Nd) – laser technology, magnetic materials,
- samarium (Sm) – cinematography, nuclear technology,
- europium (Eu) – nuclear engineering,
- gadolinium (Gd) – alloy additive, microwave technology,
- promethium (Pm) – Beta radiation source,
- terbium (Tb) – lasers, diodes,
- dysprosium (Dy) – petrochemical industry,
- holm (Ho) – nuclear technology, electronics,
- erbium (Er) – optical amplifiers,
- thulium (Tm) – magnetic materials,
- ytterbium (Yb) – microelectronics,
- lutetium (Lu) – ferrite production.

The largest deposits of rare earth elements showing their justified economic recovery are in China, USA, Russia, Australia and India. The global production of REE is at the level of 139 thousand Mg, and is dominated by China, which has 23% of the world's deposits. China also covers 93% of the global demand for these elements [2,9,10,11].

Poland does not have deposits of rare earth elements in its natural resources, therefore the following raw, secondary or waste materials may be the potential source of these elements in Poland [12]:

- fly ashes and furnace slags,
- hard coal,
- mine waste,
- sand and gravel deposits,
- waste electronic equipment.

Due to the expected presence of REE in power plant wastes and their economic importance, KOMAG Institute of Mining Technology launched an R&D program aimed at assessing the content of rare earth elements in fly ashes and furnace slag acquired from coal-fired power plants.

Currently, the Polish power industry is mainly based on hard coal and lignite - 58%. A systematic increase in electricity production is forecast in 2020-2040, reaching over 70,000 MW in 2040. The share of coal in the electric power generation in Poland will systematically decrease, while its share will still be significant, amounting to approximately 15,000 MW of electricity generated in 2040.

During the combustion of coal, large amounts of by-products are created, having a negative impact on the natural environment (emission of CO2, NOx, sulfur compounds and dust) when getting into the atmosphere. Fly ashes and furnace slags, which are the subject of the tests, are also by-products of the combustion process [13,14,15,16].

In 2019, the Polish power industry, by burning hard coal, generated about 20 million Mg of wastes, which was a mixture of fly ash and furnace slags [10,13,15].

Fly ashes are the fine particles obtained by electrostatic or mechanical precipitation from the off gases of a coal-fired furnace. According to the adopted classification, fly ashes are divided according to their chemical composition:

- silica-aluminum fly ashes with a predominance of SiO_2,
- silica-aluminum fly ashes with a predominance of Al_2O_3,
- sulphate-calcium fly ashes with a predominance of calcium compounds.

However, this division does not take into account the specificity of Polish fly ashes, which have a variable chemical composition depending on the type of coal burned. In Poland, the following types of fly ash are distinguished on the basis of chemical composition:

- silica fly ashes (K) – from burning hard coal,
- silica-aluminum fly ashes (G) – from burning lignite (Turoszów Basin), where clay minerals are the main non-flammable components,
- silica-calcium fly ashes (W) - from burning lignite (Konin and Bełchatów Basin), with a significant share of calcium compounds [17].

In the publication [1], the results of fragmentary studies on the content of rare-earth elements in fly ashes from power plants located in the Upper Silesian Industrial Region are presented (Table 1).

Table 1. Content of rare-earth elements in fly ashes [1]

Material	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sc	Y
	ppm															
GOP ashes	16-86	39-186	-	27-87	4-19	0.4-3.5	-	-	-	-	-	-	-	-	-	11-25.8
Łagisza Power Plant	39.3	79.6	9.3	35.8	7.43	1.74	6.64	0.98	5.54	1.06	2.85	0.36	2.18	0.31	15.6	26.5
Fly ashes	56.5	117.6	13.7	52.3	-	-	-	1.6	9.5	1.9	5.3	0.72	4.6	0.64	-	43.6

The data from Table 2 show that the concentration of REE in ashes vary in the range of 0.31 - 186.0 ppm. High content of cerium (39-186 ppm) and lanthanum (16-86 ppm), indicates their economic potential in fly ashes.

It should be noted, that there are inaccuracies in the results of the tests due to unknown place and date of sampling, the cognitive method determining the concentration of REE in the tested samples and the generalized name of "the GOP ashes" indicating that they may be mixtures of fly ashes from various power plants. Thus, the share of REE in the fly ashes for a given power plant of known characteristics of the furnace feed material is unknown.

Furnace slags, similarly to fly ashes, is a by-product formed after burning hard coal or lignite in the grate furnace of a power plant or a combined heat and power plant. The term raw furnace slag is defined as the residue after burning the coal on the grate, as well as on the furnace ash pan. Depending on the share of unburned coal, the following slags are distinguished:

- unburnt slag – dark gray, porous structure with pieces of unburned coal.
- burnt out slag – red, brick like colour, hard sinter and fine graining.

The furnace slags contain approx. 50% SiO_2 silica and has a significant share of Al_2O_3. Mineralogical composition showed the presence of mullite crystals, fused quartz, melilite, anorthite, burnt clay rock, magnetite and gypsum inclusions [13,16,18].

There were no extensive tests of furnace slags to determine the content of rare-earth elements in them (Table 2).

Table 2. Content of rare-earth elements in furnace slag [1]

Material	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sc	Y
	ppm															
Furnace slag	55.1	112.2	13.2	50.3	-	-	-	1.5	9.0	1.7	5.1	0.72	4.6	0.64	-	43.6

The share of REE in furnace slags is similar to that found in fly ashes, varied from 0.64 to 112.2 ppm (cerium content). The content of lanthanum, cerium, neodymium and yttrium is high, what means their economic potential.

Unfortunately, the results for furnace slags are not quite reliable due to the lack of complete data. The places and dates of sampling and the cognitive method determining the concentration of REE are not known, similarly to fly ashes. The results represent a group of furnace slags with unknown chemical composition and origin.

2. Methodology and the testing material

The power plants, the waste material of which (fly ash and energy slag) was not previously tested were selected for analyses, thus extending the knowledge on the share of REE in this type of industrial waste.

Acquisition of the material samples was preceded by a formal letter requesting the delivery of samples, which was approved by three power plants. Due to the confidentiality agreement between KOMAG and power plants supplying power plant waste, each power plant has got individual mark to unable identification of the plant.

Three power plants using different feed, a mixture of certain types of coal, differing in type and origin, were selected. Characteristics of the feed material is as follows:

- Power Plant "A" – the power boiler feed consisted of hard coal from three mining plants. The power plant does not co-incinerate biomass with hard coal. The power plant waste material was delivered on March 22, 2019.
- Power Plant "B" – the power boiler feed consisted of hard coal from one mining plant. The power plant does not co-incinerate biomass with hard coal. The power plant waste material was delivered on March 22, 2019.
- Power Plant "C" - the composition of the power boiler feed was differentiated and consisted of hard coal from various mining plants. The power plant does not co-incinerate biomass with hard coal. The power plant waste material was delivered on June 05, 2019.

The composition and characteristics of fly ashes and bottom slags, due to the different type of coal burned in power plants, may change depending on the share of each feed product.

10 kg of fly ashes and bottom slags were collected from each plant. The ashes were collected from the storage silos at the truck ash loading stations. And the slags were collected from the loading stations, after being cooled in slag settlers.

The preparation of fly ash and bottom slags consisted in taking 0.5 kg of a representative sample of the material from a 10 kg sample using the Jones divider (Fig. 1, 2).

Fig. 1. Averaging the furnace slags by the sample divider

Fig. 2. Averaging the fly ash by the sample divider

Prepared samples containing fly ashes and bottom slags were determined regarding the dry matter content, and then they were mineralised in the Material Engineering and Environment Laboratory with the use of microwave mineralizers. The obtained solution, as the test material, was then analyzed by means of mass spectrometry with inductively coupled plasma (ICP-MS). The content of each rare-earth element exceeding 5 ppm are presented in (Table 4) [17].

3. Test results and discussion

Industrial heaps, as landfills for waste rock accompanying the mined minerals or as wastes generated during industrial transformation, still contain valuable minerals. In 2019, KOMAG commenced research and development project for estimating the possibility of recovering the rare-earth elements from power plant wastes, after previous grain size analyzes to determine the content of valuable elements. The results of laboratory analyzes are presented in Table 3.

Table 3. Content of rare-earth elements in the tested power plant wastes [19]

Material	Place of obtaining the material	Content of REE [ppm]					
		Scandium (Sc)	Yttrium (Y)	Lanthanum (La)	Cerium (Ce)	Neodymium (Nd)	Europium (Eu)
Fly ashes	Power Plant „A”	**8.8**	**17.3**	**12.0**	<5	<5	**5.1**
Fly ashes	Power Plant „B”	**9.4**	**18.7**	**15.2**	**34.0**	<5	<5
Fly ashes	Power Plant „C”	**9.0**	**17.9**	**12.5**	<5	<5	<5
Furnace slags	Power Plant „A”	<5	**16.2**	<5	**1.9**	<5	**6.7**
Furnace slags	Power Plant „B”	<5	**17.5**	<5	**1.8**	<5	**7.3**
Furnace slags	Power Plant „C”	**8.7**	**29.6**	<5	**26.5**	**7.8**	**9.6**

The following six rare-earth elements were found, with some degree of content variation:

- scandium (Sc) – from 8.7 to 9.4 ppm (the highest concentration – fly ash from the "B" Power Plant),
- yttrium (Y) – from 16.2 to 29.6 ppm (the highest concentration – furnace slags from the "C" Power Plant),
- lanthanum (La) – from 12 to 15.2 ppm (the highest concentration – fly ash from the "B" Power Plant),
- cerium (Ce) – from 13.9 to 34.0 ppm (the highest concentration – fly ash from the "B" Power Plant),
- neodymium – 7.8 ppm (furnace slags from the "C" Power Plant),
- europium – from 5.1 to 9.6 ppm (the highest concentration – furnace slags from the "C" Power Plant).

Content of valuable elements in fly ashes and bottom slags is at a similar level (fly ash – from 5.1 to 34.0 ppm, bottom slag – from 6.7 to 29.6 ppm). Total content of REE in fly ashes is 159.9 ppm, while in bottom slags it is – 160.6 ppm. Considering the level of accumulation of valuable elements due to their origin, their highest share was determined for power plant waste from the "C" Power Plant – 121.6 ppm, slightly lower for the "B" Power Plant – 118.9 ppm and for the "C" Power Plant – 80.0 ppm.

The remaining rare-earth elements (praseodymium, samarium, gadolinium, promethium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium) were not found, their content was <5 ppm.

Comparing the test results with the literature data (Table 1, 2) some disproportions are noticeable, therefore only the elements determined in tests conducted so far were compared in Table 4, 5.

Table 4. Comparison of literature data of REE content in the in power plant ashes with the obtained results

Rare-earth element [ppm]	**REE content in ashes based on the literature data [ppm] [1]**	**REE content in fly ashes based on own tests [ppm]**
Scandium (Sc)	15.6	8.8 – 9.4
Yttrium (Y)	11 – 26.5 (43.8*)	17.3 – 18.7
Lanthanum (La)	16.0 – 86 (56.5*)	12.0 – 15.2
Cerium (Ce)	39.0 – 186.0 (117.6*)	34.0
Neodymium (Nd)	27.0 – 87.0	<5
Europium (Eu)	0.4 – 3.5 (1.74*)	5.1

* fly ashes

Literature data for lanthanum, cerium and neodymium significantly exceed the values given in the presented tests. The scandium concentration is similar to that measured in previous tests, while the content of yttrium is within the given range. The europium content is an exception, as its content exceeds the amount determined so far.

Table 5. Comparison of REE concentration in furnace slags with the obtained results

Rare-earth element [ppm]	REE content in furnace slags based on literature data [ppm] [1]	REE content in furnace slags based on own tests [ppm]
Scandium (Sc)	not determined	8.7
Yttrium (Y)	43.6	16.2 – 29.6
Lanthanum (La)	55.1	<5
Cerium (Ce)	112.2	13.9 – 26.5
Neodymium (Nd)	50.3	7.8
Europium (Eu)	not determined	6.7 – 9.6

In the case of furnace slags, a significant disproportion in the content of rare-earth elements is noticeable. In the analyzes conducted so far, the concentration of yttrium, lanthanum and neodymium was several times higher. In the current analyzes, scandium and europium content was determined, although the elements was not previously found.

It should be emphasized that due to the lack of a full knowledge in the literature regarding the characteristics of the material, the results are only distinctive. Due to some ambiguities in the literature tests, the comparison with own tests is indicative.

4. Conclusions

Based on a literature review, the article shows the economic importance of rare-earth elements. The power plant wastes from three power plants, consisting of fly ashes and bottom slags, after selecting a representative sample, was analyzed using the inductively coupled plasma mass spectrometry method (ICP-MS).

The results were confronted with the results of analyzes carried out so far, but the cognitive method and specificity of the material are not fully known.

The R&D project realized in this area by KOMAG Institute of Mining Technology cover the full spectrum of knowledge regarding the parameters of analyzed material and the cognitive method of analysing the given group of elements.

The highest measured concentration of rare-earth elements in fly ashes and furnace slags oscillate around 30 ppm. Due to low content of REE and lack of possibility of industrial use of power plant wastes (in transport, mining), their economic recovery on an industrial scale is not justified. It has been estimated that the economically justified level of the REE content in power plant wastes is above 1000 ppm [20]. Economic justification depends on energy consumption in extraction/recovery and coal processing.

References

[1] Całus-Moszko J., Białecka B.: Analiza możliwości pozyskania pierwiastków ziem rzadkich z węgla kamiennego i popiołów lotnych z elektrowni. Gospodarka Surowcami Mineralnymi – Tom 29, z.1. Instytut Gospodarki Surowcami Mineralnymi i Energią PAN, Kraków, 2013.

[2] Całus-Moszko J., Białecka B.: Potencjał i zasoby metali ziem rzadkich w świecie oraz w Polsce. Prace Naukowe GIG. Górnictwo i Środowisko – Kwartalnik, Tom 4, s. 61-72. Główny Instytut Górnictwa, Katowice, 2012.

[3] Jaireth, S., Hoatson, D. M., & Miezitis, Y.: Geological setting and resources of the major rare-earth-element deposits in Australia. Ore Geology Reviews, 2014. No 62, 72–128.

[4] Balaram V.: Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact, Geoscience Frontiers, Volume 10, Issue 4, pp. 1285-1303, 2019.

[5] Case M., Fox R., Baek D.,Chien W.: Extraction of Rare Earth Elements from Chloride Media with Tetrabutyl Diglycolamide in 1-Octanol Modified Carbon Dioxide, Metals 2019 No 9 (4), 429.

[6] Charalampides G., Vatalis K. I., Apostoplos B., Ploutarch-Nikolas B.: Rare Earth Elements: Industrial Applications and Economic Dependency of Europe. Procedia Economics and Finance. 2015 No 24, pp. 126 – 135.

[7] Kathryn M. Goodenough K. M.,Wall F., Merriman D.: The Rare Earth Elements: Demand, Global Resources,and Challenges for Resourcing Future Generations, Natural Resources Research. 2018. volume 27, pp. 201–216,

[8] Mariano, A. N., & Mariano, A.:Rare earth mining and exploration in North America, Elements, 2012. No 8(5), 369–376.

[9] Jarosiński A.: Możliwości pozyskania metali ziem rzadkich w Polsce, Zeszyty Naukowe – Tom 92, s. 75-88. Instytut Gospodarki Surowcami Mineralnymi i Energią PAN, Kraków, 2016.

[10] Klich M., Kozłowski J.: Odnawialne źródła energii i gospodarka odpadami oraz ochrona i gospodarowanie zasobami przyrody – wybrane problemy w Polsce s. 23-31, Wydawnictwo Państwowej Wyższej Szkoły Zawodowej w Tarnowie, Tarnów, 2016.

[11] Lai Q. T., Thriveni T., Chilakala R., Hong Ha Thi Vu, Ji W. A., Jeongyun, Leaching K: Characteristics of Low Concentration Rare Earth Elements in Korean (Samcheok) CFBC Bottom Ash Samples, Sustainability 2019. No 11(9).

[12] Kanazawa Y., Kamitani M.: Rare Earth Minerals and Resources in the World. Journal of Alloys and Compounds. 2006. 408-412(19), pp. 1339-1343.

[13] Hordyńska M.: Popioły elektrowniane w procesach stabilizacji odpadów niebezpiecznych. Praca doktorska. Wydz. Inżynieria Materiałowa i Metalurgii, Politechnika Śląska, Katowice, 2003.

[14] Paulo A.: Pierwiastki ziem rzadkich pod koniec XX wieku, Przegląd Geologiczny Tom 47, s. 34-41. Państwowy Instytut Geologiczny, Warszawa, 1999.

[15] Ministerstwo Energii: „Polityka Energetyczna Polski do 2040 r", Warszawa, 2019.

[16] Smarzewski P., Barnat-Hunek D.: Mechaniczne i mikrostrukturalne właściwości betonu wysokowartościowego z dodatkiem żużla paleniskowego, Izolacje 2015 nr. 10.

[17] https://elopole.pgegiek.pl/Technika-i-technologia/Zasada-dzialania-elektrowni [accessed: 30.10.2020]

[18] Zapotoczna-Sytek G., Łaskawiec K. i inni.: Popioły nowej generacji do produkcji autoklawizowanego betonu komórkowego", Monografia, Instytut Ceramiki i Materiałów Budowlanych, Warszawa, 2013.

[19] Baron R.: Określenie zasobności oraz analiza możliwość odzysku pierwiastków ziem rzadkich z popiołów węgla kamiennego oraz odpadów elektrownianych, ITG KOMAG, Gliwice, 2019. (unpublished).

[20] Żukowski W.: Recenzja rozprawy doktorskiej pt. „Ocena możliwości otrzymywania koncentratów metali ziem rzadkich z odpadów energetycznych", Kraków, 2018.

Publisher: KOMAG Institute of Mining Technology, Poland