DETERMINATION OF RARE EARTH ELEMENTS CONTENT IN HARD COAL TYPE 31.1

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Abstract:
The aim of the article is to present the results of laboratory analyses determining the content of rare earth elements (REE) in hard coal type 31.1. Coal was extracted directly from the mining excavation located in the Upper Silesian Coal Basin. Mass spectrometry tests with ionization in inductively coupled plasma (ICP-MS), were aimed at the quantitative analysis of the share of REE in coal, taking into account the economic aspects of recovery of these elements. Fine ground hard coal samples and ashes obtained after coal burning were assessed for the rare earth elements concentration. Results of the rare earth elements concentration (lanthanum and cerium) in hard coal are similar in the values obtained in previous tests. The current analyses present higher concentration of europium or neodymium. The article also contains the concept of possible future research work, consisting in the recovery of rare earth elements using, among others, a classifying hydrocyclone.

Key words: mining industry, processing of hard coal, rare earth elements (REE)

INTRODUCTION
Rare earths elements are of strategic economic importance, in the aspect of a development of state-of-the-art technologies. The demand for REE increases every year with a development of new technologies. Currently conducted fragmentary tests on the content of rare earths elements in Polish hard coal, showed the content of valuable metals in coal. A full range of the carbon chain for hard coal is divided into the following types due to physical and chemical properties, and hence technological usability:

- type 31 – cannel coal,
- type 32 – gas-cannel coal,
- type 33 – gas coal,
- type 34 – gas-coking coal,
- type 35 – ortho- coking coal,
- type 36 – meta- coking coal,
- type 37 – semi- coking coal,
- type 38 –loan coal,
- type 41 – anthracite coal,
- type 42 – anthracite,
- type 43 – meta-anthracite [12, 22].

Analyses at all the stages of the carbon chain starting from the youngest coal of type 31 are required to determine the REE concentration in hard coal. In connection with the above, the KOMAG Institute of Mining Technology has undertaken research and development work consisting in assessing the rare earth elements abundance in hard coal, starting from hard coal type 31.1.

LITERATURE REVIEW
Despite the name these elements are not rare, but their high dispersion is a problem. That is why, in many cases their recovery is not economically justified. REE is a group of 17 elements, which due to their specific physical and chemical properties are used in many branches of industry. The examples of their use are given below [1, 4, 7]:

- scandium (Sc) – aviation industry, construction of planes and radiotherapy,
- lanthanum (La) – optical products, hybrid vehicles,
- yttrium (Y) – ceramics, metal alloys,
- cerium (Ce) – metallurgy, dye for china, analytic chemistry,
- praseodymium (Pr) – dye for glass and stones,
- neodymium (Nd) – laser technology, magnetic materials,
- samarium (Sm) – cinematography, nuclear technology,
- europium (Eu) – nuclear engineering,
- gadolinium (Gd) – alloys admixture, microwave technology,
- promethium (Pm) – source of Beta radiation,
- terbium (Tb) – lasers, diodes,
- dysprosium (Dy) – petrochemical industry,
- holmium (Ho) – nuclear technology, electronics,
- erbium (Er) – optical amplifiers,
- thulium (Tm) – magnetic materials,
- ytterbium (Yb) – micro-electronics,
- lutetium (Lu) – manufacture of ferrites.
China, USA, Russia, India and Australia have the REE deposits, whose exploitation is economically justified [11, 13, 14, 16]. Global REE production remains at around 139 thousand Mg and is largely dominated by China, which has 23% of the world resources and covers 93% of the world demand for rare earth elements [3, 4, 12]. Poland does not have deposits of rare earth elements, thus the following natural raw materials, secondary and waste materials are potential sources of these elements [4, 19]:
- hard coal,
- post-mining wastes,
- ashes and slags from power plants,
- sand and gravel deposits,
- scrapped electronic equipment.

RARE EARTH ELEMENTS IN THE POLISH HARD COAL
Content of REE in hard coal is a result of presence of such minerals like kaolinite, biotite, hornblende and muscovite. According to the fragmentary tests of Polish hard coal from the Upper Silesian Coal Basin and the Lublin Coal Basin, it was proved that this raw material is a carrier of rare earths elements. According to the conducted tests, the coal from the Upper Silesian Industrial District has a high cerium content (2.05-108.0 ppm) compared to the global average content (23.0 ppm). A significant content of lanthanum (1.5-33.6 ppm) and scandium (1.5-20.5 ppm) was found in the coal from the Lublin Coal Basin [3, 12]. The current tests confirm the presence of rare earth elements in hard coal (Table 1).

Laboratory analyses of power plant wastes from the combustion of hard coal show a significant content of rare earth elements, exceeding the concentration of these elements in coal even by several times. A relatively high accumulation of cerium (39.0-186.0 ppm) or lanthanum (16.0-86.0 ppm) was determined [10]. Due to big hard coal resources and lack of rare earth elements deposits in Poland, research work was undertaken to determine the sources and possibilities of REE recovery from hard coal. The taken coal samples will also be used to determine the concentration of rare earth elements in ashes obtained in the combustion process in accordance with the compulsory standard. At the moment, the recovery economic aspect of these elements from hard coal is difficult to predict [3, 12].

| Region | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Th | Yb | Lu | Sc | TREE |
|--------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|------|
| Mine Sołonica Makoszowy seam 405 | nd | 78.0-100 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 17.8-20.0 |
| Mine Biskupice seam 405 | nd | 84.0 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 13.5 |
| Mine Chwaliszowice seam 405 | nd | 65.0-68.0 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 11.2-12.7 |
| Mine Jankowice seam 405 | nd | 63.0-66.0 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 10.6-12.4 |
| Poland Coal Mine Pociągw | 6.79 | 14.64 | 1.75 | 7.39 | 1.68 | 0.38 | 1.59 | 0.26 | 1.40 | 0.26 | 0.73 | 0.10 | 0.60 | 0.09 | 2.80 | 40.34 |
| Poland Coal Mine Zamořany | 8.41 | 28.82 | 1.63 | 6.19 | 1.28 | 0.28 | 1.16 | 0.19 | 1.06 | 0.21 | 0.60 | 0.09 | 0.56 | 0.09 | 3.42 | 39.63 |
| Poland Coal Mine Jankowice | 14.58 | 2.53 | 3.28 | 12.93 | 2.75 | 0.58 | 2.22 | 0.35 | 1.91 | 0.37 | 1.08 | 0.16 | 1.03 | 0.16 | 6.81 | 77.02 |
| Poland Coal Mine Bystrzyca | 1.06 | 7.0 | 0.3 | 1.37 | 0.36 | 0.09 | 0.41 | 0.07 | 0.44 | 0.09 | 0.26 | 0.04 | 0.22 | 0.03 | 0.86 | 8.13 |
| Poland Coal A | 3.5 | 2.0 | nd | 3.0 | 0.7 | nd | 0.6 | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Poland Coal B | 0.8 | nd | nd | nd | nd | 0.4 | 0.5 | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| LZW seam 378 | 7.72-23.37 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 8.45-20.56 |
| LZW seam 382 | 7.67-14.31 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 6.86-13.83 |
| LZW seam 383 | 4.07-13.58 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 4.75-12.49 |
| LZW seam 387 | 21.59-32.47 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 5.50-8.76 |
| LZW seam 389 | 0.17-19.09 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 4.25-9.38 |
| LZW seam 391 | 3.70-4.46 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 1.54-7.24 |
| LZW seam 394 | 1.54-11.24 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 4.09-7.00 |
| World | 11.0 | 23.0 | 3.5 | 12.0 | 2.0 | 0.47 | 2.7 | 0.32 | 2.1 | 0.54 | 0.93 | 0.31 | 1.0 | 0.2 | nd | 60.07 |

Source: [3].
TESTING MATERIALS AND METHODS

Hard coal type 31.1 (cannel coal), from a mine located in the Upper Silesian Coal Basin was the subject of laboratory analysis aimed at determining the concentration of rare earth elements. This type of coal, used for a combustion in industrial and domestic furnaces, is the first link of the carbon chain. In Poland coal seams of this type are deposited at relatively low depths, about 300 m. It has a high content of volatile matter and lack or poor sintering ability.

Characteristics of material

Coal samples for testing were taken directly from the geologically recognized seam, possibly from the lowest mining level, to determine the REE abundance in the newly opened deposit. The weight of the taken sample was about 50 kg.

Coal samples were taken manually from randomly selected locations along the entire length of the longwall panel to provide a representative sample characterizing the entire seam. Coal samples were taken from two seams being exploited in the mine.

Characteristics of the seams, from which the samples were taken:

- Sample 1: coal type 31.1 (cannel coal), seam 301 in the part “Podłęże S”, thickness – 2.2 – 2.7 m, depth of mining operations – from 288 to 335 m, date of taking the sample – 01.04.2019.
- Sample 2: coal type 31.1 (cannel coal), seam 212 in the part “Wschód”, thickness – 2.9 – 4.2 m, depth of mining operations – from 540 to 712 m, date of taking the sample – 01.04.2019 [25].

Preparation of samples for laboratory tests

A preparation of coal for testing consisted in selecting the representative sample of 0.5 kg from the 50 kg seam sample (Fig. 1), using a sample divider (in the case of coal lumps larger than the gap of the divider it was necessary to crush them first).

Fig. 1 Selected sample

The obtained coal sample of 0.5 kg was then crushed in a laboratory crusher (Fig. 2), to obtain grains below 2 mm in size.

Apart from the coal testing the ash, obtained after its combustion, was also analysed.

A preparation of the representative sample of ash consisted in crushing separated lumps of coal in a laboratory crusher, then milling it in a ring mill (Fig. 3). A preparation of the fine granulation material results from the standards for a sample combustion, to obtain hard coal ashes.

Fig. 2 Laboratory crusher

Then 10 crucibles were prepared and filled with 2 g of finely ground coal in each one, weighted on a laboratory scale. They were placed in the PM-6/1100A (Fig. 4) laboratory chamber furnace to obtain about 1-2 g of ash after burning. The coal was burnt in the laboratory furnace, according to the Standard PN-ISO 1171:2002 [26].

Fig. 3 Cylindrical – roller mill

Fig. 4 Laboratory furnace PM-6/1100A
The next part of the article presents the results of the analyses determining the REE concentration, included in the first stage of the task, consisting in the recovery of rare earth elements from hard coal.

Tested coal had a low ash content (Table 2).

Such a preparation of hard coal and ash samples, after hard coal combustion, enabled to conduct laboratory analyses determining the content of rare earth elements in the tested samples.

In the tested ashes, the highest content of REE was obtained for neodymium (33.6 ppm) and slightly lower for yttrium (32.3 ppm) and scandium (31.3 ppm).

Comparing the REE contents, determined in hard coal and hard coal ashes, an increase in concentration of specific elements and other valuable elements after the thermal processing is noticeable. Ashes have higher content of several elements. And so, for example: in the sample 2 the highest content was obtained for cerium (27.2 ppm), while the concentration of yttrium and europium for both seam samples were very similar.

In Table 4, the REE contents (> 5 ppm) for ashes obtained after burning the hard coal samples, are given.

In Table 5, the REE contents (> 5 ppm) for ashes resulting from the combustion of coal samples, are compared with the REE content in hard coal samples.
neodymium content in coal < 5 ppm and in ash 33.6 ppm; in sample 2, the lanthanum content in coal < 5 ppm, and in ash 27.8 ppm; in sample 1 lanthanum content in coal 12.9 ppm, and in ash 28.7 ppm. As a result of the hard coal combustion process, the presence of: scandium, praseodymium, samarium, gadolinium, dysprosium, erbium and ytterbium was found.

A hard coal thermal transformation increased in the REE concentration significantly and it increased the number of the elements which were not determined previously.

Verification of results
Comparing the results of the REE content in hard coal with the literature reports (Table 6), some similarities in the results, obtained for each element are noticeable.

| REE [ppm] | REE content based on the tests obtained from the literature [ppm] | Sample 1 | Sample 2 |
|-----------|---------------------------------------------------------------|---------|---------|
| Yttrium (Y) | not determined | 17.5 | 17.9 |
| Lanthanum (La) | 1.06 – 14.58 | 12.9 | <5 |
| Cerium (Ce) | 2.53 – 108.0 | 27.2 | 9.6 |
| Neodymium (Nd) | 1.37 – 12.93 | 14.4 | <5 |
| Europium (Eu) | 0.09 – 0.58 | 5.5 | 5.4 |

Source: [3, 9].

Referring to the results of the tests obtained from the literature (Table 1), it should be noted that they do not specify any characteristics of the tested coal (e.g. coal type, element determination method). Thus, the following comparison is indicative, taking into account the selected rare earths elements (Sc, Y, La, Ce, Nd, Eu), which were determined as a part of current research work and laboratory analyses.

The obtained REE content is within the limits of the value of previous tests for lanthanum and cerium. The current analyses confirm a higher concentration of europium or neodymium.

Apart from the issues related to the generality of the results so far, similar values confirm the correctness of the adopted cognitive method, determining the content of rare earth elements.

CONCEPT OF RARE EARTH ELEMENTS RECOVERY
In connection with the problems of rare earth elements dispersion, the recovery process is complex and requires a number of different processing methods. The initial enrichment process takes an advantage of a gravitational method, using devices such as a jig, a spiral separator, a cone concentrator, a concentration table or a hydrocyclone. The obtained concentrate undergoes further processes, such as: flotation, leaching, magnetic-electrostatic separation or the use of concentrated acid solution and extraction with concentrated sodium hydroxide [4, 6, 15, 17, 20, 21, 23].

The final stage of the work aimed at recovering or obtaining the feed with a significant concentration of rare earth elements (from the selected material with prospective sufficient REE content) in the gravitational beneficiation process. The obtained material will be a commercial product, prepared for the recovery of valuable rare earth elements in further chemical processes.

Due to the fine-grain characteristics of the material (it is necessary to obtain a small granulation < 1 mm to release REE), the concept of increasing concentration of these elements assumes the use of a classifying hydrocyclone. A hydrocyclone (Fig. 5) is a high-performance device that uses the centrifugal force in a liquid medium to separate the mixture into two components effectively.

Fig. 5 Model of hydrocyclone

This device allows a classification of very fine material, with a clear cut limit into the desired grain grades. The hydrocyclone (Fig. 6) consists of: a cylindrical part (1), giving the mixture a swirl motion; a conical part (2), where a separation occurs due to different grain sizes; an inlet nozzle (3), introducing the mixture, an overflow nozzle (4), receiving fine grains and an outflow nozzle (5), collecting coarse grains [5, 8, 18, 24].

Fig. 6 Schematic diagram of hydrocyclone
In prototype installations of rare earth elements recovery, the hydrocyclone is a device included in the system of the processing machines. In the British concept for the REE recovery from hard coal ashes, the hydrocyclone enriches the suspension based on different grain sizes, from which the organic concentrate in the turbulent mixer and the magnetic concentrate in the magnetic drum were separated previously. The results show a dozen or so percentage increase in the REE content in the hydrocyclone overflow [2].

In addition, the selected material will be used to improve the functional characteristics of the hydrocyclone, in order to improve the efficiency of its operation through computer simulation of the flow, and then to manufacture the testing prototype.

CONCLUSIONS

The article presents the results of tests and analyses of rare earth elements content in the Polish hard coal, starting from the first stage of the carbon chain, namely coal type 31.

As a part of the undertaken research work, a cooperation with the mine representatives was established and the following tasks were completed:

- a plan of testing and taking the samples of the assumed type of hard coal,
- a methodology for a determination of rare earth elements content using mass spectrometry with inductively coupled plasma ionization (ICP-MS) was developed,
- samples were prepared and the contents of rare earth elements were determined in hard coal of type 31 and also in ash from this coal,
- an analysis of the results.

Hard coal of type 31 and ash resulting from the combustion of this coal show the presence of rare earth elements. The obtained test results confirm a higher concentration of valuable elements in hard coal ash than in hard coal. At this stage of technology advance, it is difficult to talk about a possibility of recovering the REE from the coal of type 31 on the industrial scale. This is due to a low concentration level of these elements in this type of coal and a high energy consumption for separation processes. The research work has a cognitive character and it seems reasonable to conduct this type of research work and analysis for other types of hard coal.

Hard coal, showing an economic justification for the REE recovery, can be a raw material for tests aimed at a recovery of these elements using a classifying hydrocyclone.

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