Results of Pilot Research Work on the Content of Rare Earth Elements in Metallurgical Wastes from Nowa Huta

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Abstract

The article presents the results of analyses of the content of rare earth elements in Nowa Huta's metallurgical wastes deposited in two sedimentation tanks. These studies were undertaken due to strategic importance of the rare earth elements in development of state-of-the-art technologies. The waste materials were analysed using the inductively coupled plasma ionization mass spectrometry technique – ICP MS. The tests showed that the collected materials contain rare earth elements. The cumulative content of these elements in the samples was found to be slightly above 140 ppm. The article also presents proposals for further, in-depth tests of Nowa Huta's metallurgical waste.

Keywords: *rare earth elements (REE), metallurgy, metallurgical waste*

1. Introduction

Metallurgical waste dump sites are contaminated with heavy metals posing a threat to both humans and the ecosystem. The group of heavy metals includes such elements as: lead, cadmium, chromium, nickel, mercury and arsenic. In small amounts, they are necessary for life processes, while long-term exposure to hem is associated with negative health effects, such as cancer, organ damage, or changes in the circulatory system. Therefore, it is necessary to neutralize this type of dump sites [1,2,3,4].

Content of REE in the tested material samples collected from Nowa Huta waste dump site was initially analyzed to determine possibility of using the metallurgical waste materials in industrial processes. Consumption of rare earth elements, due to their economic importance, is constantly growing, with a projected doubling by 2060 [5,6]. Due to the lack of natural sources of REE in Poland, the KOMAG Institute of Mining Technology made an attempt to recover valuable elements from metallurgical waste.

Correlation between the content of heavy metals and content of REE in waste dump sites was assumed. Analyzes of usefulness of power plant and mining wastes, in the perspective of recovery of REE from this type of materials, have shown a potential of REE content [7-11].

The share of REE in samples of materials from settling tanks, which are metallurgical waste dumps is specified.

2. Rare earth elements – realization of R&D work

REE is a group of 17 valuable elements important in development of state-of-the-art technologies. Due to their physicochemical properties, they are widely used in many innovative industries [12-14]: REE is a group of 17 valuable elements important in the development of state-of-the-art technologies:

- cerium (Ce) – metallurgy, analytical chemistry,
- dysprosium (Dy) – petrochemical industry,
- erbium (Er) – lasers,
- europium (Eu) – liquid crystal displays,
- gadolinium (Gd) – CRT screens,
- holm (Ho) – nuclear technology,
- ytterbium (Yb) – optical fibers,
- yttrium (Y) – ceramics,
- lanthanum (La) – hybrid vehicles,
- lutetium (Lu) – roentgen luminophores,
- neodymium (Nd) – strong magnets,
- praseodymium (Pr) – glass colouring,
- promethium (Pm) – source of Beta radiation,
- samarium (Sm) – nuclear reactor rods,
- scandium (Sc) – aviation industry,
- terbium (Tb) – diodes,
- thulium (Tm) – magnetic materials.

REE are not rare regarding the average content in Earth's crust, but their concentrated deposits are limited. The largest concentrated deposits of REE are in China, the USA, Russia and Australia. The European Union, including Poland, in its natural resources, do not have deposits of enough concentration of REE. In Poland, the source of rare earth elements are natural resources (coal, sand and gravel) and waste (waste electronic equipment, mining and metallurgical waste) [15,16]. In view of the above and the assumed correlation of REE content with heavy metals content, a research work defining the content of REE in metallurgical waste was realized.

2.1 Collection of materials for tests

The samples were collected from the wastes after production of steel, from the sedimentation pond located in Nowa Huta in Krakow containing the following by-products from the blast furnace process [4]:

- slags,
- blast furnace gases,
- blast furnace sludge,
- blast furnace dust.

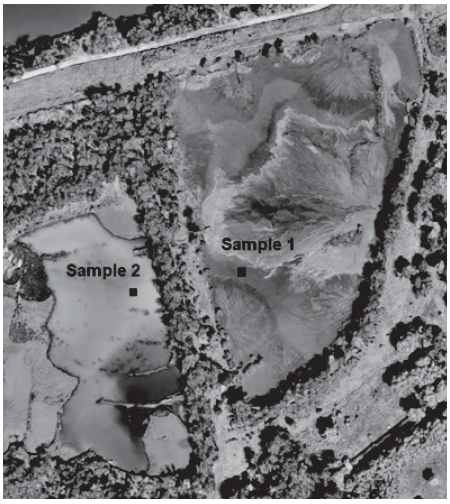

Fig. 1. Settling ponds with marked samples collecting points (own report)
Rys. 1. Widok stawów osadowych z zaznaczonymi miejscami poboru próbek (opracowanie własne)

Fig. 2. Place of collecting the sample 1 (own report)
Rys. 2. Widok miejsca poboru próbki 1 (opracowanie własne)

Fig. 3. Place of collecting the sample 2 (own report)
Rys. 3. Widok miejsca poboru próbki 2 (opracowanie własne)

On 10.06.2020 samples were taken manually from randomly selected points of two sedimentation ponds (Fig.1):

- Sample 1 – Pulp sample from the sedimentation pond 1 (Fig.2).
- Sample 2 – Pulp sample from the sedimentation pond 2 (Fig.3).

The material was collected at points approximately 25 cm deep from the surface of the settling tanks. The collected samples had a pulp consistency with a predominance of solids. 10 kg of material were collected from each of the two sedimentation ponds. The material placed in the bags was then transported to the KOMAG Institute of Mining Technology for determination of valuable elements content.

2.2 Preparation of the material

Before analysis of the chemical composition of collected material, it is important to properly prepare the samples. The material, which was analyzed with the ICP-MS spectrometer, should be standardized.

The pulp-like material was dried in a laboratory dryer (Fig. 4), and then averaged with a Jones divider (Fig. 5) to extract 0.5 kg of a representative sample.

Inductively coupled plasma mass spectrometry method (ICP-MS) was used to determine the content of REE in the analyzed representative sample. The used IPC-MS spectrometer enables fast, elemental analysis of the tested material sample. Before analysis, the samples were mineralized and dissolved, then the solution was introduced into the plasma to verify REE content [17].

2.3 REE content in metallurgical waste

The scope of analysis included determination of the dry matter content (> 99%) in accordance with the PN-ISO 11465: 1999 standard and determination of the REE content according to the testing procedure (Tab. 1).

Laboratory tests showed the presence of almost all-15 REE (except yttrium). Content of each element in the tested material samples is almost identical. The highest content of REE was determined in sample P1, containing 17.26 ppm of neodymium.

Total content of REE (Figure 6) in metallurgical waste samples is as follows:

- P1 – 147.4 ppm,
- P2 – 142.3 ppm.

When analyzing the REE content curves for samples of metallurgical waste from two settling ponds (Fig. 7), despite

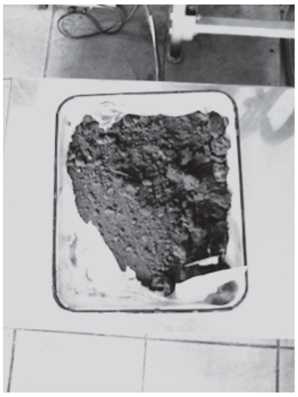

Fig. 4. Dried metallurgical waste (own report)
Rys. 4. Wysuszony odpad metalurgiczny (opracowanie własne)

Fig. 5. Jones divider (own report)
Rys. 5. Dzielnik Jones`a (opracowanie własne)

Tab. 1. Content of rare earth elements in metallurgical waste [18]
Tab. 1. Zawartość pierwiastków ziem rzadkich w odpadach metalurgicznych [18]

Item	Sample	Content of rare earth elements [ppm]							
1	Sample 1 (P1)	**Sc**	**Y**	**La**	**Ce**	**Nd**	**Pr**	**Sm**	**Eu**
		16,40	<1	3,91	13,0	17,26	5,39	13,15	5,91
		Gd	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
		16,29	5,39	13,57	4,10	11,26	2,91	14,35	4,51
2	Sample 2 (P2)	**Sc**	**Y**	**La**	**Ce**	**Nd**	**Pr**	**Sm**	**Eu**
		15,51	<1	3,62	12,5	16,76	5,18	12,81	5,70
		Gd	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
		16,08	5,17	13,20	3,90	10,89	2,76	13,92	4,33

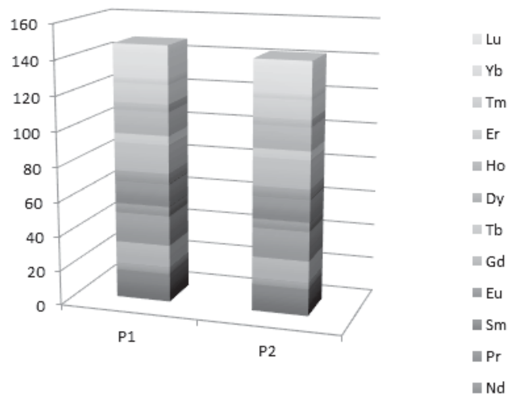

Fig. 6. Concentration of all REE in the samples (own report)
Rys. 6. Koncentracja wszystkich REE w próbkach (opracowanie własne)

the organoleptic difference (different colour of material from the settling ponds 1 and 2), an almost identical content of each element can be observed. It is concluded that metallurgical waste with very similar characteristics was/is transported to both settling ponds in Nowa Huta.

3. Conclusions

During this R&D work, content of REE in the samples of metallurgical waste from the settling ponds in Nowa Huta was determined. These results are the complementation of the previous research work realized at the KOMAG Institute of Mining Technology on REE content in the mining or power plant wastes as the another group of materials being an alternative source of REE in Poland. The intention was to give the deposited waste material a new economic significance.

The content of valuable elements (about 140 ppm) in the analysed waste material, using the method of sampling and testing, does not economically justify exploitation of these deposits, the objective of which would be the recovery of RRE. Nevertheless, further, in-depth research work on the material from these sedimentation tanks seem to be interesting too. As part of future work, the tests should be extended by including the material collected in several places of the settling pond and from a much greater depth. This material should be

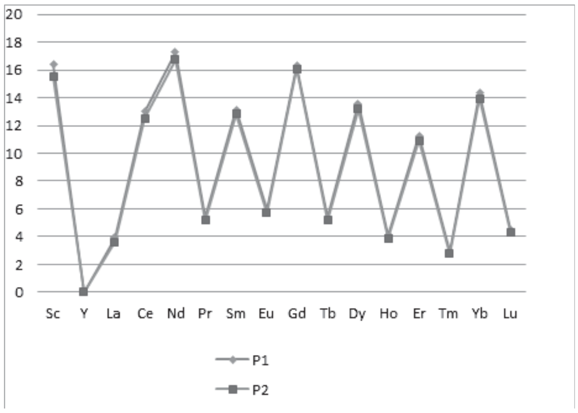

Fig. 7. Content of each REE in the samples (own report)
Rys. 7. Koncentracja poszczególnych REE w próbkach (opracowanie własne)

grain classified and different grain classes should be tested. The research work should also be extended by magnetic and electrostatic classification to determine the susceptibility of REE to classification in the magnetic field and electrostatic interactions.

In the case of higher content of REE (above 1000 ppm – economic profitability threshold [19]) resulting from planned processing, there is a possibility of economically justified recovery of REE.

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Wyniki badań pilotażowych zawartości pierwiastków ziem rzadkich w odpadach metalurgicznych Nowej Huty

W artykule przedstawiono wyniki analiz zawartości pierwiastków ziem rzadkich w odpadach metalurgicznych Nowej Huty zdeponowanych w dwóch osadnikach ziemnych. Badania te podjęto w związku znaczeniem strategicznym pierwiastków ziem rzadkich (REE) w perspektywie rozwoju nowoczesnych technologii. Analizy laboratoryjne pozyskanych odpadów przeprowadzono z zastosowaniem techniki spektrometrii mas z jonizacją w plazmie indukcyjnie sprzężonej – ICP MS. Przeprowadzone badania wykazały, że w pobranych materiałach znajdują się pierwiastki ziem rzadkich. Stwierdzono, że kumulatywna zawartość tych pierwiastków w próbkach wynosi nieco powyżej 140 ppm. W artykule przedstawiono również propozycje dalszych, pogłębionych badań odpadów metalurgicznych Nowej Huty.

Słowa kluczowe: *pierwiastki ziem rzadkich (REE), metalurgia, odpady metalurgiczne*