



SYLWESTER ŻELAZNY¹, HENRYK ŚWINDER²,
ANDRZEJ JAROSIŃSKI³, BARBARA BIAŁECKA⁴

The recovery of rare-earth metals from fly ash using alkali pre-treatment with sodium hydroxide

Introduction

The economy of EU countries is experiencing an increasing deficit of mineral resources. This forces necessary solutions to ensure the continuity of supplies of these raw materials, and thus to search for new deposits or technologies for the recovery of raw materials from waste.

Rare earth metals are used both in traditional technologies (metallurgy, glass, polishing powders) as well as in modern branches of industry (catalysts, phosphors, lasers, magnets, etc.). About 25% of rare earth metals obtained are produced in the form of pure metals, and the remaining amount in the form of various chemical compounds. The global

✉ Corresponding Author: Henryk Świnder; e-mail: hswinder@gig.eu

¹ Cracow University of Technology, Kraków, Poland; ORCID iD: 0000-0001-5254-303X;
e-mail: sylwester.zelazny@pk.edu.pl

² Central Mining Institute, Katowice, Poland; ORCID iD: 0000-0001-7976-8554; e-mail: hswinder@gig.eu

³ Mineral and Energy Economy Research Institute of the Polish Academy of Sciences, Kraków, Poland;
ORCID iD: 0000-0002-1061-0000; e-mail: ajar@min-pan.krakow.pl

⁴ Central Mining Institute, Katowice, Poland; ORCID iD: 0000-0002-6002-5475; e-mail: bbialecka@gig.eu



© 2020. The Author(s). This is an open-access article distributed under the terms of the Creative Commons Attribution-ShareAlike International License (CC BY-SA 4.0, <http://creativecommons.org/licenses/by-sa/4.0/>), which permits use, distribution, and reproduction in any medium, provided that the Article is properly cited.

REE resources are estimated at 120 million Mg* ([U.S. Geological Survey, Mineral Commodity Summaries, January 2017](#)) in terms of oxides. The largest producer of REE is China, which produces over 83% of rare earth metals in the world. This country currently has almost 37% of world rare earth resources. REEs occur in the natural environment, mainly in igneous and post-igneous rocks, in which they create their own minerals or are also admixtures in other minerals. The occurrence of scandium and lanthanum group elements in the form of isomorphic mixtures in many minerals, in very small concentrations, as well as their similar physicochemical properties, cause great difficulties in the process of their separation in the elementary form or as homogeneous chemical compounds. In addition, there are rare ores of these elements in concentrations allowing them to be economically recovered.

In many cases, the essential process of obtaining REEs from natural resources is preceded by preliminary operations such as mechanical and thermal treatment, designed to convert sparingly soluble metal compounds into chemical combinations more readily soluble in water or mineral acids. Another example of REE recovery from minerals such as monazite and xenotime is extraction, carried out in concentrated sulfuric acid (VI) or in concentrated sodium hydroxide.

The shortage of mineral raw materials rich in rare earth elements and the lack of access to them caused a significant increase in interest in secondary raw materials ([Jarosiński 2016](#)). The advantage of REE's secondary raw materials is that they generally do not contain radioactive elements as opposed to primary raw materials. These materials are significantly different in terms of REE content.

A real source of rare earth metals is considered to be apatite and give a source waste from aluminum production ([Borra et al. 2015](#)), volcanic ashes ([Randazzo 2013](#)) and electrical and electronic equipment. In recent years, interest in alternative raw materials of rare earth metals, such as hard coal combustion fly ash, has increased ([Całus-Moszko and Białecka 2013](#); [Blisset et al. 2014](#)).

Table 1 presents examples of REE content in hard coals and fly ash from coal combustion in Poland and in the world. REEs in hard coal are most often associated with two minerals, monazite and xenotime, and are admixtures in apatite and zirconium ([Hower et al. 1999](#); [Migaszewski and Gałuszka 2007](#); [Smółka-Danielowska 2010](#); [Zhuang et al. 2007](#)). REEs are associated with both organic and mineral substances ([Raask 1985](#); [Schatzel and Steward 2003](#); [Wang et al. 2006](#)). The organic substance has a higher concentration of heavy REEs, while in mineral substances – lightweight ([Seredin 1996](#); [Schatzel and Steward 2003](#); [Zivotic et al. 2008](#)). The mineral substance may be of synergistic origin ([Finkelman 1982](#)) or auto-genous ([Ruppert et al. 1993](#); [Seredin 1996](#)).

In energy waste from coal combustion, the average REE content is about 400 ppm, although they are some fly ashes know, where their content reaches 1000 or even 8500 ppm ([Ketris and Yudovich 2009](#)).

The content of REEs in waste products of hard coal combustion is influenced by many factors, such as REE initial content in burnt coal, the nature of the combustion process, the

Table 1. Content of selected REE (ppm) in hard coal and fly ash in the World and in Poland

Tabela 1. Zawartość wybranych REE [ppm] w węglu kamiennym oraz popiołach lotnych na świecie i w Polsce

Element	Hard coal		Fly ash		
	Poland	World	Poland		World
			no flue gas desulfurization	with flue gas desulfurization	
Y	~10	2.0–50.0	12.0–100.0	6.2–169.0	6.2–340.0
La	~20	3.2–300.0	6.5–78.0	27.0–70.0	27.0–280
Ce	7.7–11.5	2.0–70.0	110.0–141.0	39.0–120.0	39.0–900.0
Pr	2.2–2.7	1.0–23.0	16.4–19.6	4.5–16.5	8.7–20.0
Nd	3.7–4.7	3.0–30.0	40.0–86.0	28.0–54.0	28.0–400.0
Sm	0.4–1.6	0.5–6.0	9.1–12.1	7.0–19.0	7.0–100.0
Gd	0.2–1.5	0.4–6.8	3.8–4.9	0.4–10.0	0.4–12.1
Tb	0.1–0.3	0.1–1.0	1.4–1.8	1.2–1.5	1.6–18.0
Dy	~2.2	0.5–5.3	4.9–12.0	7.7–9.1	7.2–10.5
Er	0.3–0.6	0.5–3.0	4.4–5.0	2.2–5.6	5.0–5.7
Yb	0.5–1.0	0.3–3.2	4.2–6.1	4.2–7.4	4.2–47.0

Own study.

type of boiler and the combustion temperature. They affect both the content of REEs in ash and their content in individual mineralogical phases (crystalline or amorphous) of ash. The crystallochemistry of rare earth metals is extremely complex and is related to the content and composition of the matrix. In studies on the recovery of REEs from fly ash, preference is given to solutions of sulfuric acid(VI) with low concentration or concentrated solutions of this acid at elevated temperatures (Chi et al. 2004; Świnder et al. 2017a). Several concepts for acquiring REE from fly ash, including leaching in acidic solutions and REE separation from the solution have been proposed. For several years, work has been carried out to recover REEs from fly ash from hard coal combustion, mainly in the US and in countries where power is based on coal, e.g. Poland (Mayfield and Lewis 2013; Seredin and Dai 2012; Paulo and Krzak 2015; Jarosiński 2016).

With respect to fly ash from Polish power plants, comprehensive activities related to check them as alternative sources of obtaining rare earth metals have not been carried out so far, and studies of their physicochemical properties are fragmented (Klupa et al. 2017). In a few works (Świnder et al. 2017a, b; Żelazny et al. 2017a, b), the concepts of REE recovery from fly ash coming from hard coal combustion in several stadial multilevel leaching

with sulfuric acid (VI) with alkaline activation with sodium carbonate and acid leaching with selected mineral acids.

Available references show that there are no studies regarding the recovery of REEs from fly ash coming from hard coal combustion by preliminary thermal activation of fly ash with sodium hydroxide. In addition to economic aspects, an important factor that raises the value of fly ash from hard coal combustion is the ecological aspect. It is connected both with the protection of natural resources as well as utilization and processing of waste within the framework of the circular economy.

1. Experimental Methodology

1.1. Materials

The fly ash from the Łagisza Power Plant was subjected to tests. The tests included sodium hydroxide pure p.a. and hydrochloric acid 35% pure p.a. by Avantor Performance Materials Poland SA.

1.2. Treatment of fly ash

In the first stage, the alkaline activation of fly ash was carried out. The process was carried out for samples consisting of fly ash and sodium hydroxide containing respectively 10, 20 and 30% of NaOH by weight in relation to the weight of fly ash. Homogenization of these mixtures was carried out wet, and then they were baked at 408K, 433K and 473K, for a period of three hours. The mixture thus obtained was ground to a particle size of less than 0.1 mm and washed with hot water to remove excess NaOH.

The solid post-reaction residue was digested in concentrated HCl at 373K for 1 hour at a weight ratio solid/liquid of 1:10. After this time, concentrated HCl was added to the reaction system in an amount to obtain a solution with a pH of about 0. The solution was filtered and the filter cake was washed with hot water. The content of selected REE was determined in the filtrate.

1.3. Methodology

The ICP-MS method with plasma excitation was used to determine the content of the elemental composition, including rare earth elements. An analytical sample was prepared for analysis, based on the own procedure based on the modified method described in the work (Świnder et al. 2017a). In order to assess the reliability of the measurement results of

Ce, La, Sc, Nd and Y, a certified reference material (CRM) analysis was carried out: soil sample (NCS DC 73324 Soil; China National Analysis Center for Iron and Steel). The determination of the content of lanthanum, yttrium, cerium, neodymium and scandium was carried out using a mass spectrometer induced by ELAN 6100” argon plasma by Perkin.

The analysis of the grain composition was carried out using the Malvern Malvern G3-ID particle size and shape analyser.

The morphological analysis was carried out using the SEM scanning electron microscope by HITACH SU-3500 N, cooperating with the X-ray spectroscopy with the energy dispersion EDS UltraDry by Thermo Scientific NORAN System 7.

The phase composition was determined using X-ray powder diffraction (PANalytical Empyrean).

The amount of leached rare earth metals was determined from the analysis of samples of leached solutions with concentrated hydrochloric acid. A lanthanide standard solution containing Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, Tm, U, Y and Yb with the concentration of each of the mentioned elements of 100 mg/dm³ (InorganicVentures, USA) was used in the process of preparation of calibration solutions.

A rhenium standard solution of 1000 mg/dm³ (AccuStandard, USA) was used to prepare an internal standard solution. The blank sample was deionized water enriched with an internal standard solution and acidified with nitric acid to pH = 2. Optimization of the mass spectrometer was carried out using a multi-element standard solution containing 1 µg/dm³ Be, Ce, Fe, In, Li, Mg, Pb and U (InorganicVentures, USA). A detailed description of the applied methodology can be found in the work (Cykowska et al. 2017).

The data obtained as a result of the analysis served to determine the degree of leaching as a ratio of the amount of rare earth metals in the solution to its initial content in fly ash. Recovery of selected REE after heat treatment and leaching with hydrochloric acid, calculated on a kilogram of ash mass, was calculated according to the formula 1:

$$x = \frac{z}{m} 100\% \quad (1)$$

z – mass of the element in solution after leaching with hydrochloric acid (kg),

m – ash weight (kg).

x – recovery of the selected REE (%).

2. Results and Discussion

The chemical composition of the tested fly ash is presented in Table 2. The dominant role was played by silica (SiO₂), constituting over 50% of the weight of the ash. The total Al₂O₃ and Fe₂O content accounted for 34.54% of the mass in total. The content of alkaline components was approximately 8.9% of the mass.

Table 2. Chemical composition of the fly ash studied, % by mass

Tabela 2. Skład chemiczny badanego popiołu lotnego, % mas.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	SO ₃	TiO ₂	P ₂ O ₅
51.58	25.82	8.72	2.10	4.50	1.49	2.87	0.72	1.17	0.27

Table 3. Content of selected rare earth elements in the fly ash studied, ppm

Tabela 3. Zawartość wybranych REE w badanym popiele, ppm

Element	Ce	La	Nd	Sc	Y	Total REE
Content	176.0	91.1	71.4	52.4	63.4	454.3

The REEs content in the analyzed fly ash is presented in Table 3. This ash was characterized by a high content of elements hard to access (Nd, Sc, Y), which are on the list of critical elements. Their total share in relation to the total REEs amounted to over 41%, while the share of the so-called “excess element” (Ce) was 38.7%.

The granulometric characteristics is given in Table 4 This data shows a different grain size distribution of the tested material. The grain sizes of the tested fly ash were in the range of 0–135 µm, in which 90% of the grains were smaller than 4.26 µm.

Table 4. Grain size of the examined fly ash, µm

Tabela 4. Uziarnienie badanego popiołu, µm

Parameter		Ash
Characteristic grains	d ¹⁰	0.22
	d ⁵⁰	0.29
	d ⁹⁰	4.26
Average diameter		1.55
The maximum diameter of the grain		134.66
Standard deviation		2.69

d¹⁰, d⁵⁰, d⁹⁰ – characteristic grains diameters, below which respectively: 10%, 50%, 90% of the analyzed material is present.

Figure 1 is a graph showing the grain size interval in a sample of ash tested and the distribution of circular particles constituting 40% of the volume of the sample.

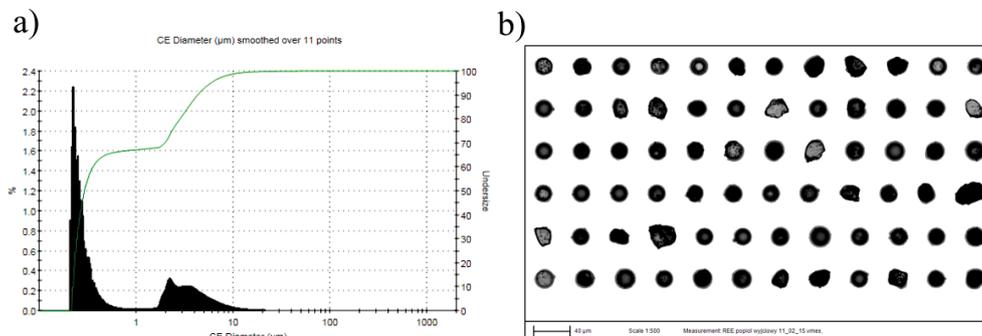


Fig. 1. Grain size distribution in ash sample
 a) histogram and cumulative curve (% by vol.); b) distribution of circular particles

Rys. 1. Rozkład wielkości ziaren w próbce popiołu wyjściowego
 a) histogram oraz krzywa kumulacyjna (% obj.); b) rozkład cząstek kolistych

Microscopic observations of the examined fly ash revealed that the material contained grains both in the form of spherical full enamel, empty inside (cenosphere) and grains of irregular shape (elongated, square in the shape of plates and rectangles) (Fig. 2). From the EDS analysis, silicon, aluminum and oxygen predominated in the fly ash. Iron, calcium, magnesium, sodium and potassium were found in much smaller quantities. A small content of sulfur, phosphorus and titanium was also found (Fig. 3).

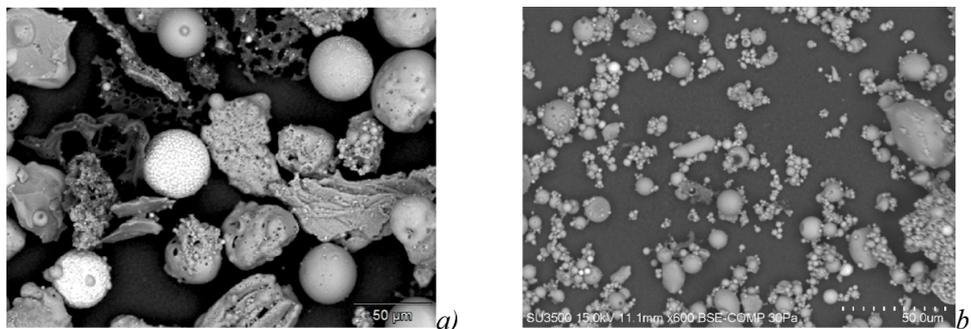


Fig. 2. SEM analysis of fly ash; morphology of grains
 a) 15 keV, 450×, b) 15 keV 600×

Rys. 2. Analiza SEM popiołu lotnego; morfologia ziaren
 a) 15 keV, 450×, b) 15 keV 600×

The mineral composition of the fly ash tested is shown in Table 5. Its basic ingredient was aluminosilicate glass.

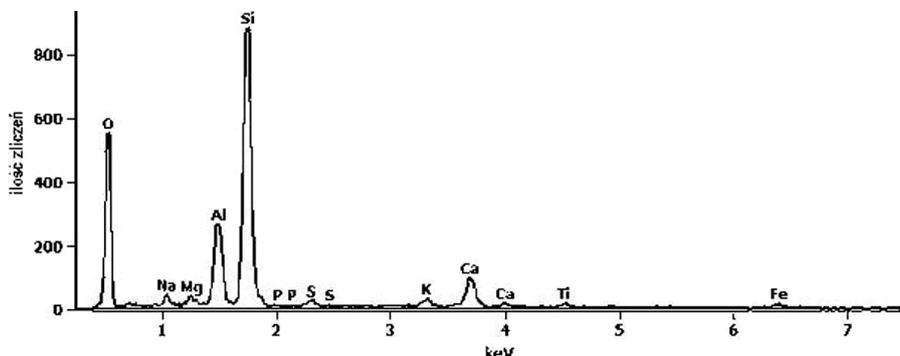


Fig. 3. SEM-EDS analysis of original fly ash sample; an exemplary qualitative X-ray spectrum

Rys. 3. Analiza SEM-EDS próbki wybranego popiołu lotnego; przykładowe jakościowe widmo rentgenowskie

Table 5. Mineralogical composition of fly ash determined by XRD

Tabela 5. Skład mineralogiczny popiołu lotnego oznaczonego metodą XRD

Phase	Share, % by weight
Quartz	6.1 ± 0.06
Mullite	17.2 ± 0.18
Anhydrite	0.6 ± 0.03
Lime	0.2 ± 0.02
Hematite	1.2 ± 0.04
Magnetite	0.3 ± 0.03
Maghemite	0.9 ± 0.04
Periclase	0.4 ± 0.04
Amorphous	73.0 ± 0.24

Table 6 shows the recovery results of selected REEs after concentrated HCl leaching of ash samples treated with NaOH at 10, 20 and 30% by weight, in relation to the fly ash mass, for a temperature of 408K.

The next stage of work included research on the influence of the thermal treatment temperature of ash with the addition of sodium hydroxide on the degree of leaching of selected REEs from fly ash.

NaOH mixtures were prepared containing 10%, 20% and 30% by weight of sodium hydroxide, respectively, based on the weight of fly ash, and then the obtained pulp was heated at temperatures of 408K, 433K and 473K.

Heat-treated samples after the grinding and washing of excess sodium hydroxide with distilled water were subjected to leaching with concentrated hydrochloric acid, similar to the above-mentioned described experiment.

The obtained post-reaction solutions were analyzed for the content of selected REE by ICP-MS.

The test results obtained in various temperatures are listed in Tables 6, 7 and 8.

Table 6. Recovery of selected REEs from fly ash after thermal treatment with NaOH at 408K and concentrated HCl leaching

Tabela 6. Odzysk wybranych REE z popiołu po obróbce termicznej z NaOH w temp. 408K i ługowaniu stężonym HCl

Weight fraction of NaOH to fly ash mass	10%	20%	30%
	Recovery (mg/kg)		
Ce	19.0	24.6	22.2
La	14.4	13.6	17.9
Nd	11.7	8.7	14.1
Sc	4.0	5.2	5.1
Y	7.2	8.3	9.1
Total	56.3	60.4	68.4

Table 7. Recovery of selected REEs from fly ash after thermal treatment with NaOH at 433K and concentrated HCl leaching

Tabela 7. Odzysk wybranych REE z popiołu po obróbce termicznej z NaOH w temp. 433K i ługowaniu stężonym HCl

Weight fraction of NaOH to fly ash mass	10%	20%	30%
	Recovery (mg/kg)		
Ce	101.7	97.1	126.1
La	40.8	83.4	82.4
Nd	19.5	25.9	32.4
Sc	13.5	13.2	20.2
Y	27.4	26.4	33.5
Total	202.9	246.0	294.6

Table 8. Recovery of selected REEs from fly ash after thermal treatment with NaOH at 473 K and concentrated HCl leaching

Tabela 8. Odzysk wybranych REE z popiołu po obróbce termicznej z NaOH w temp. 473K i ługowaniu stężonym HCl

Weight fraction of NaOH to fly ash mass	10%	20%	30%
	Recovery (mg/kg)		
Ce	89.6	121.3	130.7
La	52.3	70.7	75.5
Nd	25.0	32.4	34.6
Sc	13.8	16.9	19.6
Y	30.0	35.9	38.0
Total	208.7	277.1	298.4

Conclusions

The increase of the soda lye content in relation to the fly ash mass in the thermal activation process leads to an increase in REE leaching. At a temperature of 408K, with a 10% weight percentage of NaOH, based on fly ash, the leaching of REE from ash was 12.4%, and with the increase of NaOH to 30% by weight, the leaching step increased to 15.1%. For the thermal treatment temperature of the ash of 433K, with the participation of 10% by weight of NaOH in relation to fly ash mass, the recovery rate of selected REEs was 45.9%, and with the participation of 30% by weight of NaOH it reached 64.9%.

Figures 4 to 9 show the dependence of the degree of leaching of selected REEs depending on the amount (weight) of NaOH used for the thermal treatment of fly ash, for temperatures of 408K and 433K.

The recovery of REEs from fly ash depends, to a large extent on the temperature of the thermal treatment with NaOH. The total leaching of selected REEs, for a temperature of 473K (NaOH in the amount of 30% by weight in relation to the fly ash), was 65.7% (Fig. 10), and was significantly higher than for the equivalent sample subjected to thermal treatment at 408K, for which it amounted to only 15.1% (Fig. 6).

Figures 11 and 12 show the dependence of the degree of leaching of selected REEs on the weight fraction of NaOH used for the thermal treatment of fly ash at 473K.

The degree of REE leaching with mineral acids from fly ash subjected to alkaline activation and thermal treatment at 473K (Fig. 10) does not differ significantly from the degree of leaching from samples of fly ash activated at 433K (Fig. 9).

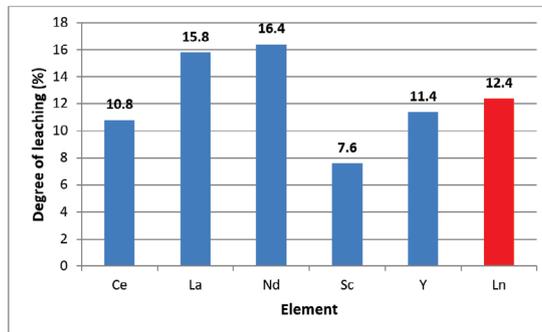


Fig. 4. Degree of REE leaching with a solution of hydrochloric acid from ash after heat treatment at a temp. of 408K, 10% NaOH by weight relative to the weight of the ash, Ln = Ce, La, Nd, Sc, Y

Rys. 4. Stopień wylugowania REE roztworem kwasu chlorowodorowego z popiołu po obróbce termicznej w temp. 408K, 10% wagowych NaOH w stosunku do masy popiołu, Ln = Ce, La, Nd, Sc, Y

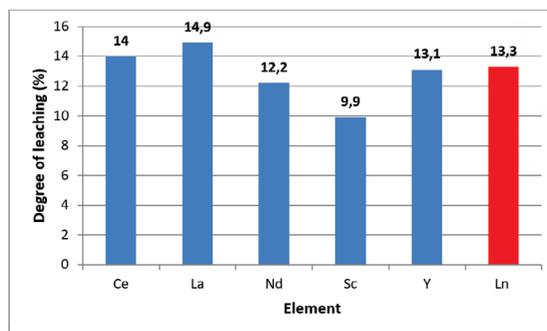


Fig. 5. Degree of REE leaching with a solution of hydrochloric acid from ash after heat treatment at a temp. of 408K, 20% NaOH by weight relative to the weight of the ash, Ln = Ce, La, Nd, Sc, Y

Rys. 5. Stopień wylugowania REE roztworem kwasu chlorowodorowego z popiołu po obróbce termicznej w temp. 408K, 20% wagowych NaOH w stosunku do masy popiołu, Ln = Ce, La, Nd, Sc, Y

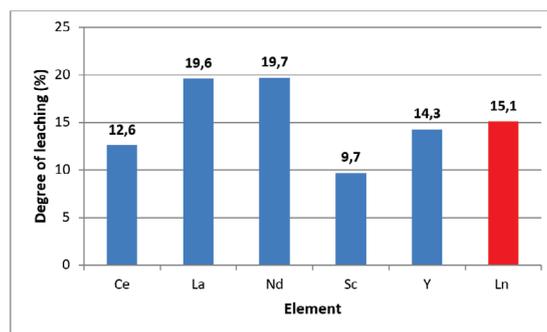


Fig. 6. Degree of REE leaching with a solution of hydrochloric acid from ash after heat treatment at a temp. of 408K, 30% NaOH by weight relative to the weight of the ash, Ln = Ce, La, Nd, Sc, Y

Rys. 6. Stopień wylugowania REE roztworem kwasu chlorowodorowego z popiołu po obróbce termicznej w temp. 408K, 30% wagowych NaOH w stosunku do masy popiołu, Ln = Ce, La, Nd, Sc, Y

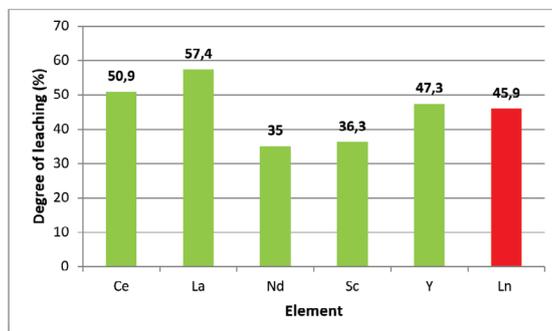


Fig. 7. Degree of REE leaching with a solution of hydrochloric acid from ash after heat treatment at a temp. of 433K, 10% NaOH by weight relative to the weight of the ash, Ln = Ce, La, Nd, Sc, Y

Rys. 7. Stopień wylugowania REE roztworem kwasu chlorowodorowego z popiołu po obróbce termicznej w temp. 433K, 10% wagowych NaOH w stosunku do masy popiołu, Ln = Ce, La, Nd, Sc, Y

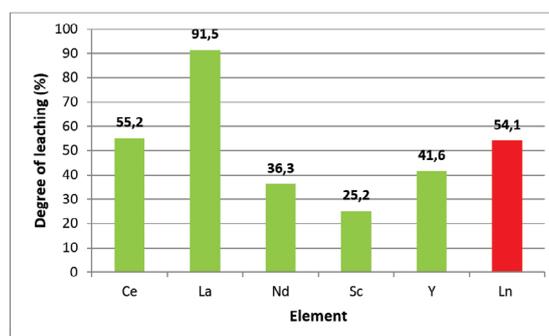


Fig. 8. Degree of REE leaching with a solution of hydrochloric acid from ash after heat treatment at a temp. of 433K, 20% NaOH by weight relative to the weight of the ash, Ln = Ce, La, Nd, Sc, Y

Rys. 8. Stopień wylugowania REE roztworem kwasu chlorowodorowego z popiołu po obróbce termicznej w temp. 433K, 20% wagowych NaOH w stosunku do masy popiołu, Ln = Ce, La, Nd, Sc, Y

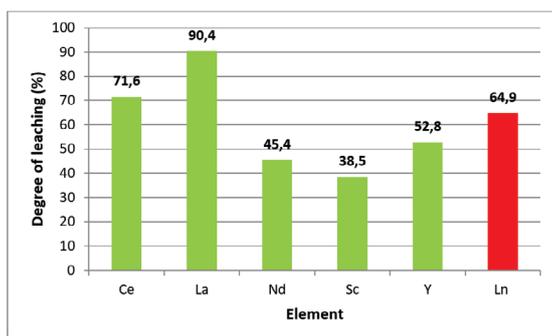


Fig. 9. Degree of REE leaching with a solution of hydrochloric acid from ash after heat treatment at a temp. of 433K, 30% NaOH by weight relative to the weight of the ash, Ln = Ce, La, Nd, Sc, Y

Rys. 9. Stopień wylugowania REE roztworem kwasu chlorowodorowego z popiołu po obróbce termicznej w temp. 433K, 30% wagowych NaOH w stosunku do masy popiołu, Ln = Ce, La, Nd, Sc, Y

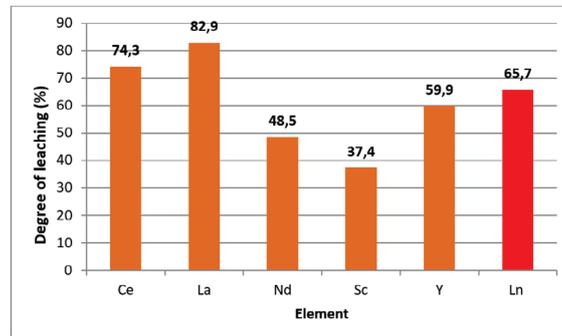


Fig. 10. Degree of REE leaching with a solution of hydrochloric acid from ash after heat treatment at a temp. of 473K, 30% NaOH by weight relative to the weight of the ash, Ln = Ce, La, Nd, Sc, Y

Rys. 10. Stopień wyługowania REE roztworem kwasu chlorowodorowego z popiołu po obróbce termicznej w temp. 473K, 30% wagowych NaOH w stosunku do masy popiołu, Ln = Ce, La, Nd, Sc, Y

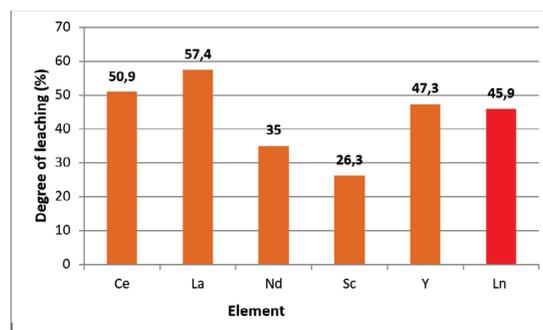


Fig. 11. Degree of REE leaching with a solution of hydrochloric acid from ash after heat treatment at a temp. of 473K, 10% NaOH by weight relative to the weight of the ash, Ln = Ce, La, Nd, Sc, Y

Rys. 11. Stopień wyługowania REE roztworem kwasu chlorowodorowego z popiołu po obróbce termicznej w temp. 473K, 10% wagowych NaOH w stosunku do masy popiołu, Ln = Ce, La, Nd, Sc, Y

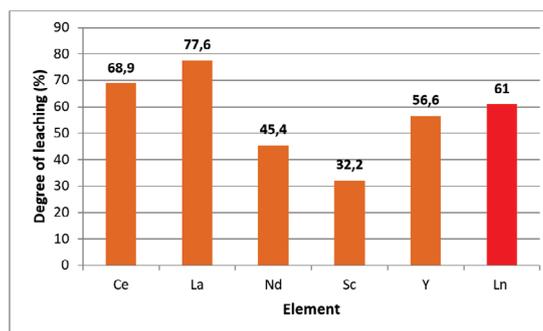


Fig. 12. Degree of REE leaching with a solution of hydrochloric acid from ash after heat treatment at a temp. of 473K, 20% NaOH by weight relative to the weight of the ash, Ln = Ce, La, Nd, Sc, Y

Rys. 12. Stopień wyługowania REE roztworem kwasu chlorowodorowego z popiołu po obróbce termicznej w temp. 473K, 20% wagowych NaOH w stosunku do masy popiołu, Ln = Ce, La, Nd, Sc, Y

The addition of 30% by weight of sodium hydroxide to fly ash and conducting the process at 473K allow the highest degree of leaching of selected REEs to be obtained, amounting to 65.7% of the total amount of selected REEs contained in fly ash (Fig. 10).

On 13 December 2018, the Patent Office of the Republic of Poland granted patent P232035 ‘The method of recovery of rare earth metals from fly ash’ to the Central Mining Institute in Katowice as a result of the presented research.

The paper has been prepared in the frames of the project: “Assessment of possible recycling directions of heavy & rare metals recovered from combustion waste products” (ERA-MIN/RAREASH/01/2015), funded by the National Centre for Research and Development under the ERA-NET ERA-MIN Programme.

REFERENCES

- Blisset et al. 2014 – Blisset, R.S., Smalley, N. and Rowson, N.A. 2014. An investigation into six coal fly ashes from the United Kingdom and Poland to evaluate rare earth element content. *Fuel* 119, 1, p. 236.
- Borra et al. 2015 – Borra, C.R., Pontikes, Y., Binnemans K. and Gerven T.V. 2015. Leaching of rare earths from bauxite residue (red mud). *Minerals Eng.* 76, p. 20.
- Całus-Moszek, J. and Białocka, B. 2013. Analysis of the possibilities of rare earth elements obtaining from coal and fly ash (*Analiza możliwości pozyskania pierwiastków ziem rzadkich z węgla kamiennych i popiołów lotnych z elektrowni*). *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 29(1), pp. 67–80 (in Polish).
- Chi et al. 2004 – Chi, R., Zhang, X., Zhu, G., Zhou, Z.A., Wu, Y., Wang, C. and Yu, F. 2004. Recovery of rare earth from bastnesite by ammonium chloride roasting with fluorine deactivation. *Minerals Engineering* 17, pp. 1037–1043.
- Cykowska M., Bebek M., Mitko K., Białocka B., Thomas M. 2017. Determination of the selected rare earth elements in environmental water samples (*Oznaczanie wybranych pierwiastków ziem rzadkich w środowiskowych próbkach wody*). *Przemysł Chemiczny* 11, pp. 2312–2316 (in Polish).
- Depoi et al. 2008 – Depoi, F.S., Pozebon, D. and Kalkreuth, W.D. 2008. Chemical characterization of feed coals and combustion-byproducts from Brazilian power plants. *International Journal of Coal Geology* 76, pp. 227–236.
- Hower et al. 1999 – Hower, J.C., Ruppert, L.F. and Eble, C.F. 1999. Lanthanide, yttrium and zirconium anomalies in the Fire Clay coal bed, Eastern Kentucky. *International Journal of Coal Geology* 39, pp. 141–152.
- Finkelman, R.B. 1982. *The origin occurrence and distribution of the inorganic constituents in low rank coal*. Proceedings of the Basic Coal Science Workshop. US Department of Energy, Huston T.X, pp. 69–90.
- Jarosiński, A. 2016. Selected issues from the technology of harvesting metals with rare earth (*Wybrane zagadnienia z technologii pozyskiwania metali ziem rzadkich*). Kraków: MEERI PAS (in Polish).
- Karayigit et al. 2001 – Karayigit, A.I., Onacek, T., Gayer, R.A. and Goldsmith, S. 2001. Mineralogy and geochemistry of feed coals and their combustion residues from the Cayirhan power plant, Ankara, Turkey. *Applied Geochemistry* 16, pp. 911–919.
- Ketris M.P., Yudovich Y.E. 2009. Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents in black shales and coals. *Intern. J. of Coal Geol.* 78, p. 135–148.
- Kłupa et al. 2017 – Kłupa, A., Adamczyk, Z. and Harat, A. 2017. Lanthanides in mineral elements found in fly ashes from the Rybnik Power Plant. *17th International Multidisciplinary Scientific Geoconference SGEM 2017*, 11, pp. 883–888.
- Marrero et al. 2007 – Marrero, J., Polla, G., Rebagliati, R.J., Gomez, D. and Smichowski, P. 2007. Characterization and determination of 28 elements in fly ashes collected in a thermal power plant in Argentina using different instrumental techniques. *Spectrochimica Acta part B* 62, pp. 101–108.

- Mayfield, D.B. and Lewis, A.S. 2013. Environmental Review of Coal Ash as a Resource for Rare Earth and Strategic Elements. *World of Coal Ash (WOCA) Conference* – April 22–25, in Lexington, KY.
- Migaszewski, Z.M. and Gałuszka, A. 2007. Fundamentals of environmental geochemistry (*Podstawy geochemii środowiska*). Warszawa: WNT (*in Polish*).
- Paulo, A. and Krzak, M. 2015. Rare metals (*Metale rzadkie*). Kraków: AGH (*in Polish*).
- Pires, M. and Querol, X. 2004. Characterization of Candiota (South Brasil) coal and combustion by-product. *International Journal of Coal Geology* 60, pp. 52–72.
- Raask, E. 1985. The mode of occurrence and concentration of trace elements in coal. *Program Energy Combustion Sciences* 11, pp. 97–118.
- Randazzo, L.A. 2013. Effects of Dissolved Complexation on REE Fate During Interactions between Volcanic Ash and Coexisting Fluids *Proc. Earth and Planetary Sci.* 7, p. 721.
- Ruppert et al. 1993 – Ruppert, L.F., Neuzil, S.G., Cecil, C.B. and Kane, J.S. 1993. Inorganic constituents from samples of a domed and lacustrine peat, Sumatra, Indonesia. [In:] *Modern and Ancient Coal Forming Environments. Geological Society of America Special Papers* 286, pp. 83–96.
- Schatzel, S.J. and Steward, B.W. 2003. Rare earth elements sources and modification in the Lower Kittanning coal bed, Pennsylvania: implications for the origin of coal mineral matter and rare earth element exposure in underground mines. *International Journal of Coal Geology* 54, pp. 223–251.
- Seredin, V.V. 2005. Rare earth elements in germanium-bearing coal seams of the Spetsugli deposit. *Geological of Ore Deposits* 47, pp. 265–284.
- Seredin, V.V. and Dai, S. 2012. Coal deposit as potential alternative sources for lanthanides and yttrium. *International Journal of Coal Geology* 94, pp. 67–93.
- Smółka-Danielowska, D. 2010. Rare earth elements in fly ashes created during the coal burning proces in certain coal-fired power plants operating in Poland-Upper Silesian Industrial Region. *Journal of Environmental Radioactivity* 101, pp. 965–968.
- Świnder et al. 2017a – Świnder, H., Białecka, B. and Jarosiński, A. 2017a. Study on recovering the rare earth metals from fly ash by multi-stage leaching with sulfuric(VI) acid (*Badanie odzysku metali ziem rzadkich z popiołów lotnych przy zastosowaniu wielostopniowego ługowania kwasem siarkowym(VI)*). *Przemysł Chemiczny* 96/11, pp. 2238–2243 (*in Polish*).
- Świnder et al. 2017b – Świnder, H., Białecka, B. and Jarosiński, A. 2017b. Recovery of rare earth elements from coal combustion fly ashes 17th International Multidisciplinary Scientific Geoconference SGEM 2017 v.17, 11, pp. 995–1002.
- U.S. Geological Survey, Mineral Commodity Summaries, January 2017.
- Wang et al. 2006 – Wang, W., Qin, Y., Wei, Ch., Li, Z., Guo, Y. and Zhu, Y. 2006. Partitioning of elements and macerals during preparation of Antaibao coal. *International Journal of Coal Geology* 68, pp. 223–232.
- Zhuang et al. 2007 – Zhuang X., Querol X., Alastuey A. Plana E., Moreno N., Andres J.M., Wang J. Mineralogy and geochemistry of the coals from the Chongqing and Southwest Hubei coal mining districts, South China. *International Journal of Coal Geology* 71, pp. 263–275.
- Zivotic et al. 2008 – Zivotic, D., Wehner, H., Cvetkovic, O., Jovancevic, B., Grzetec, I., Scheeder, G., Vidal, A., Sajnovic, A., Ercegovac, M. and Simic, V. 2008. Petrological, organic geochemical characteristics of coal from the Soko mine, Serbia. *International Journal of Coal Geology* 73, pp. 285–306.
- Żelazny et al. 2017a – Żelazny, S., Świnder, H., Białecka, B. and Jarosiński, A. 2017a. Recovery of rare earth elements from fly ash. Part 1, Leaching (*Odzysk pierwiastków ziem rzadkich z popiołów lotnych. Cz. I Ługowanie*). *Przemysł Chemiczny* 96/11, pp. 2279–2283 (*in Polish*).
- Żelazny et al. 2017b – Żelazny, S., Świnder, H., Białecka, B. and Jarosiński, A. 2017b. Recovery of rare earth elements from fly ash. Part 2, Precipitation (*Odzysk pierwiastków ziem rzadkich z popiołów lotnych. Cz. II Wytwarzanie z roztworu*). *Przemysł Chemiczny* 96/11, pp. 2284–2290 (*in Polish*).

**THE RECOVERY OF RARE-EARTH METALS FROM FLY ASH USING
ALKALI PRE-TREATMENT WITH SODIUM HYDROXIDE**

Key words

fly ash, REE, leaching

Abstract

The aim of the work was to draw attention to the usefulness of the alkaline thermal activation process with sodium hydroxide in the process of rare earth metal leaching (REE), from fly ash with hydrochloric acid and nitric acid(V). The work is a part of the authors' own research aimed at optimizing the REE recovery process coming from fly ash from hard coal combustion.

The article contains an assessment of the possibility of leaching rare earth metals (REE) from fly ash originating from the combustion of hard coal in one of the Polish power plants. The process was carried out for various samples consisting of fly ash and sodium hydroxide and for different temperatures and reaction times. The process was carried out for samples consisting of fly ash and sodium hydroxide containing respectively 10, 20 and 30% on NaOH by weight in relation to the weight of fly ash. Homogenization of these mixtures was carried out wet, and then they were baked at 408K, 433K and 473K, for a period of three hours. The mixture thus obtained was ground to a particle size of less than 0.1 mm and washed with hot water to remove excessive NaOH. The solid post-reaction residue was digested in concentrated HCl at 373K for 1 hour at a weight ratio f_s/f_c of 1:10. The results of chemical analysis and scanning microscopic analysis along with EDS analysis and X-ray analysis were used to characterize the physicochemical properties of the tested material.

The results indicated that REE recovery from fly ash strictly depends on heat treatment temperature with NaOH, and an increase in REE recovery from alkaline-activated fly ash along with increasing the amount of NaOH in relation to fly ash mass.

**ODZYSK METALI ZIEM RZADKICH Z POPIOŁÓW LOTNYCH
PRZY ZASTOSOWANIU WSTĘPNEJ OBRÓBKİ ALKALICZNEJ WODOROTLENKIEM SODU**

Słowa kluczowe

popioły lotne, REE, ługowanie

Streszczenie

Celem pracy było zwrócenie uwagi na przydatność alkalicznego procesu aktywacji termicznej wodorotlenkiem sodu w procesie ługowania metali ziem rzadkich (REE) z popiołu lotnego z kwasem chlorowodorowym i azotowym (V). Praca jest częścią badań własnych autorów mających na celu optymalizację procesu odzyskiwania REE z popiołów lotnych ze spalania węgla kamiennego. Artykuł zawiera ocenę możliwości ługowania metali ziem rzadkich (REE) z popiołów lotnych pochodzących ze spalania węgla kamiennego w jednej z polskich elektrowni. Proces przeprowadzono

dla próbek składających się z popiołu i wodorotlenku sodu zawierającego odpowiednio 10, 20 i 30% wagowych NaOH w stosunku do masy popiołu. Homogenizację tych mieszanin przeprowadzono na mokro, a następnie spiekano je w temperaturze 408K, 433K i 473K przez okres trzech godzin. Tak otrzymaną mieszaninę zmielono do wielkości cząstek mniejszej niż 0,1 mm, a następnie przemyto gorącą wodą w celu usunięcia nadmiaru NaOH. Stałą pozostałość poreakcyjną trawiono stężonym HCl w temperaturze 373K przez 1 godzinę, przy stosunku wagowym f_s/f_c wynoszącym 1:10. Wyniki analizy chemicznej i skaningowej analizy mikroskopowej wraz z analizą EDS i analizą rentgenowską wykorzystano do scharakteryzowania właściwości fizykochemicznych badanego materiału.

Otrzymane wyniki wskazują, że odzysk REE z popiołu zależy ściśle od temperatury obróbki cieplnej za pomocą NaOH, oraz że odzysk REE z popiołu aktywowanego alkalicznie rośnie wraz ze wzrostem ilości NaOH w stosunku do masy popiołu.

