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# THE CONCENTRATION OF RARE EARTH ELEMENTS IN THE POLISH POWER PLANT WASTES

The article presents the results of laboratory tests determining the concentration of rare earth elements (REE) in coal-burning wastes to assess their economic usefulness. The content of valuable elements was determined by the technique of inductively coupled plasma mass spectrometry (ICP-MS) in the material collected from three regions of southern Poland. A mixture of waste (including fly ash, furnace slag) from heat and power plants using coal for thermal transformation processes was an object for testing. Part of the research project was to identify a share of the rare elements in the collected samples with a selected grain class of <0.045 mm.

**Keywords:** coal burning wastes; rare earth elements (REE); granulometric classification

## 1. Introduction

Rare earth elements (REE) is a group of 17 elements of key economic importance for developing advanced technologies. They have a critical status, awarded by the European Commission for Raw Materials Supply, due to the effects of economic scarcity. They are used, among others, for the production of automotive catalysts, aviation fuselages or hard drives. Commodity market forecasts show a steady increase in the demand for REE, doubling by 2060. Contrary to their name, rare earth elements are not rare in the Earth's crust, but their dispersion makes a problem of their recovery. Due to the high dispersion of rare earth elements, their concentration in the tested material samples is expressed in ppm. The rare earth market is extremely susceptible to changes in the economic situation. The largest deposits of these elements are found in China, the USA and Russia, whilst in European Union countries, including Poland, do not have deposits

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as the exploitation of which is economically justified. It is necessary to identify REE alternative sources to conventional deposits to maintain competitiveness in the global raw material market. In Poland, electrical waste equipment, hard coal, or fly ashes and power plant slags are the sources of REE [1-11].

The production of electricity and heat by burning coal generates a large amount of coal-burning waste. In Poland, approx. annually 20 million tons of waste is produced during the production of electricity and heat. 40% of this waste cannot be reused [12]. In the Silesian Voivodeship alone, there are the following 29 industrial waste landfills:

- landfills of dangerous and neutral wastes – 13,
- landfills of dangerous wastes – 9,
- landfills of asbestos-containing wastes – 4,
- landfills of mine wastes for neutralization – 2,
- landfill of neutral wastes – 1 [13]

The presence of rare earth elements in coal ashes is related to the minerals in the coal, such as biotite, hornblende, kaolinite and muscovite. The share of these minerals in coal directly influences the increase in REE concentration.

Analysis of rare earth elements concentration in fly ashes and furnace slag from three power plants located in the Upper Silesian Industrial District (Tab. 1) showed the presence of 6 REE, with some diversification in their concentrations. Wastages from coal-fired power plants, which to a large extent, had economic usefulness (as an admixture in the concrete production), were the object of analysis [14-17].

TABLE 1

Content of rare earth elements in fly ashes and furnace slags [17]

| **Material** | **REE content [ppm]** | | | | | |
|---|---|---|---|---|---|---|
| | **Scandium (Sc)** | **Yttrium (Y)** | **Lanthanum (La)** | **Cerium (Ce)** | **Neodymium (Nd)** | **Europium (Eu)** |
| Fly ashes – powerplant 1 | 8.8 | 17.3 | 12.0 | <5 | <5 | 5.1 |
| Fly ashes – powerplant 2 | **9.4** | **18.7** | **15.2** | **34.0** | <5 | <5 |
| Fly ashes – powerplant 3 | **9.0** | **17.9** | **12.5** | <5 | <5 | <5 |
| Furnace slags-powerplant 1 | <5 | **16.2** | <5 | **13.9** | <5 | **6.7** |
| Furnace slags-powerplant 2 | <5 | **17.5** | <5 | **16.8** | <5 | **7.3** |
| Furnace slags-powerplant 3 | **8.7** | **29.6** | <5 | **26.5** | **7.8** | **9.6** |

Content of rare earth elements in fly ashes and furnace slag is on the same level varies from 5.1 (europium) to 34.0 ppm (cerium). The total content of valuable elements in fly ashes is 159.9 ppm, while in furnace slag is 160.6 ppm. Content of the remaining elements (praseodymium, samarium, gadolinium, promethium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium) is <5 ppm [17].

Currently, the European Union is implementing numerous projects aimed for greater raw materials independence on the rare earths market. Supporting the activities in developing innovative technologies for the recovery of rare earth elements is the „Horizon" program objective [18]. It is requested to support projects related to the determination of REE content in fly ashes from burning the hard coal and lignite in the European coal-fired power plants.

KOMAG Institute of Mining Technology has the experience recommended by the Polish and foreign contractors in implementing innovative technologies. In connection with plans of energy transformation and departing from coal-based energy, KOMAG has recently developed numerous research projects in determining the concentration of rare earth elements. An example of this is in hard coal products and coal flotation tailings [19,20]. Based on the results of REE concentration in hard coal and the literature knowledge in this field, the Institute undertook research and development work, determining the concentration of valuable elements in coal-burning wastes deposited in heaps. In this project, under the developed sampling methodology, the necessary amount of material determines its suitability in the planned recovery of rare earth elements. Under the confidentiality agreement between ITG KOMAG and the entity managing the material resources, the information on the entity and the sampling sites is confidential.

## 2. Materials and methods

The acquired material, consisting of the mixture of fly ashes, furnace slags and unspecified industrial waste from the selected places of a heap, was collected in the form of 10 kg samples. The sample's origin resulted from the technological processes of power plants, combined heat and power plants, as well as power boilers and other units of energy conversion from coal. The samples were selected from coal-burning waste landfills in the first quarter of 2020 in consultation with the Polish energy tycoon. The location of the heaps covers the vicinity of Krakow (1 sample) and the vicinity of Wrocław (2 samples). Material samples from different mining levels and sampling sites were collected manually from the landfill surface in each heap.

### 2.1. Preparation of raw material for testing

Correct preparation of the raw sample (Fig. 1) is necessary for reliably determining the concentration of rare earth elements in the tested material sample. The preparation of the mixture of power plant waste consisted of selecting the representative 0.5 kg sample using the Jones divider (Fig. 2).

Grains larger than 2 mm in size were crushed using a laboratory crusher to loosen the material and release valuable elements (Fig. 3).

Material samples prepared in this way were the subject of laboratory analys es for determining the REE content.

### 2.2. Preparation of fine fractions for testing

Based on the literature knowledge in determining rare earth elements content, an increased concentration of valuable elements in the smallest grain size classes was found [21]. Therefore, the share of REE in the separated class <0.045 mm was analysed. The desired, narrow grain size

Fig. 1. Raw coal burning waste for testing

Fig. 2. Classification of the material using the sample divider

Fig. 3. Laboratory crusher

class due to the fine-grained nature of the material was obtained by wet particle sieve analysis using the vibration classifier with sieves of a mesh 2 mm and sieves of a mesh 0.045 mm. The 2 mm sieve eliminated the classes with the largest grains, while the 0.045 mm sieve separated the material of the required grain class.

Fig. 4. Wet separation with use of the vibrating classifier

The product fraction in the <0.045 mm class was fed by gravity to a tank, where the solids sunk by gravity in water (sedimentation). The sediment, after filtration, was dried in a laboratory dryer, becoming the material for the laboratory analysis.

### 2.3. Cognitive method

The contents of rare earth elements in the power plant waste were determined at the KOMAG Laboratory of Material Engineering and Environment. The solids content in the sample was determined, followed by the mineralisation process. The wet mineralisation process was carried out in a closed system with the use of microwave mineralisers. The mixture was dissolved to a colourless, clear solution. The content of rare earth elements is determined by the mass spectrometry method with inductively coupled plasma ionisation (ICP-MS). This method measures the intensity of ions stream formed in the plasma, allowing for their separation and detection. The application of this cognitive method results from the fine graining of the material and the diverse chemical composition of the samples [22,23].

## 3. Results

The scope of laboratory analyses, according to the testing procedure and the PN-ISO 11465: 1999 standard, included determining the dry solids content and then determining the REE content in the tested samples (Table 2). Depending on the origin, the following symbols were given to the samples:

P1 – coal burning waste from Wrocław area.
P2 – coal burning waste from Wrocław area.
P3 – coal burning waste from Kraków area.

TABLE 2

Content of REE in coal burning waste

| Sample | REE content [ppm] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| P1 | **Sc** | **Y** | **La** | **Ce** | **Nd** | **Pr** | **Sm** | **Eu** |
| | 32.64 | 20.47 | 6.69 | 9.40 | 28.58 | 9.01 | 21.66 | 10.32 |
| | **Gd** | **Tb** | **Dy** | **Ho** | **Er** | **Tm** | **Yb** | **Lu** |
| | 27.37 | 9.02 | 22.47 | 6.95 | 18.62 | 5.03 | 23.63 | 7.56 |
| P2 | **Sc** | **Y** | **La** | **Ce** | **Nd** | **Pr** | **Sm** | **Eu** |
| | 31.03 | 18.81 | 5.72 | 13.0 | 47.76 | 7.96 | 19.01 | 9.05 |
| | **Gd** | **Tb** | **Dy** | **Ho** | **Er** | **Tm** | **Yb** | **Lu** |
| | 23.79 | 7.97 | 19.75 | 6.23 | 16.45 | 4.56 | 20.91 | 6.73 |
| P3 | **Sc** | **Y** | **La** | **Ce** | **Nd** | **Pr** | **Sm** | **Eu** |
| | 34.40 | 19.80 | 6.34 | 12.5 | 27.92 | 8.90 | 21.50 | 10.54 |
| | **Gd** | **Tb** | **Dy** | **Ho** | **Er** | **Tm** | **Yb** | **Lu** |
| | 27.17 | 9.01 | 22.16 | 6.87 | 18.44 | 4.94 | 23.52 | 7.46 |

According to the adopted standard, the content of rare earth elements in the separated grain class <0.045 mm of the waste from the coal-burning process were also analysed.

TABLE 3

Content of rare earth elements in the separated grain class <0.045 mm of the waste from coal burning process

| Sample | REE content [ppm] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| P1 | **Sc** | **Y** | **La** | **Ce** | **Nd** | **Pr** | **Sm** | **Eu** |
| | 18.88 | <0.1 | 3.50 | 15.14 | 3.57 | 1.54 | 0.97 | 0.85 |
| | **Gd** | **Tb** | **Dy** | **Ho** | **Er** | **Tm** | **Yb** | **Lu** |
| | 1.45 | 0.10 | 1.14 | 0.17 | 0.62 | <0.1 | 0.66 | <0.1 |
| P2 | **Sc** | **Y** | **La** | **Ce** | **Nd** | **Pr** | **Sm** | **Eu** |
| | 17.64 | <0.1 | 3.76 | 28.12 | 6.94 | 2.03 | 0.30 | 1.12 |
| | **Gd** | **Tb** | **Dy** | **Ho** | **Er** | **Tm** | **Yb** | **Lu** |
| | 3.06 | 0.40 | 3.10 | 0.58 | 1.83 | 0.21 | 1.94 | 0.19 |
| P3 | **Sc** | **Y** | **La** | **Ce** | **Nd** | **Pr** | **Sm** | **Eu** |
| | 16.67 | <0.1 | 2.10 | 12.63 | 2.42 | 1.30 | 0.45 | 0.70 |
| | **Gd** | **Tb** | **Dy** | **Ho** | **Er** | **Tm** | **Yb** | **Lu** |
| | 1.19 | <0.1 | 0.98 | 0.14 | 0.51 | <0.1 | 0.55 | <0.1 |

## 3.1. Analysis of the results

The tests of fractions below 0.045 mm using the mass spectrometry technique with ionisation in inductively coupled plasma, showed a diversified content of each rare earth element from power plant waste. From this, sixteen elements were discovered. The amount and concentration of these elements exceeded the contents of the samples, which consisted of fly ashes and furnace slags before classification. For a significant part of the elements, their contents in fine grains class were several times higher. Consequently, the material of lower economic usefulness has a higher potential for economically viable recovery of valuable elements.

### 3.1.1. Results of the REE concentration of the collected material Samales

Analysis of rare earth elements content showed the presence of almost all valuable elements:

- Scandium (Sc) – within the range of 31.03-34.40 ppm.
- Yttrium (Y) – within the range of 18.81-20.47 ppm.
- Lanthanum (La) – within the range of 5.72-6.69 ppm.
- Cerium (Ce) – within the range of 9.40-13.00 ppm.
- Neodymium (Nd) – within the range of 27.92-47.76 ppm.
- Praseodymium (Pr) – within the range of 7.96-9.01 ppm.
- Samarium (Sm) – within the range of 19.01-21.66 ppm.
- Europium (Eu) – within the range of 9.05-10.54 ppm.
- Gadolinium (Gd) – within the range of 23.79-27.37 ppm.
- Terbium (Tb) – within the range of 7.97-9.02 ppm.
- Dysprosium (Dy) – within the range of 19.75-22.47 ppm.
- Holmium (Ho) – within the range of 6.23-6.95 ppm.
- Erbium (Er) – within the range of 16.45-18.62 ppm.
- Thulium (Tm) – within the range of 4.56-5.02 ppm.
- Ytterbium (Yb) – within the range of 20.91-23.52 ppm.
- Lutetium (Lu) – within the range of 6.73-7.56 ppm.

Content of each element, presented in Fig. 5, shows a very similar distribution of REE, regardless of the place of the sample origin.

The highest concentration of rare earth elements was found in sample P2, containing 47.76 ppm of neodymium. The lowest concentration of elements was also recorded in sample P2 – 4.56 ppm of thulium.

The total concentration of all rare earth elements in each sample was the following:

- P1 – 259.4 ppm.
- P2 – 258.7 ppm.
- P3 – 261.5 ppm.

It was estimated that the concentration of REE at 1000 ppm makes their economic recovery possible. The analyses showed that the found valuable elements do not meet the economic recovery conditions.

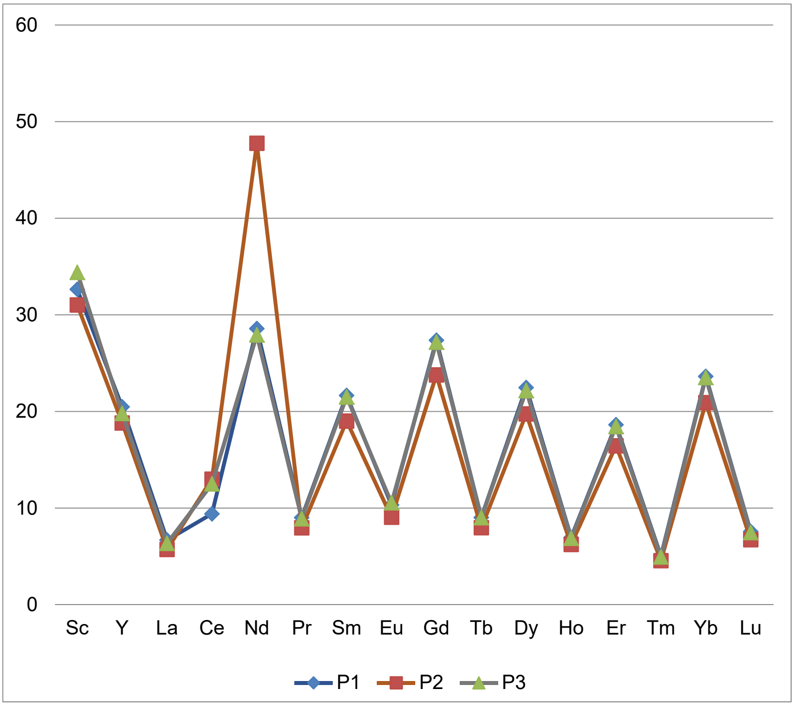


Fig. 5. Concentration of each REE in coal burning waste

### 3.1.2. Results of REE concentration analysis in the selected grain class

Based on the literature knowledge, the REE content in the class <0.045 mm was analysed, and results of the content for each element were as follows:

- Scandium (Sc) – within the range of 16.67-18.88 ppm.
- Yttrium (Y) – <0.1 ppm.
- Lanthanum (La) – within the range of 2.10-3.76 ppm.
- Cerium (Ce) – within the range of 12.63-28.12 ppm.
- Neodymium (Nd) – within the range of 2.42-6.94 ppm.
- Praseodymium (Pr) – within the range of 1.30-2.03 ppm.
- Samarium (Sm) – within the range of 0.30-0.97 ppm.
- Europium (Eu) – within the range of 0.70-1.12 ppm.
- Gadolinium (Gd) – within the range of 1.19-3.06 ppm.
- Terbium (Tb) – within the range of <0.1-0.40 ppm.
- Dysprosium (Dy) – within the range 0.98-3.10 ppm.
- Holmium (Ho) – within the range of 0.14-0.58 ppm.
- Erbium (Er) – within the range of 0.51-1.83 ppm.
- Thulium (Tm) – within the range of <0.1-0.21 ppm.
- Ytterbium (Yb) – within the range of 0.55-1.94 ppm.
- Lutetium (Lu) – within the range of <0.1-0.19 ppm.

The results of the concentration of each rare earth element in the class <0.045 mm (except for scandium and cerium) showed their trace share. Content of each element, is shown in Fig. 6

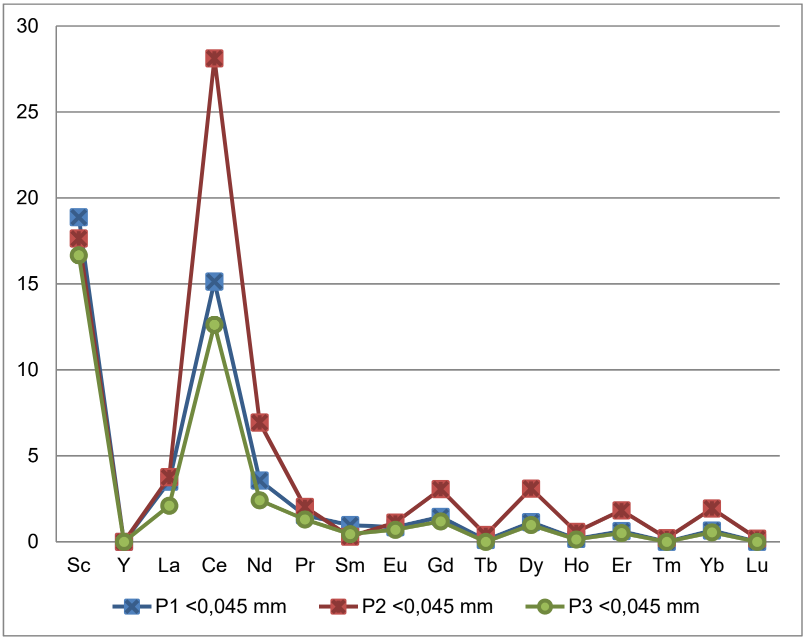


Fig. 6. Concentration of each REE in the separated class <0.045 mm of coal burning waste

Sample P2 had the highest REE concentration, containing 28.12 ppm of cerium, while the concentration of terbium, thulium, and lutetium was <0.1 ppm.

The total concentration of all rare earth elements in each sample for the class <0.045 mm was as follows:

- P1 – 48.6 ppm.
- P2 – 71.2 ppm.
- P3 – 39.6 ppm.

## 3.2. Comparison of the results

When comparing the concentration of rare earth elements in coal-burning wastes, a significant disproportion in their content is noticeable between the sample containing all grain classes and the selected class <0.045 mm (Fig. 7).

In the class <0.045 mm, the content of rare earth elements is much lower compared to the results of the entire sample. The exception is the cerium content, showing increased concentration in the separated fine-grain class.

The presented relationship proves the uneven distribution of rare earth elements in each grain class after the sieve analysis.

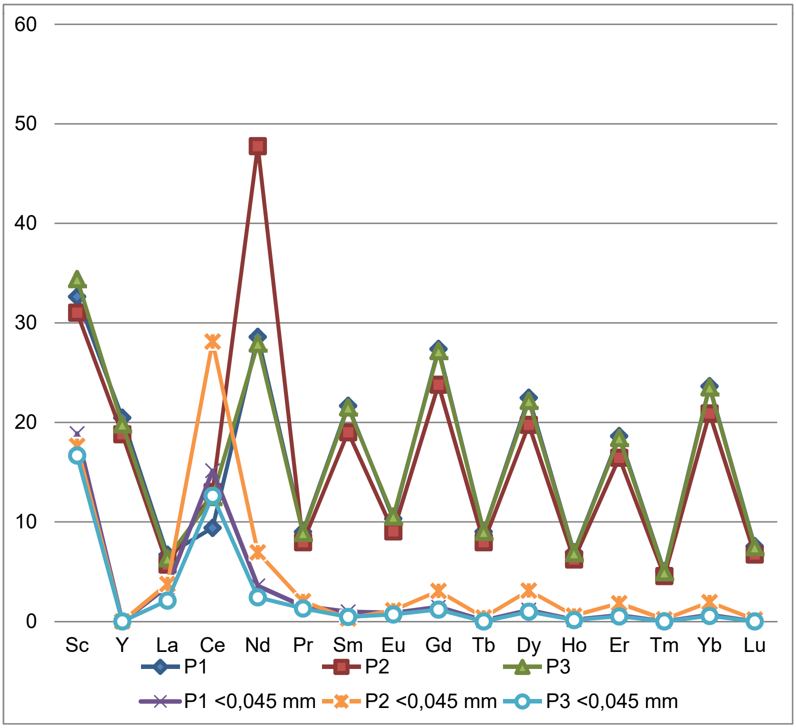


Fig. 7. Comparison of REE content in coal burning wastes in the entire sample and in the separated grain size class <0.045 mm

The total concentration of rare earth elements in the collected samples is very close, oscillating around 260 ppm. The content of valuable elements in the selected classes <0.045 mm of three samples is divergent, differing almost by the concentration fold (the REE concentration in the P3 sample is 44.38% lower than in the P2 sample).

When interpreting the obtained results, it should be assumed that the higher concentration of valuable elements is in the grain classes of higher granulation. Due to the uneven distribution of REE in the selected grain class and the balanced equation, the share of grain classes (>0.045 mm) should be assumed, containing more than 260 ppm (concentration in REE in the raw feed) of valuable elements.

## 4. Discussion

Due to the growing demand and the lack of natural deposits of rare earth elements in Poland, the concentration of elements dispersed in the earth's crust was analysed. Due to the economic usability of energy waste and the proven share of valuable environmental waste in fly ash and furnace slag, waste from power plants was the subject of laboratory analysis.

The applied cognitive method (ICP-MS) determining the content of rare earth elements showed their presence in the waste from power plant heaps. The share of REE in products being a mixture of waste from thermal coal conversion processes is higher than in raw fly ash and furnace slag from power plants. The disproportion in the content of REE between raw material and in the selected class <0.045 mm, in connection with the balance equation, proves an increase in the content of rare earth elements in classes of higher granulation. Therefore the full-grain size samples should be analysed to determine the grain class of the highest content of valuable elements.

## References

[1] A. Jarosiński, Możliwości pozyskania metali ziem rzadkich w Polsce. Zeszyty Naukowe. Instytut Gospodarki Surowcami Mineralnymi i Energią PAN, Kraków, **92**, 75-88 (2016).

[2] Y. Kanazawa, M. Kamitani, Rare Earth Minerals and Resources in the World. Journal of Alloys and Compounds **408-412**, 1339-1343 (2006). DOI: http://dx.doi.org/10.1016/j.jallcom.2005.04.033

[3] M. Kathryn, K. M. Goodenough, F. Wall, D. Merriman, The Rare Earth Elements: Demand, Global Resources, and Challenges for Resourcing Future Generations, Natural Resources Research **27**, 201-216 (2018). DOI: https://doi.org/10.1007/s11053-017-9336-5

[4] V. Balaram, Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. Geoscience Frontiers **10**, 4, 1285-1303 (2019). DOI: https://doi.org/10.1016/j.gsf.2018.12.005

[5] J. Całus-Moszko, B. Białecka, Potencjał i zasoby metali ziem rzadkich w świecie oraz w Polsce. Prace Naukowe GIG. Górnictwo i Środowisko – Główny Instytut Górnictwa, Katowice, **4**, 61-72 (2012).

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

[7] A.N. Mariano, A. Mariano, Rare earth mining and exploration in North America. Elements **8** (5), 369-376 (2012).

[8] S. Jaireth, D.M. Hoatson, Y. Miezitis, Geological setting and resources of the major rare-earth-element deposits in Australia”. Ore Geology Reviews **62**, 72-128 (2014). DOI: https://doi.org/10.1016/j.oregeorev.2014.02.008

[9] G. Charalampides, K.I. Vatalis, B. Apostoplos, B. Ploutarch-Nikolas, Rare Earth Elements: Industrial Applications and Economic Dependency of Europe. Procedia Economics and Finance 2**4**, 126-135 (2015). DOI: https://doi.org/10.1016/S2212-5671(15)00630-9

[10] M. Mehmood, Rare Earth Elements – a Review. Journal of Ecology & Natural Resources **2** (2) (2018). DOI: https://doi.org/10.23880/jenr-16000128

[11] S. Jaireth, D.M. Hoatson, Y. Miezitis, Geological setting and resources of the major rare-earth-element deposits in Australia. Ore Geology Reviews, (62), 72-128 (2014). DOI: https://doi.org/10.1016/j.oregeorev.2014.02.008

[12] M. Stępień, B. Białecka, Inwentaryzacja innowacyjnych technologii odzysku odpadów energetycznych. System Wspomagania w Inżynierii Produkcji. Sposoby i Środki Doskonalenia Produktów i Usług na Wybranych Przykładach **6** (8), 108-123 (2017).

[13] Plan gospodarki odpadami dla województwa śląskiego. Załącznik E, Katowice (2010).

[14] A. Bocheńczyk, M. Mazurkiewicz, E. Mokrzycki, Fly ash energy production – a waste, byproduct raw material. Mineral Resources Management, Kraków **31**, 139-150 (2015). DOI: https://doi.org/10.1515/gospo-2015-0042

[15] R.S. Blissett, N. Smalley, N.A. Rowson, An investigation into six coal fly ashes from United Kingdom and Poland to evaluate rare earth element content. Fuel – the science and technology of Fuel and Energy **119**, 236-239, United Kingdom (2013). DOI: https://doi.org/10.1016/j.fuel.2013.11.053

[16] H. Zhang, Y. Zhao, Study on Physicochemical Characteristics of Municipal Solid Waste Incineration (MSWI) Fly Ash, International Conference on Environmental Science and Information Application Technology **1**, 28-31 (2009). DOI: https://doi.org/10.1109/ESIAT.2009.33

[17] R. Baron, Determination of rare earth elements in power plant wastes. Mining Machines **4**, 24-30 (2020). DOI: https://doi.org/10.32056/KOMAG2020.4.3

[18] https://ec.europa.eu/info/sites/info/files/research_and_innovation/strategy_on_research_and_innovation/presentations/horizon_europe_en_investing_to_shape_our_future.pdf, accessed: 13.04.2021.

[19] R. Baron, Determination of rare earth elements content in hard coal type 31.1. Management Systems in Production Engineering **4**, 240-246 (2020). DOI: https://doi.org/10.2478/mspe-2020-0034

[20] P. Friebe, Tests of neodymium content in selected materials. Mining Machines **2**, 38-47 (2020). DOI: https://doi.org/10.32056/KOMAG2020.2.4

[21] F. Cavalcante, C. Belviso, G. Piccarreta, S. Fiore, Grain-Size Control on the Rare Earth Elements Distribution In the Late Diagenesis of Creataceous Shales from the Southern Apennines. Journal of Chemistry (2014). DOI: https://doi.org/10.1155/2014/841747

[22] A. Ammann, Inductively coupled plasma mass spectrometry (ICP MS): A versatile tool. Journal of Mass Spectrometry **42**, 419-27 (2007). DOI: https://doi.org/10.1002/jms.1206

[23] J.L. Fernandez-Turiel, J.F. Llorens, F. Lopez-Vera, Strategy for water analysis ICP-MS. Fresenius Journal of Analytical Chemistry **368**, 601-606 (2000). DOI: https://doi.org/10.1007/s002160000552