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Chapter 2

Perspective of Obtaining Rare Earth Elements in Poland

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Abstract

Along with the increasing development of electric and electronic industries, the demand for rare earth elements is also growing due to their high position in many applications. In Poland, there are minerals containing REE; however, the concentration of these elements in raw materials is rather low, so they do not have a big impact on the national economy. The potential source of REE is secondary materials; among them are phosphogypsum, uranium tailings, and the waste electrical and electronic equipment (WEEE). Lanthanides as accompanying metals of uranium in Polish uranium ores were leached in the technology of uranium recovery from these resources. The recovery of REE from pregnant liquors was conducted by solvent extraction and ion exchange. Novel apparatus solutions like membrane contactors in extraction stage were tested. Different types of matrices (uranium ore, phosphorites, etc.) were used.

Keywords: rare earth elements, phosphogypsum, uranium deposits, waste electrical and electronic equipment, separation of lanthanides

1. Introduction

The group of rare earth elements (REE) is considered as 1 of 20 critical mineral raw materials important for the EU economy [1]. Due to the high demand for these metals, their resources are systematically exhausting. Actions aimed at ensuring continuity of REE supply, that is, exploration and exploitation of new deposits, reduction of consumption of these precious metals in technological processes and their recovery from waste, are very important from an

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economic point of view. The REE are widely used in the industry. For example, Nd, Pr, Sm, Tb, and Dy constitute the most important component of magnets used among others in mobile computers, mobile phones, cameras, electric motors, hybrid cars, and equipment for magnetic resonance; La, Ce, Pr, and Nd are used for the production of batteries of hybrid vehicles and hydrogen-absorbing alloys; Eu, Y, Tb, La, Dy, Ce, Pr, and Gd are a part of luminophores used in mobile phones, tablets, LED diodes, and energy-saving light bulbs; Ce, La, and Nd are added to the powders for polishing of screens of TV sets, monitors, tablets, mirrors, and computer processors (in the form of nanoparticles) [2]. The new applications of REE are still being found, and in the most of cases, it is impossible to replace them by other materials.

In Poland, the concentration of REE in minerals is rather low; their impact on the national economy is small. Potential sources of these metals are secondary materials such as phosphogypsum,

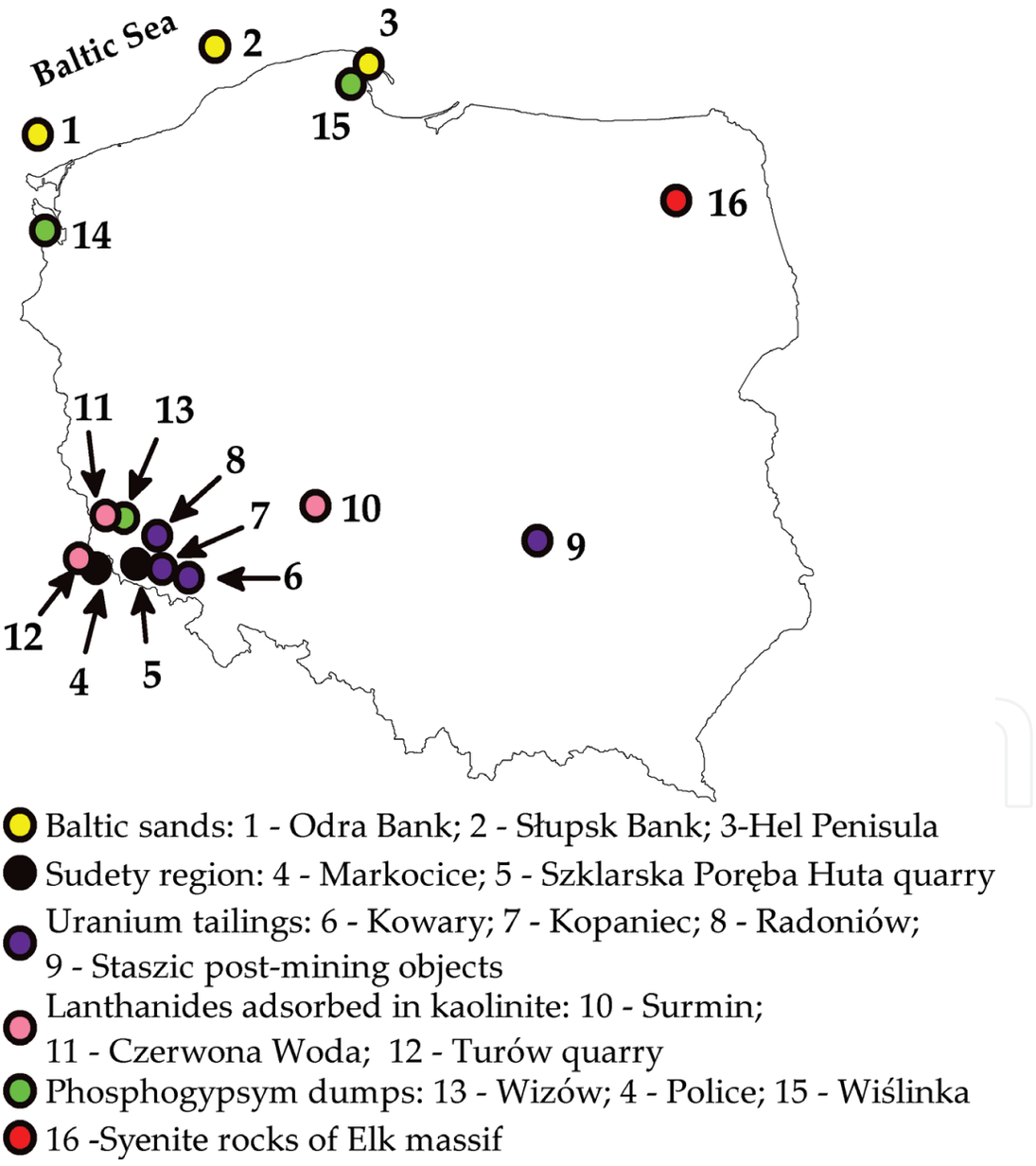


Figure 1. The location of potential REE raw materials in Poland.

the uranium tailings, and the waste electrical and electronic equipment (WEEE). In this chapter, the perspectives of recovery of REE from the Polish reserves are presented. The location of potential REE resources in Poland is shown on **Figure 1**.

2. Rare earth elements in Poland: natural sources

Natural resources of lanthanides in Poland were identified in alkaline intrusive Elk massif, Baltic sands, granite rock of Szklarska Poręba Huta quarry and Michałowice quarry (Karkonosze massif), pegmatites of Bogatynia (Sudety mountains), and Lower Silesia kaolinite [3–6].

The Elk alkaline massif belongs to group of intrusive centers within the crystalline basement of the precambrian Baltic shield (northeastern Poland). It is composed mainly of syenite rocks such as nepheline syenite (E2, E3), fold-less syenite (E3), amphibola syenite (E4), monzogabbro (G1), and quartz syenite (K1, P1, P2). The whole massive is about 400 km^2 in areal extent and the lanthanide-bearing rock is buried beneath 800–900 m of sedimentary rocks. For all rocks of Elk massif light REE enrichment has been found [3].

In the 1950s of the last century, a geological survey was carried out (seven drills has been digged, near the Elk city). It was showed that the concentration of lanthanides in this region is in the range of 207 up to 1224 ppm. The highest average concentration of lanthanides (963.9 ppm) is related to amphibola syenite, on a depth 950–1639 m, and the lowest one (354.7 ppm) is related to monzogabbro. The whole REE bearing layer is located on the depth 900–2500 m [3]. Distribution of the %REO (rare earth oxides) content depending on the depth of residual resources was shown on **Figure 2**. The calculation was done on the basis of the data published in the Geological Survey [3].

For all rocks of Elk massif light REE enrichment has been found and almost all samples have negative Eu anomaly [3].

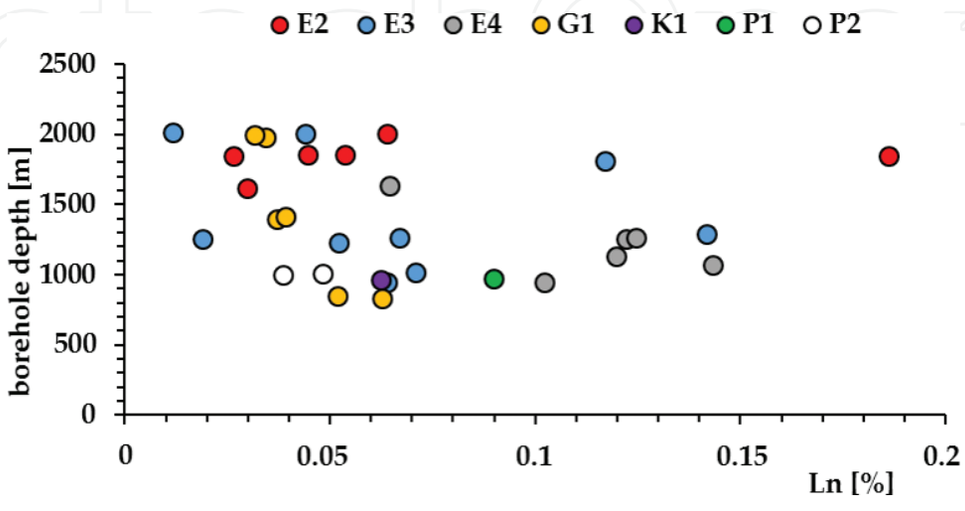


Figure 2. Distribution of %REO depending on the borehole depth (calculation based on data [3]).

The lanthanides mineralization has been also found in the Baltic marine sands, which are enriched in heavy metals, from the Odra and Slupsk Bank and from Hel Peninsula. All the samples were enriched in LLn_2O_3 (light lanthanides oxide). The highest REE (including Y and Sc) content is related to heavy minerals of Hel Peninsula sands (1371.2 ppm) and Odra Bank (up to 8787.7 ppm) [4].

In southwestern Poland (Sudety Mountains) REE occurrences are associated with uranium- and thorium-bearing rocks. In Szklarska Poręba Huta quarry, lanthanides are associated with Nb, Ta, and Li pegmatites and granites. The total concentration of %REO is 0.5 wt%, and prospective resources are estimated at 305 tonnes of these metals. In Markocice (near Bogatynia), REE content has been estimated at 150 tonnes, with average REO concentration of 1.5 wt%. In this area, lanthanides occur in metamorphic cover with the main REE bearing minerals such as zirconolite, gadolinite, fersonite-formanite, aeschynite, uraninite, monazite, zircon, and xenotime [5, 6].

The occurrence of lanthanides, which are adsorbed in kaolinite (Surmin, Czerwona Woda, and Turów), has been found in the area of Lower Silesia (southwestern Poland). The average concentration of lanthanides in this mineral is 288.7 ppm for Surmin, 106.9 ppm for Czerwona Woda, and 41.6 ppm for Turów. These clays are enriched in light lanthanides [7].

3. Potential secondary materials for REE recovery

3.1. Uranium tailings

Uranium mining and uranium tailings are also rich sources of metals from the lanthanide group. Uranium mining residues in Poland were studied under various projects demonstrating the presence of REE and possibility of their extraction. The investigations were conducted in the Sudety region—Kowary (adit and sorting station), Radoniów (small and big dump), Kopaniec (dump), and in iron sulfide deposit in Rudki ("Staszic" mine) in the Holy Cross Mountains—where the soil and water from the mine pit lake and surrounding soils were analyzed. For waste materials from the Sudety region, the average concentration of Ln (excluding Tm) was as follows: Kowary adit, 64.9 ppm; sorting place, 95.9 ppm; Radoniów, 77.3 ppm (big dump) and 109.8 ppm (small dump); and Kopaniec dump, 103.9 ppm, with majority of light lanthanides (calculation based on data from [8]). For the Staszic post-mining objects, the average concentration of Ln was 993.3 ppm in water from open pit lake and 82.6 ppm in soils (calculation based on data [9]). All tested samples were enriched in medium lanthanides [9].

3.2. Phosphoric fertilizer manufacturing process: imported phosphates, phosphogypsum, and phosphoric acid

One of perspective secondary materials for recovery of REE is phosphate ores, which are used in the production of phosphoric acid. Phosphate ores can be divided into two main types according to their origin: sedimentary and igneous phosphate rocks. Sedimentary phosphate rocks (phosphorites) are found in Florida, Morocco, and the Middle East, while igneous

phosphate rocks in the Kola Peninsula (Russia) and in Brazil [10]. The REE content in phosphate rocks depends on the type of rocks; in sedimentary phosphate rocks, it is 0.01–0.1 wt%, while in igneous phosphate rocks it is much richer (1–2 wt%). Apatite is the main phosphate mineral in most phosphate deposits [11]. These phosphate ores generally contain only 0.1–1% Me_2O_3, but they are present in huge quantities, c.a. 67 billion tonnes and are spread around the world; thus they have the potential to be an important source of REE. In apatite ores, REE either take the place of Ca^{2+} in the apatite itself or is presented as mineral inclusions in the ores. REE can be extracted from apatite ores during the production of phosphoric acid. In the technological process, c.a. 70% of REE present in the raw material is transferred to insoluble gypsum in precipitation process. In phosphoric fertilizer manufacturing process in Poland, phosphate rocks imported from Morocco, Tunisia, and Syria are used. The example concentration of lanthanides in these materials is presented in **Table 1**.

Phosphogypsum is primarily $CaSO_4 \cdot 2H_2O$, but it also contains impurities such as fluoride, heavy metals, and naturally occurring radionuclides such as ^{210}Po, ^{226}Ra, ^{234}U, ^{238}U, and ^{210}Pb [13]. The composition of impurities within phosphogypsum can vary greatly depending on the source of the phosphate rock used in phosphoric acid production.

Phosphogypsum waste generated during production of phosphoric acid process in Poland is stored on the heaps in Police, Wizów, and Wiślinka near Gdańsk. It is estimated that every year, all plants in Poland produce about 2.2–2.6 mln tonnes of phosphogypsum. In Wizów, apatites originating from the Kola Peninsula (Russia) were processed. The phosphate rock coming from the Kola region contained an average 0.8–1.0 wt%. lanthanide oxides (as Ln_2O_3). Phosphogypsum waste generated in the Wizów Chemical Plant in southwestern Poland was stored on a huge heap in the vicinity of the plant. The phosphogypsum stored in Wizów mainly consists of calcium sulfate hemihydrate which undergoes physical and chemical changes during storage [14]. The analyses of the composition of this waste showed that the average content of lanthanides was in the range 0.3–0.7 wt%. (as Ln_2O_2). It was confirmed that this waste is a potential raw material for the manufacture of 6–10 kt of REE [15]. The phosphogypsum waste heap in Wiślinka (northern Poland) is located between the Martwa Wisła River and farm fields, close to the Gdańsk agglomeration. It contains about 16 million tonnes of phosphogypsum stored on 40 ha of land. The phosphogypsum waste heap is the result of production of phosphorite fertilizers by phosphoric fertilizer industries in Gdańsk. The concentration of lanthanides in phosphogypsum stored in Wiślinka is collected in **Table 2**.

Lanthanides	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Yb**
Origin of phosphorite	**Concentration, ppm**											
Morocco	90	38	14	62	13	3	18	3	18	4	14	13
Syria	26	22	4	18	4	1	5	1	4	1	4	3
Tunisia	64	100	13	55	11	3	12	2	9	2	6	5

Table 1. Concentration of lanthanides in the phosphates of different origin [12].

3.3. Fly ash from coal combustion in conventional power plants

Fly ash is considered as a potential future source of lanthanides and other valuable metals (e.g., uranium, thorium, aluminum, etc.).

Usually concentration of metals in solid fossil materials such as anthracite, hard coal, and lignite is not very high. During combustion or co-firing processes, a lot of valuable metals is concentrated several times in coal fly ash (CFA) [16, 17].

Poland is the second biggest consumer of coal in European Union countries. Polish energy mix has been shown in **Figure 3**. Almost 80% of electric energy comes from combustion of hard coal, lignite, and biomass [18].

Only 25% of CFA that comes from Polish coal-fired power plants is utilized, and 75% is disposed as a waste material. Fly ash is used mainly as an admixture for concretes and cements or for production of synthetic zeolites. In the fly ash, 81 metals have been analyzed, including REE, which concentration is much higher than in raw material.

Average concentration of lanthanides in coal and lignite is not very high (in Polish solid fossil fuel is approximately 100 ppm of Ln), but during combustion process the total concentration of lanthanides grows 3–4 times [16]. Assessment of Polish fly ash, which comes from combustion of solid materials (biomass, hard coal, and lignite), showed that concentration of REE (including Y and Sc) is in the range 101.1–443.3 ppm, always with majority of LL_2O_3 fraction [17, 19].

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb
Concentration, ppm	40	53	8	34	7	2	9	1	7	2	5	4

Table 2. The concentration of lanthanides in phosphogypsum stored on Wiślinka heap [15]

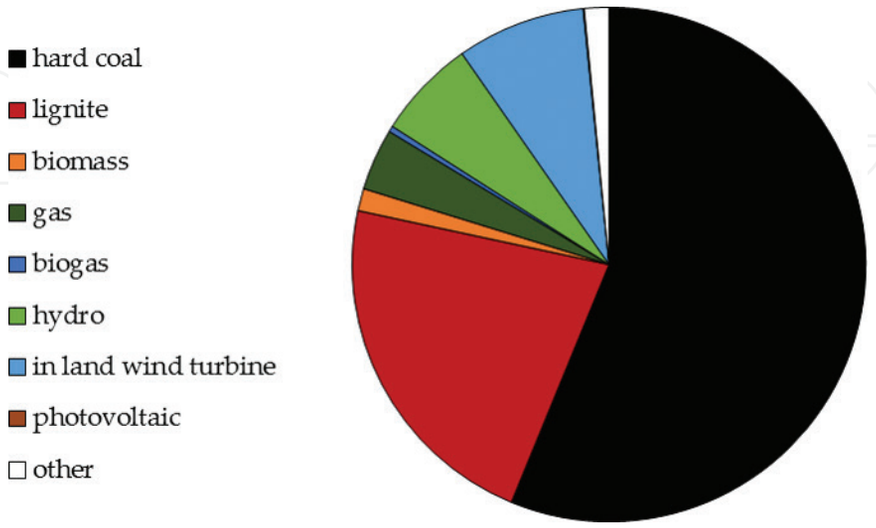


Figure 3. Polish electricity production energy mix (in shares %).

3.4. Waste electrical and electronic equipment (WEEE)

In view of the growing demand for rare earth elements (REE) and requirements of environmental protection, the treatment of waste electrical and electronic equipment becomes a very good secondary source of the REE in a modern economy. Recycling of the waste electrical and electronic equipment is also one of the possibilities of obtaining the rare earth metals and limiting their purchase from China. According to the European Commission, waste electrical and electronic equipment is one the fastest growing waste streams in the European Union, with almost 9 million tonnes produced in 2005 and probably will increase to more than 12 million tonnes by 2020 [20].

Also in Poland, a potential raw material of the rare earth elements is secondary material, which is a waste of electrical and electronic equipment (WEEE). In the recycling process of WEEE, developing an appropriate scheme for the management of WEEE by improvement of collection and treatment of electronics scrap is very essential. In Poland, the new WEEE Act has been in force from January 1, 2016 (dated September 11, 2015) [21], which transposes the European Directive WEEE 2 (No. 2012/19 / EU) [22]. The European Directive WEEE 2 introduces, among others, increased obligations to collect and process WEEE–65% of weight from 2021 and a new division into six groups of WEEE from 2018, as well as the obligation to collect WEEE free of charge in the place of delivery of new equipment. Stores also have the obligation to collect small WEEE without any quantitative restrictions if the dimensions do not exceed 25 cm. The European Directive WEEE 2 groups a total of 10 categories of waste electrical and electronic equipment (WEEE) [22]:

- Large household appliances
- Small household appliances
- IT and telecommunications equipment
- Consumer equipment
- Lighting equipment
- Electrical and electronic tools
- Toys, leisure, and sports equipment
- Medical devices
- Monitoring and control instruments
- Automatic dispensers

It is estimated that about 11 million tonnes of WEEE such as computers, laptops, TV sets, LCD glass panels, fridges and mobile phones, smartphones, batteries, car batteries, accumulators, fluorescence lamps, magnets, etc. are produced in Europe annually, which accounts for 22% of the total volume of WEEE generated in the world [1]. The largest growth rate among WEEE is seen in the use of IT and telecommunications devices, for example, mobile phones and

laptops [1]. The recovering and processing of the WEEE have become very important because of the huge amount of the collected WEEE in Poland and in the European Union. Only 25% of the mass of WEEE produced in the EU-27 is stored and processed, and the remaining 75% is not processed. In Poland, an overall of 1.48 kg per capita of WEEE was collected in 2008 and 4.39 kg per capita in 2014; it is roughly 168,900 tonnes of WEEE. In 2021 Poland will be obliged to collect 11 kg per capita [23].

Based on the data of the Chief Inspectorate for Environmental Protection (CIEP), Poland, there are a lot of Polish Organisation of Electrical and Electronic Equipment Recovery (OEEER), for example, Elektroeko, the European Recycling Platform, AURAEKO, Biosystem Elektrorecykling, CCR RELECTRA, Electro-System, DROP, and TOM, which are responsible for meeting the collecting and recycling obligations on behalf of enterprises [23]. In Poland, there are also a number of companies collecting and processing WEEE, which cooperate with companies belonging to OEEER, for example, Elektrorecykling Sp. z o.o. [24], REMONDIS Electrorecycling Sp. z o.o. [25], Baterpol S.A. [26], and P.P.H.U. POLBLUME Zbigniew Miazga [27].

A total of 168,932 tonnes of WEEE was collected in the country, including 159,756 tonnes (94.56%) from households and 9175 tonnes (5.44%) from other sources in 2014. The largest volume of this waste is composed of large household appliances, 79,562 tonnes (47.09%), and IT and telecommunication equipment (e.g., computers, laptops, mobile phones, etc.), 24,965 tonnes (14.72%). The smallest part is composed of wastes of automatic dispensers, 115 tonnes (0.06%) [28].

4. Hydrometallurgical process of REE recovery

In order to separate the individual REEs, at first they have to be recovered from the raw material such as REE ores or the WEEE, in hydrometallurgical process. The technological scheme of REE extraction from minerals usually consists of grinding and cracking mined ore, preliminary enrichment to produce mixed REO concentrates, and then further concentration, separation and purification of REE oxides. To concentrate the REE extracted from minerals, the methods such as flotation, gravity separation, electrostatic separation, or magnetic processes are used [2].

Various methods and solutions are used for the extraction of REE from solid materials. As lixiviants, inorganic acids, alkalines, electrolytes, and chlorine gas are used. The leaching reagent should be selected to fit specific characteristics of the source material, for example, acids are commonly used to extract REE from silicate ore mineral such as gadolinite, eudialite, and allanite, and the alkaline reagents and sulfuric acid are mainly used to leach REE from phosphate ore minerals like monazite and xenotime. Electrolyte solutions are used to extract of REE from ion adsorption clay deposits. The chlorination process can be used to treat majority of rare earth minerals.

The obtained solution is a mixture of various REE with other metals, present in the raw material. The separation of individual metals is one of the most major challenges in hydrometallurgy. Currently the solvent extraction is the most preferable method of purification due

its continuous nature and possibility to handle large amounts of diluted post-leaching solution. Selection of the ligand used for forming the organic soluble metal-ligand complex can have profound effects on separation of metals and overall process efficiency and economics. Generally all three major classes of extractants: acidic, neutral, or basic extractants can be utilized for separating rare earths [29].

The extraction step is always followed by scrubbing. The organic phase from extraction step is contacted with scrubbing solution in order to remove any undesirable solutes that are entrained in the organic solution and improve the purity of valuable elements. Typically scrubbing is carried out by using water, dilute acid, or base solution. It is worth to note that a relatively high amount of valuable metals may pass to the scrubbing solution. For this reason, it should be recycled back to extraction stage and mixed with the feed aqueous solution.

The metals extracted to the organic phase should then be stripped back to aqueous phase for further recovery. The stripping is the reverse operation to the extraction. As a stripping solution, typically concentrated acid, alkaline, or salt solutions are used. Likewise extraction, stripping may be performed in a one-stage, two-stage, or multi-stage process [30].

REE can be separated using ion-exchange techniques. The separation of lanthanides can be achieved by using the combination of chelating eluents that are selective for individual lanthanides with resins that is characterized by little selectivity. The other possibility is the extractions with the chemically modified resins; among them are resins coated with extractant [31].

Several REE can be separated basing on their redox properties [31]. The example is cerium and europium which have been isolated on an industrial scale using reduction-oxidation reactions. Cerium (III) was oxidized to +4 that forms sparingly soluble oxides or hydrates. The precipitate was separated to give pure cerium solid (99% of purity) and cerium free liquor. Europium was reduced to +2 and precipitated as sulfate from mixed rare earth elements solution. The purity of europium obtained in this way was >99%.

The industrial process of purification of lanthanum, gadolinium, terbium, and dysprosium uses fractional crystallization techniques. This method is based on the different solubility of rare earth bromate, nitrate, and sulfate complexes. A lot of repetition of crystallization is necessary to obtain pure metal. For example, the lanthanide with 99.98% purity was obtained from a mixture of REE with using ammonium nitrate after 16 repetitions of crystallization ([31], and references therein).

Summarized, the separation of REE is the most difficult aspect of their production. The expanding global demand of these metals is the reason for the intensive increase of research in this field.

5. Separation of REE from polish resources

Initiating the nuclear power program in Poland generated interest in domestic uranium resources and the study of the recovery of uranium from Polish uranium ores [32, 33]. Most

Polish uranium ores are black shale and sandstone-type deposits [34, 35]. Uranium is usually accompanied by other valuable metals, among them REE [36]. These metals could be recovered at the same time as uranium, to improve the economy of processing of low-grade uranium ores predominated in the country. The content of lanthanum in Polish ores is 31–62 ppm in dictyonema shales and 4–53 pm in Triassic sandstones. The studies performed in the scope of national projects have shown 66% efficiencies of leaching of La from dioctynemic shales by 10% H_2SO_4 at 80°C [36]. The leaching under elevated pressure (2, 3, 5, 7 bar) did not improve the efficiencies, however shortened the time of process from 8 to 2 hours. Zakrzewska-Koltuniewicz et al. developed the second-order regression models to predict the leaching efficiencies of valuable chemical elements. They carried out the statistically designed experiments to investigate the recovery of U, V, and Mo chemical elements and representative lanthanides like La and Yb from low-grade uranium ore using sulfuric acid as a leaching reagent [37]. Lanthanum can also be extracted from sandstones with high efficiency (80%) at temperature 60°C with 10% HCl [38].

Very interesting, the novel method used for processing Polish uranium ores was a leaching in the membrane contactor with helical flow equipped with tubular metallic membrane. In this process, lanthanum was co-extracted with uranium from dictyonema shales with 78% of efficiency [39]. The process was carried out at ambient temperature, and the yield of leaching was higher than obtained in the stationary reactor with heating and mixing. The additional advantage of using the membrane contactor is a possibility of conducting two processes: leaching and solid-liquid separation in one apparatus.

The post-leaching solution obtained from the separation of solid residue from liquid is a mixture of various metal ions. The further purification and separation of metals can be achieved by solvent extraction followed by stripping to aqueous phase or by ion exchange. By using solvent extraction, we cannot avoid some of the problems associated with this process. A third phase between aqueous and organic phases is often formed in solvent extraction process. It is related to the solubility of the metal-extractant complex in the organic solution. The formation of the third phase may cause many difficulties; first of all, it leads to organic solvent loss. The minimization of the formation of the third phase can be achieved by addition of a modifier to the organic phase [40] or by application of membrane contactors, a multistage mixer-settler arrangement with concurrent flow of two phases—aqueous and organic [41].

Ion exchange proved also itself as an effective separation method of metals from water solutions. Danko et al. proposed to use Dowex 1X10 and Dowex 50WX4 for valuable metals extraction from pregnant leach liquors from extraction of Polish ore. The recovery of lanthanides was 99% [42].

6. Separation of REE from waste and products of phosphate fertilizer industry

The process of the recovery of REE from phosphogypsum has been studied in Poland for over 30 years. As a leaching solution, a concentrated sulfuric acid, nitric acid, or their mixture have been applied. For separation of rare earth elements, different methods have been

used: precipitation and extraction in liquid-liquid systems with the participation of an organic phase as well as crystallization methods, among others [43, 44]. Results of this work confirmed higher efficiency of leaching lanthanides from phosphogypsum by the application of nitric acid (c.a. 90%) than sulfuric acid (c.a. 60%). However, in the case of using nitric acid, an additional waste threatening the environment is generated.

The possibility of recovery of REE from phosphogypsum stored in Wizów heap with simultaneous recovery of P_2O_5 and production of anhydrite cement was also a subject of work [14]. The technology was examined at laboratory scale by the processing of 1 Mg/h of phosphogypsum. The technological flowsheet consisted of three steps: (i) leaching of lanthanide from the phosphogypsum using sulfuric acid at a concentration of 15%, (ii) crystallization of the rare earth concentrate (containing up to 25% Ln_2O_3) from the leach solution, and (iii) recrystallization of gypsum. In this way, insoluble high-quality anhydrite, phosphoric acid, and concentrate of rare earths concentrate containing more than 90% of oxides were products of the process. The composition of the rare earth concentrate is presented in **Table 3**.

The leaching of valuable metals from phosphogypsum stored in Wiślinka heap was also studied. The experiments were performed in laboratory scale. Lanthanum and other REEs were recovered with high efficiencies (**Figure 4**). Initially, the phosphogypsum was treated with 30% NaOH at 60°C, and then the solid residue was leached with 10% HCl at 60°C [12, 45].

Zielinski et al. studied the recovery of lanthanides from Kola apatite used for the phosphoric acid production in Polish phosphoric fertilizer factory [46]. It was found that a stage of the hydration of hemihydrate provides the best conditions for the recovery of lanthanides. In this stage for the removal of lanthanides, a solvent extraction has been applied and consequently a precipitation-stripping process for the removal of lanthanides from the solvent has been employed. As a result, a concentrate enriched with lanthanides has been obtained in which lanthanides were recovered with an efficiency of 80–85%. The similar results were obtained by the El-Didamony et al. in the studies of reduction in the concentration of radionuclides in phosphogypsum by using suitable organic extractants. This process was accompanied by reduction in the concentration of REE up to 80.1% [47–49].

Component	%	Component	%
La_2O_3	24.8	Dy_2O_3	0.2
CeO_2	50.5	Tb_4O_7	0.1
Nd_2O_3	15.9	Ho_2O_3	<0.1
Sm_2O_3	1.9	Er_2O_3	<0.1
Gd_2O_3	0.9	Tm_2O_3	<0.1
Eu_2O_3	0.44	Yb_2O_3	<0.1
Y_2O_3	0.3	Lu_2O_3	<0.1
ThO_2	0.2		

Table 3. The composition of the concentrate of REO [14]

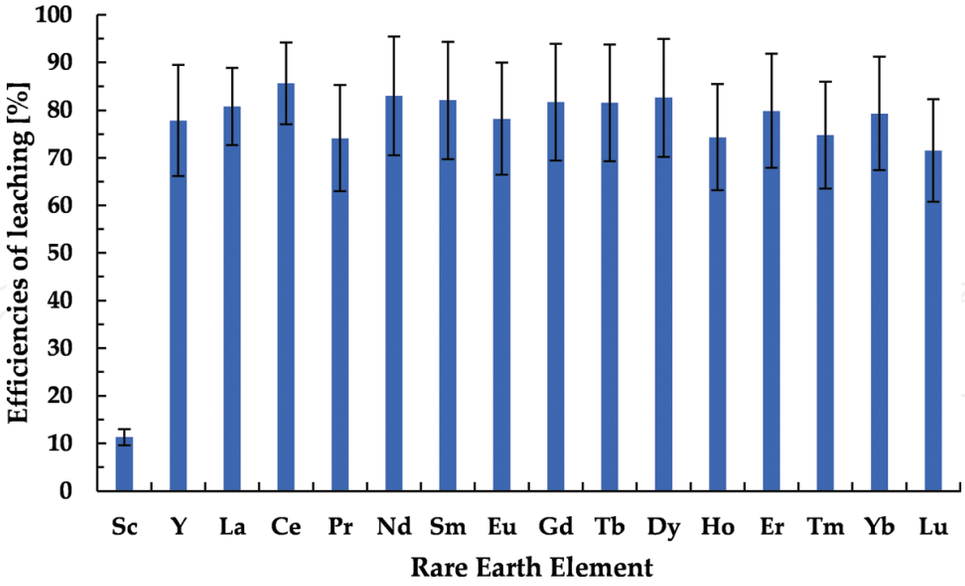


Figure 4. The efficiencies of leaching REE from phosphogypsum stored in Wislinka heap, Poland.

The possibilities of separation of rare earth elements from phosphoric acid solution have been also investigated [50]. A strongly basic ion-exchange resin with quaternary ammonium functional groups (Dowex 1) has been used for this purpose. The effect of temperature and resin cross-linking on the column performance and the ion-exchange reactions of phosphate complexes of several rare earths were determined. It was found that the resolution increases with increase of temperature, and the best separation was obtained at temperature of 85°C.

A separation of lanthanides form phosphoric acid through a crystallization process has been also investigated [51]. The effect of temperature and H_3PO_4 concentration on lanthanide solubility was tested. As a result of the experiments, highly crystalline solids of lanthanide phosphates were obtained.

7. Recovery of REE from WEEE

A complete strategy of recycling of waste electrical and electronic equipment consists of policies of waste management, research and development in new methods of processing, and challenges in elaboration of new technologies. For many countries, mainly those having limited access to mineral resources of REE, the development and improvement of the recycling processes of valuable metals from WEEE are significant aspects from the economic and environmental point of view. In Poland, obtaining a concentrate of REE from the discussed secondary raw material on an industrial scale is currently an economic issue. Unfortunately, about 70% of collected WEEE waste is processed in China [52].

In general, waste electrical and electronic equipment (WEEE) is a mixture of different materials and can consist of steel, printed circuit boards, batteries, permanent magnets, hard drives, plastic, aluminum foils, phosphors, photovoltaic materials, cables, separators, active

materials, carbon, organic binders, organic solvents, salts, additives, valuable metals, etc. Very important steps for the hydrometallurgical recovery of metals from a wide range of WEEE are mechanical pretreatment and dismantling.

Usually, a recycling of different types of waste electrical and electronic equipment is very complex because of the complexity of the material; the content of metals, for example, low-grade or high-grade material; the solubility and/or thermal stability; etc. Recovery of REE from WEEE using pyrometallurgical treatment is energy demanding, and often, the final products that are obtained require another processing to get pure compounds of the material [53]. As an alternative to pyrometallurgical processes, the metallurgical industry has been examining for hydrometallurgical treatment, due to some benefits related to hydrometallurgical processing, mainly for low-grade and chemically difficult streams [53].

Rare earth elements are used in the production of metal alloys (25%), catalysts (16%), permanent magnets (23%), polishing materials (11%), glass (7%), and materials containing phosphors (7%). The applications of these metals should provide the opportunities for strategic recycling and material recovery after their use. Recycling of spent fluorescent lamps can be a useful secondary source of Y, Eu, and Tb, and recycling of permanent magnets, which are used in water and wind energy as well as in HEV and EV vehicles, can become an important source of secondary acquisition of Nd, Pr, Dy, and Tb [54–56].

The amount of REE depends significantly on the type of waste electrical and electronic equipment (WEEE) and can range from several hundred ppm to several dozen percents. Particularly rich in rare earth elements are wasted permanent magnets of type $Fe_{14}Nd_2B$ (about 24% of Nd) or Sm_2Co_5. Some magnets of this type include additionally about 5% of Dy [1].

Usually, the processes of obtaining rare earth from permanent magnets are preceded by pretreatment, which includes such operations as mechanical disassembly of waste, physical separation, grinding to the proper grain size, thermal treatment, pyrometallurgy, hydrometallurgy, etc. Methods are adequate to the particular type of waste electrical and electronic equipment. The basic technologies include such unit processes as rare earth recovery through thermal or hydrometallurgical processing. For example, the recovery process of the neodymium from the $Fe_{14}Nd_2B$ magnet scrap consists of the extraction of neodymium with liquid magnesium, the separation of the liquid phase from the solid phase, and the evaporation of liquid magnesium. After these operations, the obtained final product contains about 96% of Nd [57].

The recycling and separation processes of Nd and Dy from permanent magnet scrap has been also studied by a hydrometallurgical method using liquid emulsion membranes in an integrated process [58]. In this method, the removal of ions is the result of processes taking place in one apparatus, that is, the production of liquid emulsion membranes and extraction. The extraction process involves the steps of transporting metal ions of Nd and Dy through the membrane phase of the emulsion to the phase of internal droplets, where they are separated by the extraction.

Nickel-metal hydride batteries (NiMH) that are used in the production of hybrid vehicles are another secondary source of valuable rare earth elements. The typical NiMH car batteries

contain approximately 3 kg of REE, 11 kg of nickel, and 1.5 kg of cobalt. A hydrometallurgical technology has been carried out for the recovery of valuable metals from spent car NiMH batteries in a continuous countercurrent solvent extraction process using a mixer-settler system in a pilot plant scale [59].

At the Institute of Mechanised Construction and Rock Mining, Warsaw, Poland, a method for recovery of yttrium and europium from used phosphors was developed, that is the subject of the patent PL-200095, 2008 [60, 61]. Acidic leaching, hydrolytic precipitation, and/or solvent extraction methods have been used in the recovery of Eu and Y from waste fluorescent lamps containing ~0.3% Eu and 7% Y. The best results of leaching efficiency were reached in 3 M HCl or 3 M HNO_3 at 80°C, about 90% for Eu, and 95% for Y [62].

A mixture of fluorescent lamps of a different kind was processed for the recovery of REE especially Y and Eu [63].

The high efficiency of oxide containing 99.96% REE (94.61% yttrium, 5.09% europium, and 0.26% of the other REE) was reached in solution with 35 vol% Cyanex 923 in kerosene using mixer-settler systems of three extraction and four stripping stages.

8. Summary: current status and perspectives

Due to the depletion of natural resources, increased environmental pollution, and dependence on suppliers from China, the recovery of valuable metals from WEEE is currently of great importance. Broadly understood economic development and new technologies in the electrical and electronic market are beneficial for people, but they also harm the surrounding environment and, consequently, all of us. Therefore, the intensively developing industry of recovery of metals from secondary sources has many positive aspects such as less hazardous waste, reduction of greenhouse gas emissions and CO_2, or a reduction in the use of natural resources and thus reducing the destruction of the natural environment.

Despite the small amount of recycling of REE, the worldwide production of these metals currently exists at about 130,000 metric tonnes of REO equivalent content per year, with the 2014 REE market worth about US$2051 million [64]. A large amount of REE is used in the production of catalysts, glass, lighting, and in the metallurgy industry, 59% in 2011, and the remaining 41% in new increasing markets such as magnets, batteries, and ceramics [64].

Development of modern technologies both in the field of electronics and green motorization is heavily dependent on rare earth elements. Also in Poland, the constantly growing consumption of REE is observed. Poland does not actually have its own REE natural deposits. The demand for these metals is mainly covered by import from China, West Europe, and USA. Alternative sources can be rich hard coal resources and a large share of fossil fuels in energy production. No wider studies on the occurrence of REE have been conducted in the country so far, for example, for the assessment of the hard coal deposits and power fly ashes as reasonable sources of lanthanides. Fragmentary data not allow to determine the full volume of REE in Polish hard coal.

A prospective direction in obtaining REE from domestic resources can be processing of WEEE. In recent years the interest of small entrepreneurs in this subject is noticeable. Many small companies have been established, dealing primarily with the collection and segregation of electric and electronic waste materials. With the help of national assets and money from EU structural funds, many innovative projects in the field of metal recycling are carried out. Innovative REE recovery projects can meet the expectations of satisfying the demand for these valuable, irreplaceable metals in today's life.

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