



Study of Extraction of Rare Earth Elements from Hard Coal Fly Ash

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Abstract

Rare earth elements (REEs) extraction from wastes and/or by-products is alternative possibility of their winning. The occurrence of REEs, namely 50.1 ppm of La, 100.1 ppm of Ce and 44.3 ppm of Nd was confirmed in solid fly ash samples from the coal fired heating plant (TEKO, Inc. Košice, eastern Slovakia). The submitted contribution presents laboratory results of REEs leaching from coal fly ash using 3M HCl, HNO₃, H₂SO₄ and H₃PO₄ at 80°C during 120 min.

It was found, that recoveries 65.5% of La, 64.4% Ce and 64.3% of Nd into liquor may be attained after grain size reduction to below 5 μm.

Keywords: coal fly ash, REEs extraction, inorganic acids

Introduction

Recently, REEs consumption continually increases due to their extensive application in various areas.

The content and distribution of lanthanides in rocks and coal is confirmed by the presence of REE-bearing uncommon minerals, such as monazite (Ce,La,Nd,Th)PO₄, allanite (Ce,Ca,Y)₂(Al,Fe³⁺)₃(SiO₄)₃(OH), zircon (Zr,REE)₃SiO₄, xenotime YPO₄ (Kolker et al., 2017; Finkelman, 1981), rhabdophane (Ce,La,Y)PO₄·H₂O (Dai et al., 2014), florencite CeAl₃(PO₄)₂(OH)₆ and Ce-Nd-bearing (fluoro)carbonates, e.g. bästnasite (Ce,La,Y)CO₃F (Dai et al., 2016; Dai et al., 2017; Zhao et al., 2017). Besides electronic scrap, the wastes from mining and metallurgical industry and also coal combustion (by)products (CCPs), e.g. fly ash can consider to be a potential source of REEs. CCPs landfills often negatively influence the surroundings by their elutriation and in such way contaminate surface and ground waters. On the other hand performed scientific studies confirmed an interesting content of REEs in CCP. Moreover, within the frame of European Union REEs were recognized as critical raw materials by European Commission. All above mentioned facts caused the intensive research on REEs winning from coal fly ash.

Generally, the extraction of REEs from mineral resources is energy intensive and ecologically undesirable process. Moreover, from technological viewpoint, this process is also complicated and it includes various physical separation methods to obtain REE-bearing mineral concentrates and hydrometallurgical techniques for processing the concentrates, i.e. metals extraction from minerals by using suitable leaching agents.

Lin et al. (2017) dealt with the enrichment of REEs from coal, coal by-products and shales.

The samples of fly ash contained 312–623 ppm of REE or 378–754 REY, respectively. An enrichment of REEs was attained in non-magnetic product using magnetic separation.

As to gravity concentration, it is interesting that the highest REE content was not found in the heaviest fraction, probably due to insufficiently liberated REE-bearing minerals from others ones.

Blisset et al. (2014) evaluated the REEs content in six coal fly ashes from the United Kingdom (UK) and Poland. Apart from other things they presented REO content of four samples obtained from semi-anthracitic coal combustion at various places of processing scheme (flotation/rougher product to magnetic separation/non-magnetic product to hydrocycloning) at upgrading of fly ash. Thus, they assayed organic concentrate (REO 398 ppm) from rougher froth, magnetic concentrate (REO 270 ppm), fines from hydrocyclone overflow (REO 637 ppm) and coarse from hydrocyclone underflow (REO 560 ppm) from the feed of REO 505 ppm. After above mentioned it seems that REEs concentrate in inorganic non-magnetic matter.

Naturally, an application of hydrometallurgical techniques in REEs winning from coal fly ashes is also intensively investigated. The researchers pay attention to several technological parameters of leaching with the aim to attain maximal attainable REEs recovery. So, various leaching agents, pH value at leaching, influence of temperature, pressure, and stirring speed in consideration of coal fly ash composition are studied.

Cao et al. (2018) studied the coal fly ash containing 489 ppm REE. The leaching of fly ash in 3M HCl at 60°C, at 200 rpm during 120 min. resulted in the following values of recovery: 71.9% La, 66.0% Ce and 61.9% Nd. Kashiwakura et al. (2013) studied the extraction of REE from coal fly ashes by leaching using H₂SO₄. King et al. (2018) dealt with acid and alkaline leaching of REEs from fly ashes from combustion of various coals. In dependence on origin of fly ash and pH of leaching they observed leachability of REEs. It was shown that acid leaching is suitable for one group of coal fly ashes, but

Tab. 1. Chemical analysis of coal fly ash
 Tab. 1. Analiza chemiczna popiołu węglowego

SiO ₂ [%]	MgO [%]	CaO [%]	Fe ₂ O ₃ [%]	Al ₂ O ₃ [%]	MnO [%]	K ₂ O [%]	La [ppm]	Ce [ppm]	Nd [ppm]	LOI [%]
44.6	1.68	4.22	6.22	21.20	0.085	1.07	55.6	100.1	49.5	15.22

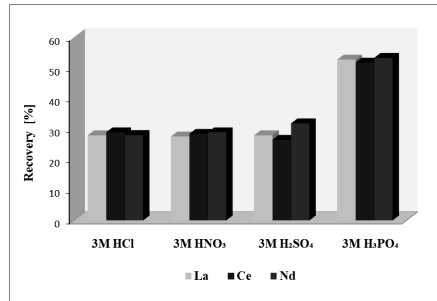


Fig. 1. Extraction La, Ce and Nd from coal fly ash (grain size –100 μm)
 Rys. 1. Ekstrakcja La, Ce oraz Nd z popiołu węglowego (wielkość ziarna – 100 μm)

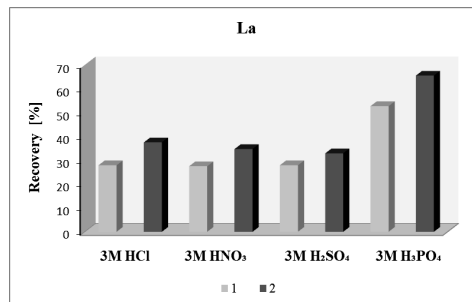


Fig. 2. Influence of grain size on extraction for La in 3M HCl, 3M HNO₃, 3M H₂SO₄ and 3M H₃PO₄ 1 – grain size –100 μm, 2 – grain size –5 μm
 Rys. 2. Wpływ wymiaru ziarna na ekstrakcję La w 3M HCl, 3M HNO₃, 3M H₂SO₄ i 3M H₃PO₄ 1 – wielkość ziarna – 100 μm, 2 – wielkość ziarna – 5 μm

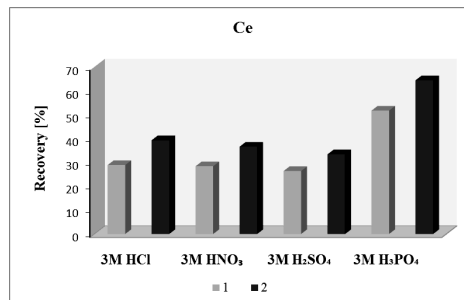


Fig. 3. Influence of grain size on extraction for Ce in 3M HCl, 3M HNO₃, 3M H₂SO₄ and 3M H₃PO₄ 1 – grain size –100 μm, 2 – grain size –5 μm
 Rys. 3. Wpływ wielkości ziarna na ekstrakcję Ce w 3M HCl, 3M HNO₃, 3M H₂SO₄ i 3M H₃PO₄ 1 – wielkość ziarna – 100 μm, 2 – wielkość ziarna – 5 μm

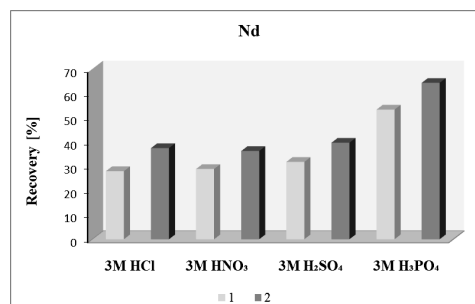


Fig. 4. Influence of grain size on extraction for Nd in 3M HCl, 3M HNO₃, 3M H₂SO₄ and 3M H₃PO₄ 1 – grain size –100 μm, 2 - grain size –5 μm
 Rys. 4. Wpływ wielkości ziarna na ekstrakcję Nd w 3M HCl, 3M HNO₃, 3M H₂SO₄ i 3M H₃PO₄ 1 – wielkość ziarna – 100 μm, 2 – wielkość ziarna – 5 μm

on the other hand higher REEs recoveries into liquor were achieved using alkaline leaching in the case of the second sample group.

Wang et al. (2019) performed the study of bottom and fly ashes from the Luzhou power plant in Sichuan, (Southwest China) as a promising alternative resource for rare earth elements and yttrium (REE+Y or REY) recovery. The fly ash is characterized by an aluminosilicate composition with a low CaO content and it consists of >70% amorphous glass and <30% mineral phases such as mullite, quartz and iron oxides. Dissolution of the fly ash with 4% HF showed that ~90% of all the REY are associated with the amorphous glass. The optimal NaOH-HCl sequential leaching resulted in 41.10% removal of active silica from the fly ash and 88.15% REY extraction.

Materials and methods

The sample of fly ash from the coal fired heating plant (TEKO, Inc. Košice, Slovakia) was subjected to leaching experiments on REEs extraction. The content of major components and lanthanides in fly ash is introduced in Table 1. The extraction was realized in glass banks in water bath at the temperature 80°C in 3M solutions of HCl, HNO₃, H₂SO₄ a H₃PO₄. The time of leaching was 120 min at the stirring speed 200 rpm. The ratio of leaching agent to solid phase was 100 ml of solution to 1g of solid sample. The content of lanthanides, namely La, Ce and Nd was determined by ICP-MS (Agilent 7700, USA). Silicon dioxide and Loss On Ignition (LOI) were assayed using gravimetric analysis (GA). The content of other metals was determined by AAS (Varian AA240FS, Australia).

The grain size reduction of fly ash sample to ~100 µm was performed using a vibrating mill (VM-1, KSMH – Hranice, Czech Rep.). Further diminishing to grain size below 5 µm realised by means of a planetary mill (Pulverisette 6, Fritsch, Germany) in grinding bowls at rotational speed of main disk 550 rpm. Tungsten carbide balls with diameter 10 mm were used as grinding media.

Results and Discussion

The results of laboratory experiments of lanthanides extraction from fly ash sample of grain size bellow 100 µm in

3M HCl, HNO₃, H₂SO₄ and H₃PO₄ at 80°C during 120 min are shown in Fig. 1. Thus, leachability of observed lanthanides was confirmed by using all acid solutions. The highest recoveries 52.7% of La, 51.7% of Ce and 53.3% of Nd were attained using 3M H₃PO₄.

Naturally, a grain size reduction of fly ash sample to ~5 µm favourably resulted in the enhancement of REEs recovery into liquor by 5–12.8%. The highest recoveries into liquor, namely 65.5% of La, 64.4% of Ce and 64.3% of Nd and the highest recovery increases by 12.8 of La, 12.7% of Ce and by 11% of Nd were again received by using 3M H₃PO₄. The influence of grain size reduction on individual REE recovery is graphically illustrated in Figs. 2–4.

Conclusion

An attention to REEs recovery from hard coal fly ash was paid in submitted contribution. The samples of grain size below 100 µm and 5 µm, respectively were subjected to acid leaching by using 3M HCl, HNO₃, H₂SO₄ and H₃PO₄. Firstly, as to grain size below 100 µm the recoveries 27.5–52.7% of La, 26.4–51.7% of Ce and 28–53.3% of Nd into liquor were obtained. Secondly, in the case of grain size below 5 µm the recoveries 32.9–65.5% of La, 33.4–64.4% Ce and 36.3–64.3 % of Nd were won. The highest REEs recoveries were attained using 3M H₃PO₄. Conversely, the application of HNO₃ and H₂SO₄ as leaching agents seems to be inadequate. Finally, it can be stated, that grain size reduction resulted in higher REEs recovery into liquor by 5–12.8 %, mostly using H₃PO₄ (by 11–12.8 %).

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Badanie ekstrakcji pierwiastków ziem rzadkich z popiołu węgla kamiennego

Ekstrakcja pierwiastków ziem rzadkich (REEs) z odpadów oraz/albo z produktów jest alternatywną możliwością ich uzyskania. Obecność REEs, konkretnie 50,1 ppm La, 100,1 ppm Ce oraz 44,2 ppm Nd została potwierdzona w próbkach popiołu z węgla z elektrociepłowni (TEKO, Inc. Košice, wschodnia Słowacja). Prezentowany artykuł pokazuje wyniki laboratoryjne ługowania REEs z popiołu węglowego za pomocą 3M HCl, HNO₃, H₂SO₄ oraz H₃PO₄ w 80°C w czasie 120 minut. Odkryto, że odzysk 65,5% La, 64,4% Ce oraz 64,3% Nd w formie ciekłej może być osiągnięte przy redukcji wymiaru ziaren do poniżej 5 μm.

Słowa kluczowe: popiół węglowy, ekstrakcja REEs, kwasy nieorganiczne