https://doi.org/10.32056/KOMAG2021.3.2

Assessment of rare earth elements content in the material from mine heaps

Received: 06.05.2021

Accepted: 24.06.2021

Published online: 30.09.2021

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Abstract:

The paper contains the results of laboratory tests aimed at determination of rare earth elements (REE) in mine wastes The material for testing was collected from mine heaps located in Lower Silesian Coal Basin (LSCB). Laboratory analyses of the material of different granulation (coal mud and the material of coarser granulation) were conducted with use of inductively coupled plasma mass spectrometry (ICP-MS) method. The tests were an extension of the scope of the projects aimed at searching for valuable elements in waste material from hard coal mining realized at the KOMAG Institute of Mining Technology. Basing on the results of laboratory analyses, the economic viability of the recovery of valuable elements from the mine wastes was formulated.

Keywords: rare earth elements (REE), mine wastes, Lower Silesian Coal Basin.

1. Introduction

Rare earth elements (REE) belong to the group of raw materials of high economic importance, resulting from the perspective of the development of state-of-the-art technologies. The European Union includes REE among the group of 20 critical raw materials in economic terms. According to the analyses of the raw material market experts, the demand for rare earth elements will double by 2060. Due to the lack of deposits with valuable elements, the Community countries are forced to import the raw material. Recovery of REE from waste products an alternative solution is [1,2,3].

Analyses of rare earth elements content indicate for their presence in hard coal. Unfortunately, due to the low concentration, they cannot be an alternative source of REE from economic point of view [4,5]. The described tests were aimed at determining the concentration of REE in mine wastes and at identifying technologies that would allow increasing this concentration to the economically justified level to process them.

1.1. Rare earth elements

Rare earth elements are a group of 17 elements with specific physicochemical properties. They are used in state-of-the-art, advanced technologies. These elements are [6,7,8,9]:

- scandium - aviation,
- lanthanum - automotive industry (batteries of electric vehicles),
- yttrium - ceramics,
- cerium-metallurgy,
- praseodymium - glass dye,
- neodymium - laser technology, magnetic materials,
- samarium - cinematography,
- europium - nuclear technology,
- gadolinium - microwave technique,
- promethium - laser technology,
- terbium - laser technology,
- dysprosium - petrochemical industry,
- holm - electronics,
- erbium - optical amplifiers,
- thulium - materials with significant magnetic susceptibility,
- ytterbium - electronics,
- lutetium - ferrite products.

The term "rare" is misleading as the presence of REE in the earth's crust is common. The problem, however, is their considerable dispersion. The content of REE in a given material, due to its dispersion, is expressed in ppm. Consequently, recovery of rare earths is often economically unjustified. The largest deposits of REE are in China, the USA, Australia, Russia and India. The rare earths raw materials industry is dominated by China, which has 23% of the world's deposits and covers 93% of the world's demand [10,11,12].

Poland, like other countries of the European Union, does not have deposits of rare earth elements, hence the need to identify alternative sources. It is assumed that the following materials have some potential in Poland [1,10,11,13]:

- hard coal and lignite,
- mining industry waste,
- power plant waste (fly ashes and slag),
- mineral resources (sand and gravel),
- electronic waste.

Due to potential content of rare earth elements in mine waste (including the cerium content of 27.2 ppm) [4] and the possibility of giving the degraded post-mining areas economic importance, the KOMAG Institute of Mining Technology realized the research projects in this area (e.g. regarding power plant wastes) [4, 14]. Determination of REE content of in mine waste obtained from the Lower Silesian Coal Basin was this research project objective.

1.2. Mine wastes

For over 100 years, coal mining and coal processing in Poland have been generating significant amounts of mine waste. This type of waste, which includes mined rock with coal, is deposited in heaps, dump sites and sedimentary ponds. Currently, there are 153 such facilities in Poland (Śląskie, Dolnośląskie, Małopolskie and Lubelskie Voivodeships), with an estimated area of 11,304.8 hectares. In 2015-2017, 72,139.0 thousand tonnes of mining waste was generated [15,16,17].

Mining waste poses an environmental hazard by contaminating soil, surface and ground waters and air. The heaps containing a significant share of hard coal also pose a serious threat due to thermal activity. The endogenous fires, resulting from the tendency of hard coal to self-heating, emit fire gases (H_2S, CO, CO_2, SO_2), smoke and odour. Due to the high temperature, loosening the heaps overlayer is possible, causing material slides. It is possible to recultivate and make such objects harmless by recovering the hard coal deposited in them [17].

In connection with the above and rare earth elements found in hard coal, the material for analyses was taken from the thermally active heap located in the Lower Silesian Coal Basin.

2. Materials and Methods

The material for analyses of rare earth elements, came from the heap adjacent to the closed LSCB mine in Nowa Ruda. The mine exploited lean coal and anthracite coal deposits [16]. The heap has a significant content of hard coal, what was confirmed by numerous endogenous fires. The material being the subject of laboratory analyses was collected on June 16, 2020, from three selected locations on the heap (Fig. 1).

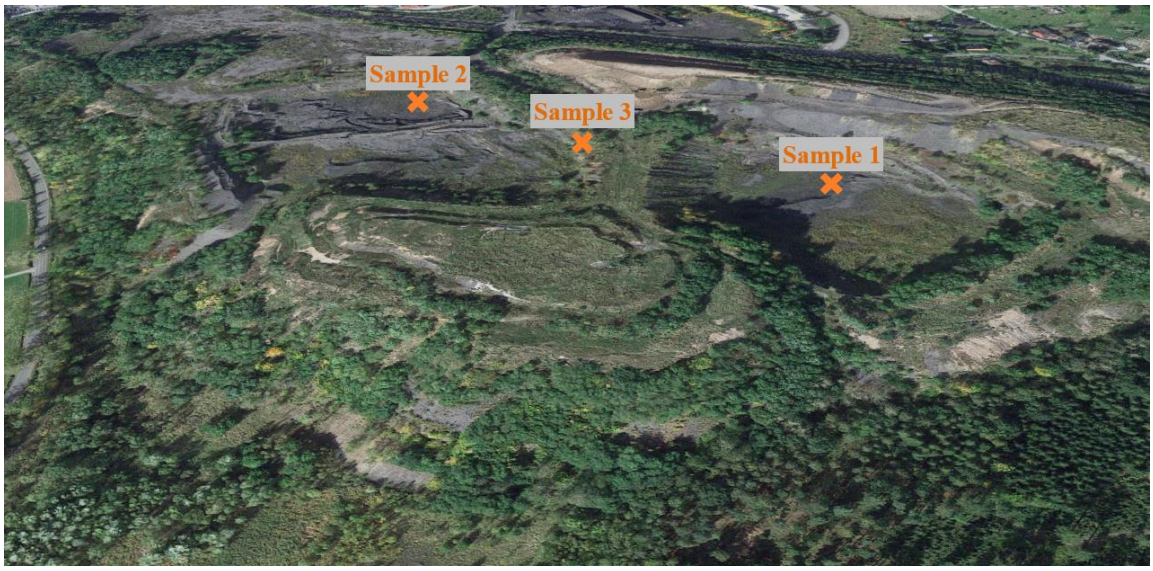

Fig. 1. Place of sampling the material from the heap [own source]

About 10 kg of material were collected from each of the three sampling points. The location in the heap and the characteristics of the collected material were as follows:

- sample 1 – mud in the upper part of the heap (Fig.2),
- sample 2 – mud in the lowest part of the heap (Fig.3),
- sample 3 - material taken from the vertical slope in the lower part of the heap (Fig.4).

The collected samples were transported to KOMAG for analysis of rare earth element content.

Fig. 2. "Nowa Ruda" heap – mud collected from the upper layers of the heap [own source]

Fig. 3. "Nowa Ruda" heap – mud collected from the lower layers of the heap [own source]

Fig. 4. "Nowa Ruda" heap – material taken from the slope [own source]

Due to the significant amount of water content in the mud, the first stage of preparatory work consisted in drying the samples 1 and 2 in a laboratory dryer (Fig. 5). Sample 3 taken from the slope of the heap, due big size of grains, was crushed in a laboratory crusher to the granulation of sand (Fig. 6). Necessity of crushing results from the requirements of the device determining the content of valuable elements.

Fig. 5. Laboratory dryer [own source]

Fig. 6. Laboratory crusher [own source]

Then the representative sample of 0.5 kg of the material for testing was selected using the sample divider (Fig.7).

Fig. 7. Jones sample divider (own source)

3. Results

Rare earth elements content in the tested samples was determined using the inductively coupled plasma mass spectrometry (ICP-MS) method. The IPC-MS spectrometer enables fast multi-element analysis of the tested material sample. The samples were mineralized prior to testing. Resulting solution was entered to plasma using the laser beam to verify share of REE in the analysed samples [18].

The results given in Table 1 were obtained using the developed testing procedure [19].

Table 1. Content of REE in the tested mining waste [19]

Item	REE content [ppm]							
1	Sample 1 (P1)							
	Sc	**Y**	**La**	**Ce**	**Nd**	**Pr**	**Sm**	**Eu**
	33.49	<1	7.52	14.0	29.03	9.23	21.56	10.34
	Gd	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
	27.03	9.15	22.29	7.13	18.55	5.28	23.36	7.70
2	Sample 2 (P2)							
	Sc	**Y**	**La**	**Ce**	**Nd**	**Pr**	**Sm**	**Eu**
	40.49	<1	7.38	19.1	29.14	9.69	22.34	10.64
	Gd	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
	27.93	9.55	22.99	7.54	19.13	5.56	24.13	8.19
3	Sample 3 (P3)							
	Sc	**Y**	**La**	**Ce**	**Nd**	**Pr**	**Sm**	**Eu**
	20.96	<1	4.56	38.4	17.91	5.82	13.54	6.50
	Gd	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
	16.99	5.77	13.81	4.50	11.56	3.26	14.63	4.87

The laboratory analyses showed the presence of 15 rare earth elements. Distribution of each REE in the tested material samples is similar. The highest content of REE was found in sample P2, containing 40.49 ppm of scandium.

Content of all rare earth elements in the analysed samples is as follows:

- P1 – 245.7 ppm,
- P2 – 263.8 ppm,
- P3 – 183.1 ppm.

Based on the literature analysis indicating for increased concentration of rare earth elements in the finest grain class <0.045 mm [20], this separated grain size class was additionally analysed to verify the literature information.

A set of two sieves with 2 mm mesh size and 0.045 mm mesh size were used for material classification. Due to the fine-granulation of the material, the grain class <0.045 mm was separated in water medium using the vibrating classifier (Fig. 8).

Fig. 8. Wet vibrating classifier (own source)

The suspension, containing grains <0.045 mm, was transported by gravity to a tank for sedimentation. The clarified water was pumped out, and the material from the bottom of the tank was dried in a laboratory dryer. The material prepared in this way was then analysed to determine the content of rare earth elements.

Contrary to the expectations in the selected fine grain class, there was a decrease in the content of each rare earth element and a smaller number of elements, reduced to 13 (Table 2).

Table 2. REE content in tested mine waste for grain size classes <0.045 mm [19]

Item	REE content [ppm]							
1	Sample 1 (P1)							
	Sc	**Y**	**La**	**Ce**	**Nd**	**Pr**	**Sm**	**Eu**
	18.68	<0.1	2.00	8.39	2.60	1.31	0.75	0.82
	Gd	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
	1.30	0.11	1.42	0.24	0.88	<0.1	0.99	<0.1
2	Sample 2 (P2)							
	Sc	**Y**	**La**	**Ce**	**Nd**	**Pr**	**Sm**	**Eu**
	14.73	<0.1	2.07	9.75	2.19	1.23	0.56	0.66
	Gd	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
	1.02	<0.1	0.89	0.14	0.51	<0.1	0.52	<0.1
3	Sample 3 (P3)							
	Sc	**Y**	**La**	**Ce**	**Nd**	**Pr**	**Sm**	**Eu**
	15.23	<0.1	2.89	15.49	2.34	1.28	0.65	0.89
	Gd	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
	1.19	<0.1	0.94	0.15	0.55	<0.1	0.59	<0.1

Content of each element is very similar, reaching the maximum for scandium in sample 1 (18.68 ppm).

Total content of REE in the analyzed samples in the grain class <0.045 mm is as follows:

- P1 – 39.5 ppm,
- P2 – 34.3 ppm,
- P3 – 42.2 ppm.

4. Results

Increased content of REE in samples P1 and P2 probably results from the washing out of these elements from the adjacent slope, so the concentration of REE in the slope is 60-80 ppm lower. Content of each rare earth element in the analysed samples are presented in Fig. 9.

Content of rare earth elements in the class <0.045 mm for mine waste is not as high as for the samples before classification (Fig. 10).

In the finest grain class, scandium and cerium makes the majority of all determined REE.

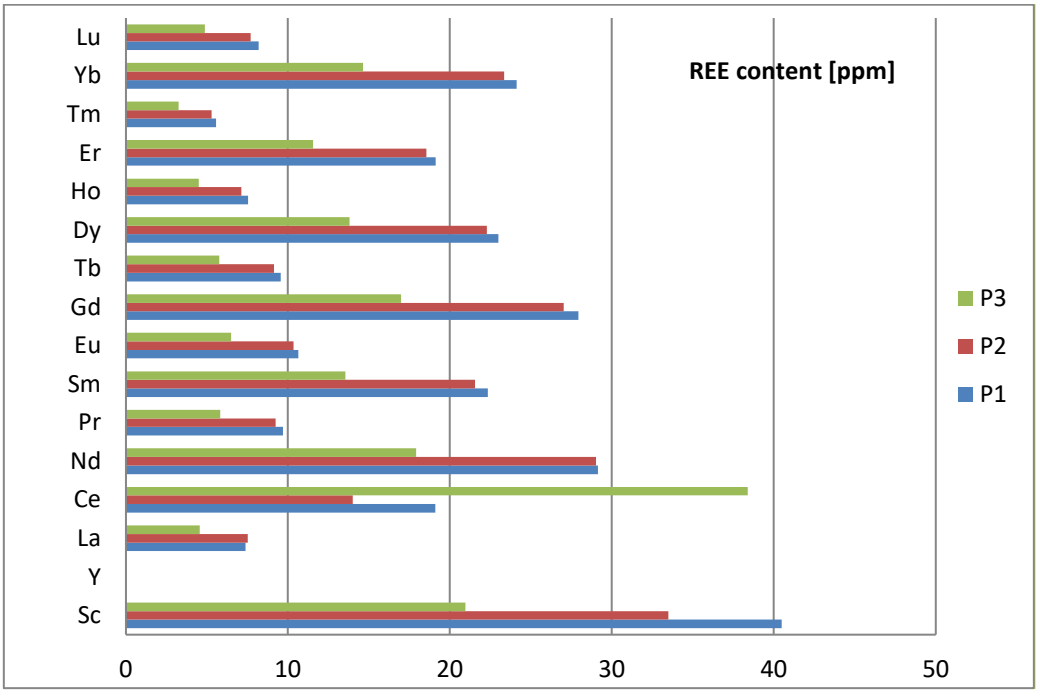

Fig. 9. Content of each rare earth element in the tested mine waste [own source]

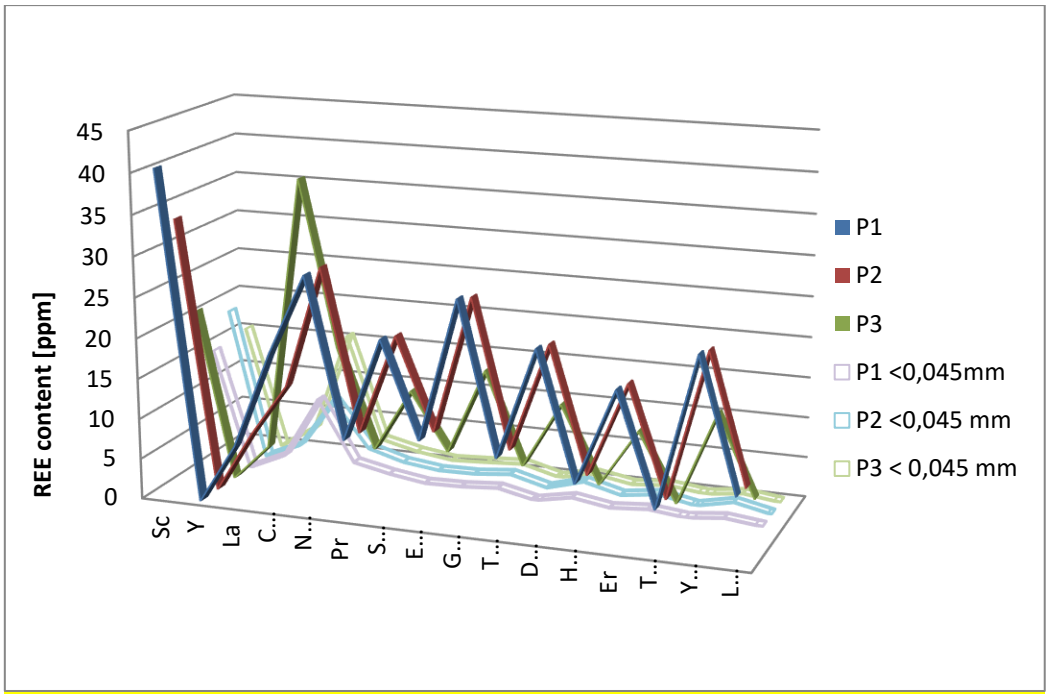

Fig. 10. REE content in the tested mining waste, depending on the grain size distribution of the samples [own resource]

5. Conclusions

Research and development work related to determination of the REE content in mine waste from the heap located in Nowa Ruda, allowed for establishing cooperation, resulting in the acquisition of materials for testing. Preparation of materials, combined with the developed methodology for determining the content of valuable elements in the material with the use of a spectrometer (ICP-MS), allowed to determine the share of the REE in mine waste samples.

The paper shows that mining waste, which has no economic use, is a carrier of rare earth elements.

The content of valuable elements (about 260-180 ppm) in the collected samples, when compared with the estimated level for economic REE recovery (about 1000 ppm) [21], is, however, unsatisfactory. The REE content, for the grain class <0.045 mm, showed a decrease (about 40 ppm), contrary to the literature knowledge. The discrepancy shown indicates a different content of elements, depending on the grain size class of the material and its origin.

Therefore, the range of grain classes of the tested mining waste will be analyzed in the further part of the work on REE to determine the grain class with the highest REE content. Determination of such a grain class, if the economic condition is met, will allow for the management of devastated post-mining areas and for creating an alternative source of rare earth elements in Poland.

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