

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/330816603>

Rare Earth Elements—Separation Methods Yesterday and Today

Chapter · January 2019

DOI: 10.1007/978-3-030-10430-6_8

CITATIONS

2

READS

503

5 authors, including:



Dorota Kołodziejka

Maria Curie-Skłodowska University in Lublin

138 PUBLICATIONS 2,034 CITATIONS

[SEE PROFILE](#)



Dominika Fila

Maria Curie-Skłodowska University in Lublin

7 PUBLICATIONS 15 CITATIONS

[SEE PROFILE](#)



Jerzy Gega

Częstochowa University of Technology

26 PUBLICATIONS 274 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



New complex lanthanide compounds for fiber lasers and optical amplifiers technology [View project](#)



IONOMIC APPROACH IN AGRICULTURAL, FOOD AND ENVIRONMENTAL RESEARCH [View project](#)

Chapter 8

Rare Earth Elements—Separation Methods Yesterday and Today



Dorota Kołodyńska, Dominika Fila, Bernadeta Gajda, Jerzy Gęga and Zbigniew Hubicki

Abstract Rare earth elements (REEs) belong to the group of strategic elements. Their separation together with the spectral, magnetic and coordinative properties of REEs is essential for their further applications. However, separation of individual REEs on an industrial scale is very complex. Obtaining REEs of high purity requires purification of their concentrates. This is usually achieved by precipitation of REEs such as double sulphates $\text{NaLn}(\text{SO}_4)_2$ or oxalates $\text{Ln}_2(\text{C}_2\text{O}_4)_3$ as well as extraction and/or ion exchange method application. Currently, the recovery of rare earth metals from secondary sources is also very important. The details connected with the rare earth element recovery from nickel–metal hydride batteries and permanent magnets as well as their separation will be described in the paper.

8.1 Introduction

Due to their unique electrical, optical and magnetic properties, rare earth elements are very popular and used in many different areas of life. Although these elements have long been used in the production of glass, lighting and catalysts are also sought after by developing markets such as battery alloys and permanent magnets. The constantly growing demand for elements requires searching for alternative sources of their recovery. Although rare earth elements quite often occur in nature,

D. Kołodyńska (✉) · D. Fila · Z. Hubicki
Department of Inorganic Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, M. Curie Skłodowska Sq. 2, 20-031 Lublin, Poland
e-mail: d.kolodynska@poczta.umcs.lublin.pl

B. Gajda
Department of Metals Extraction and Recycling, Faculty of Production Engineering and Materials Technology, Czestochowa University of Technology,
J.H. Dąbrowskiego 69, 42-201 Częstochowa, Poland

J. Gęga
Department of Chemistry, Faculty of Production Engineering and Materials Technology, Czestochowa University of Technology, J.H. Dąbrowskiego 69, 42-201 Częstochowa, Poland

their extraction and separation have been big problems, mainly due to their high chemical similarities. The difficulty is also due to the fact that they occur very often together in the natural environment. Because of their similar physicochemical properties, their separation is problematic [1, 2].

Rare earth elements belong to the group of strategic elements. Their production is unequally distributed around the world. Their largest deposits are located in China, which is the main exporter of these materials. China is responsible for more than 80% of current global mining production and controls over 50% of the global mineral resources of these elements. China has become an industry leader, owing to which it has gained an advantage in every segment of production: ore mining, separation of elements, refining metals, creating alloys and processing them into production components. By introducing dumped prices, the Chinese degraded competing suppliers and dominated the world market for rare earth metals. Ultimately, China drastically raised commodity prices and almost completely limited their exports, thereby blocking the activities of global electronics companies. With the declining availability of rare earth elements in the global market, there is a need to search for and develop effective and economical methods of recovering these elements from secondary sources [2–4].

Currently, the recovery of rare earth metals from secondary sources, such as electronic and electrical equipment, is carried out using traditional pyrometallurgical or hydrometallurgical methods. In these technologies, many indirect operations can be distinguished to obtain the pure metal. These operations can be divided into four basic stages: homogenization, concentration, dissolution and separation of metals and their purification. The chemical similarities of rare earth metals and their ability to create isomorphic mixtures have resulted in difficulty of their separation. Therefore, physicochemical methods of their recovery from secondary sources are of great importance. Common methods of concentration, recovery and separation of rare earth ions include precipitation and coprecipitation, ion exchange, solvent extraction, electrochemical and membrane processes, adsorption as well as oxidation and reduction methods. Among the mentioned methods, ion exchange has played a significant role in the chemical technology of recovery and separation of rare earth ions from solutions with different concentrations for a long time. Application of ion exchange in the sorption and separation processes of rare earth ions is an important aspect towards separation of pure metals from wastewaters as well as from the solutions obtained after the leaching process of raw materials containing these elements [5–8].

8.2 Rare Earth Elements

8.2.1 *General Characteristics*

Rare earth elements (REEs), also known as rare earths (REs) or rare earth metals (REMs), according to the classification by the International Union of Pure and

Applied Chemistry (IUPAC) are a group of 17 elements including scandium (Sc), yttrium (Y) and 15 lanthanides (Ln): lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). The discovery of lanthanides dates back to 1794 when a mixture of lanthanides was first extracted from iterbite mineral by the Finnish chemist Johan Gadolin [9–13]. These elements can be divided into light rare earth elements (LREE): from La to Eu and heavy rare earth elements (HREE): from Ga to Lu. The basis for this division is the significant difference in atomic masses between Eu (151.964) and Gd (157.250) [10, 14–16].

The amount of these elements is not as small as results from their name. They occur in the Earth's crust in larger quantities than, for example, silver which content is about $6 \times 10^{-6} \%$ or platinum. The average distribution of yttrium is $3.3 \times 10^{-3} \%$, lanthanum $3 \times 10^{-3} \%$ and the other lanthanides from 6×10^{-3} to $5 \times 10^{-5} \%$. However, despite their relatively common occurrence, they are rarely found in a concentrated form that would be favourable for their extraction [17].

The amount of lanthanides depends on the atomic number of a given element. The increase in the atomic number causes a decrease their occurrence. In addition, elements with an odd atomic number are less common than those with even atomic numbers [18, 19].

8.2.2 The Occurrence of Rare Earth Elements

Rare earth elements belong to the group of lithophile elements. They do not occur in the Earth's crust in a free state but in the form of mixtures, usually isomorphous which makes their extraction and separation problematic. All lanthanides generally occur together except for promethium which nucleus is unstable. These are found in nature as abundant but rare minerals present in igneous or sedimentary rocks which include argillaceous. In the acidic igneous rocks, contents of rare earth are higher than in the basic ones. Relative abundance of lanthanides is presented in Fig. 8.1. The sedimentary rocks are characterized by a lower content of REE than the igneous ones [20]. Table 8.1 presents the average contents of rare earth elements in the igneous and sedimentary rocks.

There have been about 250 identified minerals containing rare earth elements. These can be divided into minerals containing light lanthanides, i.e. from La to Sm and those containing Y as well as heavy lanthanides, i.e. from Gd to Lu. Lanthanides occur in the form of silicates, phosphates, carbonates and fluorocarbons. Among the richest sources of rare earth elements are minerals such as monazite $(\text{Ce,La})\text{PO}_4$, bastnasite $(\text{La,Ce})\text{CO}_3\text{F}$, allanite $(\text{Ce,Ca,Y,La})_2(\text{Al,Fe})_3(\text{SiO}_4)_3(\text{OH})$ and xenotime $(\text{Y})\text{PO}_4$ [13, 16, 20–24].

Monazite, bastnasite and allanite are minerals that are the main source of light rare earth metals. They are primarily characterized by high contents of lanthanum and cerium. Xenotime is the main source of heavy rare earth elements which

Fig. 8.1 Relative abundance of lanthanides (own elaboration based on [19])

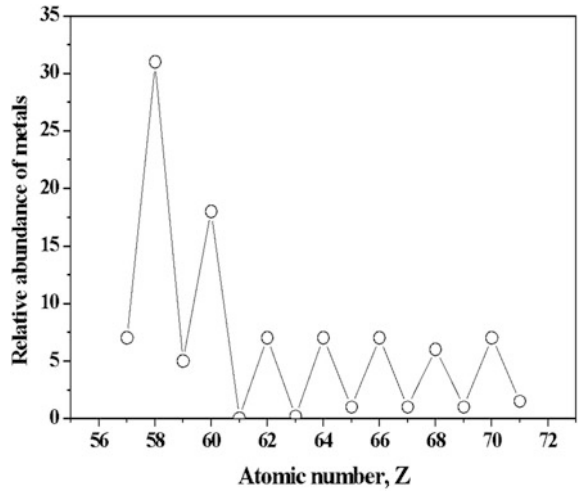


Table 8.1 Average REE contents in rocks (mg/kg) (own elaboration based on [20])

REE	Igneous rocks		Sedimentary rocks
	Acid	Basic	Argillaceous
La	30–150	2–70	30–90
Ce	80–250	4–60	3–90
Pr	6–30	1–15	6–10
Nd	18–80	2–30	18–35
Sm	6–11	0.1–1.7	5–7
Eu	1–2	0.01–4	1–2
Gd	4–10	0.1–8	5–7.5
Tb	1–1.25	0.1–1.2	0.9–1.1
Dy	5–8	0.05–7	4–6
Ho	1.3–2	0.1–1.5	1–1.8
Er	3.4–0.7	0.1–1	2.5–4
Tm	0.3–0.7	0.1–0.6	0.2–0.6
Yb	3–4.5	0.1–3.5	2.2–4
Lu	0.5–1.2	0.1–0.6	0.5–1.2

contains a high concentration of yttrium; hence, its general formula is (Y)PO₄. Monazite and bastnasite deposits account for approximately 99% of the total production of rare earth. These minerals contain about 60–75% of rare earth metal oxides and other elements [24]. Monazite and xenotime contain thorium and uranium which create problems related to the safe operation, processing and economical utilization. The bastnasite deposits are very valuable because these do not contain radioactive elements [9, 13, 16, 17].

The composition of individual minerals depends on the place of their occurrence. Although mineral deposits are scattered all over the world, their main mining is

currently taking place in China [12]. Bastnasite deposits constitute the two largest sites of rare earth elements. These are the Bayan-Obo in Inner Mongolia in North China and the Mountain Pass in Southern California [15, 22, 25]. Abundant monazite deposits are found on the beaches in India and coastal sands in Brazil, Australia and Malaysia [2, 9, 10, 22, 26].

Promethium is the only element that does not occur in nature. It was obtained as a result of artificial nuclear transformations and detected in uranium fission products. Lanthanides can be also found in small amounts in marine waters, biosphere as well as in plants and animals as secondary components. Their occurrence was registered on the Sun, Moon and stars as components of meteorites [9, 20].

8.2.3 *Physicochemical Properties of Rare Earth Elements*

REEs are an unusual group of metallic elements with unique properties: chemical, catalytic, magnetic, metallurgical and phosphorescent which consists of seventeen elements belonging to lanthanides [27, 28]. Lanthanides in the free state are silvery white, soft and malleable metals. About 25% of produced RE metals are used in the metallic form as the so-called mischmetal including [29]: 45–50% cerium, 22–25% lanthanum, 18% neodymium, 5% praseodymium and 1% samarium with deoxidizing and desulphurizing properties. Lanthanides are characterized by very similar chemical and physical properties. This is due to the fact that they have similar atomic and ionic radii and the same electronic structure of valence shells. As the f-electron elements, these have the electronic configuration of $4f^{1-14}5d^{0,1}6s^2$ (Table 8.2).

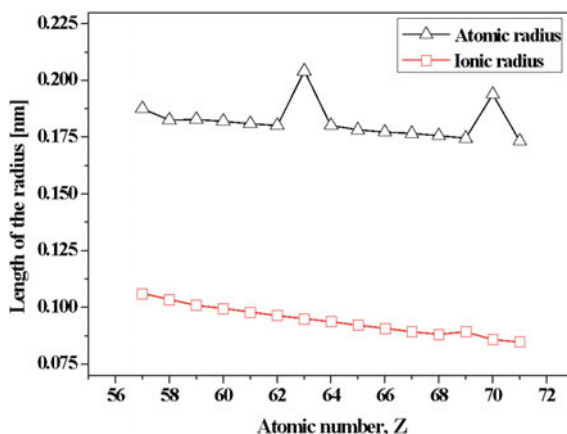
All lanthanides are very reactive metals and strongly electropositive, and in contact with the air gets tarnished. Their oxides and hydroxides have evidently basic properties. Lanthanide hydroxides do not dissolve in excess of bases. The basic properties of lanthanides decrease with the decreasing ionic radius (from La to Lu). Some elements additionally form ions on the second or fourth oxidation state which is associated with obtaining the more stable electronic configuration $4f^0$, $4f^7$ or $4f^{14}$, for example, Ce(IV), Tb(IV), Yb(II), Eu(II). II and IV oxidation states are unstable in aqueous solutions except for cerium(IV) salts. Europium forms the most durable compounds on the second oxidation state. Lanthanides are characterized by low electronegativity and high boiling or melting points. Lanthanide ions except for La(III) and Lu(III) exhibit strong paramagnetism which is associated with the presence of the unpaired electrons subshell 4f. La(III) and Lu(III) ions are diamagnetic. At low temperatures, Gd(III), Dy(III), Eu(III), Er(III) and Ho(III) ions become ferromagnetic. The colour of lanthanide ions is associated with f-f electronic transitions. All ions absorb light in the visible and near ultraviolet ranges. Many of them show a characteristic colour in both the solid state and in the solution. The orbitals f located deep inside the atom are largely shielded from external influences which indicate that they do not participate in the bond formation, and as a result, sharp absorption bands are observed [30, 31].

Table 8.2 Physicochemical properties of rare earth elements (own elaboration based on [11])

Element	Symbol	Atomic number	Atomic weight	Electron configuration
Scandium	Sc	21	44.9559	$3d^1 4s^2$
Yttrium	Y	39	88.9059	$4d^1 5s^2$
Lanthanum	La	57	138.9055	$5d^1 6s^2$
Cerium	Ce	58	140.12	$4f^2 6s^2$
Praseodymium	Pr	59	140.9077	$4f^3 6s^2$
Neodymium	Nd	60	144.24	$4f^4 6s^2$
Promethium	Pm	61	145.0	$4f^5 6s^2$
Samarium	Sm	62	150.36	$4f^6 6s^2$
Europium	Eu	63	151.96	$4f^7 6s^2$
Gadolinium	Gd	64	157.25	$4f^7 5d^1 6s^2$
Terbium	Tb	65	158.9254	$4f^9 6s^2$
Dysprosium	Dy	66	162.50	$4f^{10} 6s^2$
Holmium	Ho	67	164.9304	$4f^{11} 6s^2$
Erbium	Er	68	167.26	$4f^{12} 6s^2$
Thulium	Tm	69	168.93	$4f^{13} 6s^2$
Ytterbium	Yb	70	173.04	$4f^{14} 6s^2$
Lutetium	Lu	71	174.967	$4f^{14} 5d^1 6s^2$

A characteristic phenomenon found in a series of lanthanides is the so-called lanthanide contraction. As the charge of the nucleus increases, the atomic and ionic radii of lanthanides decrease with the increasing atomic number. Passing from La (III) to Lu(III), the ionic radius decreases from 0.106 to 0.085 nm. The contraction comes from the interactions of the increasing nuclear charge on a slightly changing electron shell in which the subshell 4f got extended. When it is filled up with electrons, the nucleus is less and less affected by the electrons of external subshells. This phenomenon is characteristic of lanthanides on various oxidation states; however, it is the most visible for ions on the third oxidation state (Fig. 8.2) [30, 32].

Fig. 8.2 Lanthanide contraction (own elaboration based on [30, 32])



8.2.4 Application of Rare Earth Metals

Consumption of REEs in individual countries around the world is a measure of their technological level and modernity which is associated with the production of new and multifunctional materials for medical diagnostics, optics, nuclear technologies, laser production, telecommunications, metal alloys, aviation and cosmonautics as well as petrochemistry. Progress in the above fields is possible due to the development of technologies for separation and purification of REEs. According to the data of the US Geological Survey published in 2015, approximately 97% of REEs production came from China. From the point of view of the use of secondary sources—apatite phosphogypes from the Kola Peninsula (containing about 1% of rare earth oxides (REO)) stored at the former Chemical Plant “Wizów”/Bolesławiec (Poland) seems to be an attractive source [19, 33].

REEs are essential in everyday life all over the world in both developed and developing countries in the use of the greener technologies. They have many desirable properties, such as clear optical properties including fluorescence and coherent light emission which is necessary for laser devices, the ability to create with other metals very durable and light magnetic materials as well as unique nuclear, metallurgical, chemical, catalytic, electrical, magnetic and optical properties. These properties contributed to their increasing variety of applications. They are primarily used in many high-tech sectors, in metallurgy, glass and ceramics, electronics, petrochemical industry, nuclear energy production, agriculture, medicine, in the production of military and defence systems as well as renewable energy sources. Due to the continuous development of modern and advanced technologies, lanthanides are constantly gaining importance. Rare earth elements are also used in high-performance magnets ($\text{Nd}_2\text{Fe}_{14}\text{B}$ and SmCo_5 , $\text{Sm}_2\text{Co}_{17}$), rechargeable nickel–metal hydride batteries (NiMH), TV sets, computer hard drives, plasma and LCD screens, laptop computers, cell phones, DVD players, cameras, electric motors and generators of hybrid cars. Figure 8.3 shows the use of rare earth elements in various

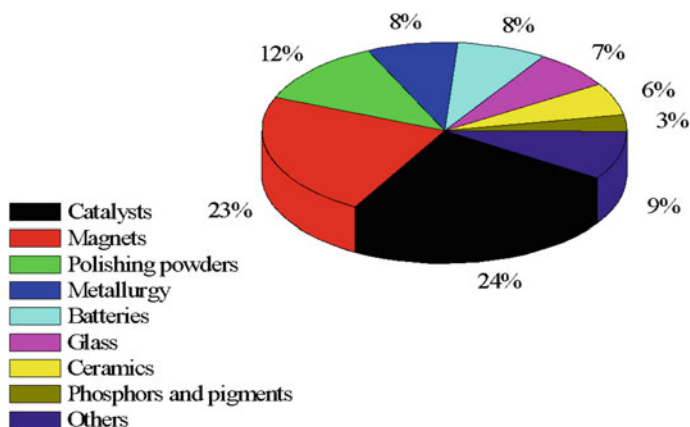


Fig. 8.3 Main applications of rare earth elements (own elaboration based on [36, 37])

areas of life. Due to their characteristic magnetic, spectroscopic and optical properties, REEs are widely used not only in various branches of industry such as electronics, nucleonics, optoelectronics, powder metallurgy or the nuclear industry but also in many fields of science (physics, biochemistry, medicine and pharmacy). For example, REE compounds are used as catalysts for cracking heavy hydrocarbons in oil refineries, exhaust catalysts as well as methane conversions, in the computer industry, mobile telephony, lasers and medicine. The mischmetal alloy, i.e. a mixture of rare earth elements such as Ce, La, Nd, Pr and smaller amounts of Sm, Tb and Y, is used as a deoxidizer and a desulphurizing agent of steel [12, 34, 35]. Table 8.3 presents the most important applications of individual rare earth elements.

Table 8.3 Most important industrial applications of rare earth elements (own elaboration based on [12, 15, 34, 35, 38])

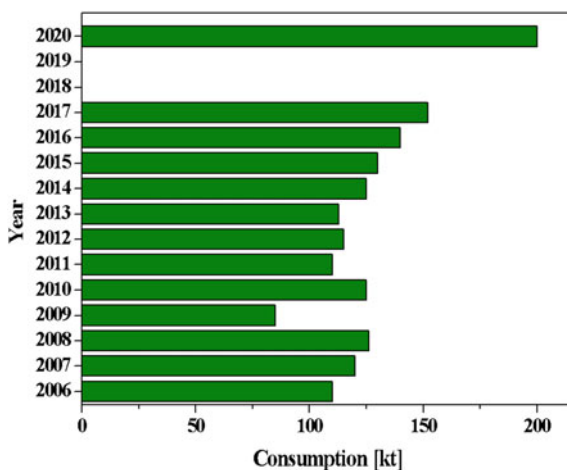
Symbol of element	Application
La	Catalyst in the oil refining, production of hybrid car engines, batteries, lenses, projectors, X-ray films, polishing powders
Ce	Additive to steel, production of polishing powders, lenses, cathode-ray tubes, as a yellow dye in dyeing glass and ceramics, catalyst
Pr	Anticorrosive component, signal amplifier in fibre optics, additive to protective glasses, as a green dye
Nd	Production of lasers, batteries, supermagnets, wind turbines, engines for hybrid cars, wind generators in wind power plants, loudspeakers
Pm	As a source of beta radiation, production of nuclear batteries, portable X-ray equipment, paints
Sm	Production of supermagnets, reactor rods, lasers
Eu	Production of LCD televisions, fluorescent lighting, lasers, mercury lamps, construction of control rods in atomic reactors
Gd	Production of lasers, magnets, hard discs, contrast agent in magnetic resonance, production of control rods in nuclear reactors, alloy additive
Tb	Production of magnets, lasers, fluorescent lamps, phosphors for lamps and displays, as radiological screens and fuel cells
Dy	Production of strong magnets, lasers, hybrid engines, hard disc drives
Ho	Production of magnets, lasers, dyeing glass and zirconia, used in nuclear reactors
Er	Production of lasers used in medicine, phosphors, photographic filters, control rods in nuclear reactors, used in the dyeing glass
Tm	Production of ceramic magnetic materials, surgical lasers, reactors, portable X-ray devices
Yb	Manufacture of optical fibres, solar cells, lasers, oxidizer in the alloys
Lu	Lutetium isotope is used in radioactive dating
Sc	High-strength Al–Sc alloys, metal alloys for the aerospace industry, dentistry
Y	Production of capacitors, phosphors, oxygen sensors, radars, lasers, superconductors, radioactive yttrium isotopes in radiotherapy

8.2.5 Production and Consumption of Rare Earth Elements in the World

REEs have been designated as strategic metals due to the risk of supply limitation, environmental hazard related to the limitation of production possibilities conditioned by the need to maintain environmental quality standards as well as economic effects of supply limitation. In 2014, the total global production of REEs was estimated to be 110,000 tons [24, 39]. The value of production has been growing year by year. In 2016, the value of REEs production was estimated to be 126,000 tons which were 85% in China, 10% in Australia and the rest in Malaysia, Brazil, India, Russia and Vietnam [40, 41]. According to the estimates by Curtin University and IMCOA, the demand for REEs by 2020 may increase by more than 50% compared to the level from 2014, reaching around 200,000–250,000 tons (Fig. 8.4) [41].

However, according to the US Geological Survey (USGS) based on REEs production data from 2015, the top six rare-earth-producing countries include (1) China with the mine production of 105,000 tons. China dominates rare earth mineral production to such a degree that its export practices were recently challenged by the USA, European Union and Japan, resulting in the World Trade Organization (WTO) ruling against the country's rare earth export quotas in 2014 (in the past China exported only 31,000 tons of its rare earth production); (2) Australia with the mine production of 10,000 tons is the world's third-largest known rare-earth-producing country; (3) the USA with the mine production 4,100 tons. The Molycorp's Mountain Pass mine is the only one producing rare earth minerals in the USA. Overall, the US rare earth production drops from 5,400 tons in 2014 to 4,100 tons in 2015; (4) Russia with the mine production of 2,500 tons is expected to be able to meet Russian rare earth demand and increase

Fig. 8.4 Consumption of rare earths in 2006–2020 (own elaboration based on [41])



production. However, Russian rare earth production stayed flat in 2015 at 2,500 tons; 5) Thailand with the mine production of 1,100 tons. Thailand has raised production of rare earth minerals by 300 tons in 2014 to 1,100 tons in 2015; and (6) Malaysia with the mine production of 200 tons. Malaysia is home to the world's largest rare earth refinery, Lynas Corporation's Lynas Advanced Materials Plant (LAMP). The LAMP facility handles refining duties for Lynas's mines in Australia.

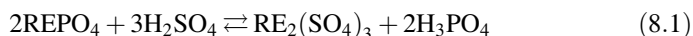
It should be mentioned that China is the only country in the world that can provide rare earth products of all grades and specifications such as not only metals, alloys or carbonates but also most of the final products, e.g. phosphors, LEDs, catalysts, NiMH batteries, magnets etc. The main process steps of REEs production are connected in mining (open-pit mining and underground mining) and processing. In open-pit mining, the first step is soil, waste rock and vegetation removal. The second step is milling. The ore is crushed, ground to fine powder in the mill in order to obtain the high surface needed for the further separation. The third step is the separation of valuable REEs from the rest of the ore by physical separation methods. The most commonly used methods have been magnetic separation and flotation with consumption of water, chemicals as well as a high amount of energy.

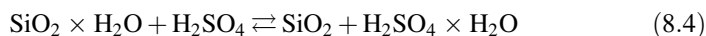
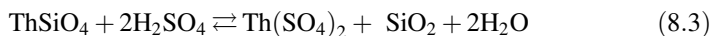
RE minerals have different magnetic susceptibilities. Some of these are paramagnetic which is connected with the Fe and Mn contents or contribution of REEs themselves. In magnetic separation, no chemicals are used. The method can be wet or dry depending on grain size, water availability and dust issues. It is characterized by the low operating cost but on the other hand by significant power requirements. However, with a good release, recovery can be very high.

As for flotation, its product is enriched to obtain the concentrates (30–70%). Finally, the concentrates are further extracted and separated; however, the MREEs and HREEs such as Sm, Eu, Tb and Dy are obtained by metallothermic reduction in a vacuum. In this case, the reaction proceeds at 1723–2023 K and needs the inert gas presence.

Separation of individual REEs is difficult due to their chemical similarity. Monotonic evolution from La(III) to Lu(III) makes the separation between two ions very difficult and only possible by the complexation process.

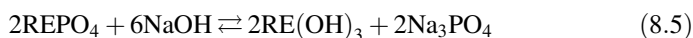
The Bayan-Obo Mines in Inner Mongolia and Sichuan in China are the largest rare earth mines in the world. The main product is iron ore with LRE as a side product. The surface mining extracts a bastnasite–monazite mix containing LREE and also thorium. Monazites are processed by acid and alkaline methods. In the acid method, ground (100–150 mesh) concentrate is subjected to the reaction with acid at 473 K. The ore decomposition takes place in the steel or cast iron apparatus operated periodically or continuously. The principal processes run according to the following reactions:





At low temperature, acid excess and longer reaction time are needed. Additionally, at temperatures, 573–623 K, water-insoluble thorium pyrophosphate is formed. However, in the presence of an appropriate excess of acid, the decomposition process itself is not selective. Further possibilities for thorium separation from rare earth are by the leaching process.

In the alkaline method, the ground rare earth is melted with sodium hydroxide or sodium carbonate or treated with the aqueous solution of sodium hydroxide. As a result, phosphates become hydroxides:



To prevent the formation of Ce(IV) which impedes the dissolving of the precipitate, the addition of some reductants, e.g. glucose, is recommended [42].

Since 1970s, the solvent extraction (SX) is the only industrial technology for REE separation. However, the families of thorium and uranium are responsible for the radioactivity of REE-based products. The most popular isotopes are as follows: ^{232}Th family (^{232}Th , ^{228}Ra , ^{228}Th), ^{238}U family (^{238}U , ^{234}U , ^{230}Th , ^{226}Ra , ^{210}Pb) and ^{235}U family (^{235}U and ^{227}Ac).

As for the solvent extraction process, there should be taken into account the following extractants:

- (1) strongly acidic (alkylphosphoric derivatives) such as HDEHP, D2EHPA, P204, bis(2-ethylhexyl) hydrogen phosphate, phosphoric acid bis(2-ethylhexyl)ester; HEHEHP, HEHEHPA, PC88A, P507, Ionquest 801, 2-ethylhexyl hydrogen-2-ethylhexyl phosphonate, phosphonic acid (2-ethylhexyl)-mono(2-ethylhexyl) ester or cyanex 272, LIX 272, P229, di-isooctylphosphinic acid and Ionquest 290, bis (2,4,4-trimethylpentyl)phosphinic acid. These extractants extract REE in the acidic medium systems, and the extraction increases with the atomic number of REE (Y(III) occurs between Ho(III) and Er(III)). Additionally, anions and diluents have a very limited impact on selectivity. The effectiveness of the process is dependent largely on acidity of the aqueous phase (in the case of less acidic extractants, saponification is required to extract REE). Moreover, alkyl-phosphorics are stronger extractants but more difficult to back-extract (increasing reactant costs in processes).
- (2) weakly acidic extractants (carboxylic acids) such as versatic acids (versatic 10, versatic 911), naphthenic acids (NOR180), CA-100 (sec-nonylphenoxyacetic acid). These are much less acidic than phosphorous acidic extractants and can be applied in neutral aqueous solutions. For example, versatic acids extract REE in the pH 4–6 range, naphthenic acids have been widely used but the

composition of the extractant is often not stable and CA-100 extracts at lower pH value than versatic ones.

- (3) neutral extractants/molecular extractants—in this group, the most popular are TBP (tri n-butyl phosphate), DBBP (dibutyl butyl phosphonate), TOPO, cyanex 921 (trioctylphosphine oxide), cyanex 923, cyanex 925—the liquid mixture of four trialkylphosphine oxides. These extractants only extract REE nitrates with no or limited extraction of REE chlorides or sulphates. In the case of the neutral extractants, the efficiency of the process can be increased by a salting out effect with non-extracted salts (i.e. sodium or ammonium nitrate). It should be noticed that TBP selectivity is relatively low and highly influenced by REE concentration in the aqueous phase.
- (4) basic extractants/anion exchangers—primary amines (Primene™ JM-T (t-alkyl primary amine) or N1923 (sec C-alkyl amine)), quaternary ammonium salts (Aliquat 336, Adogen 464—tricaprylmethylammonium chloride). The primary amines extract REE sulphates, and quaternary ammonium salts extract REE nitrates or REE thiocyanates. However, no extraction occurs in the chloride medium. This system offers possibilities for separation of non-REEs by amine extractants. Additionally, primary amines are efficient extractants to separate Th from U and REEs (after sulphuric acid leaching from the monazite). The selectivity between adjacent REEs is rather low ($F = 1.2\text{--}1.9$) and not really large enough for separation [43].

While carrying out the liquid–liquid extraction process, the low mutual solubility of both extracted and extractant phases and the difference in phase density (the greater the difference in density between the solvent and the sample, the faster and more accurate the separation of layers) should be taken into account. Unfortunately, in practice, emulsions at the interface are often formed. These are readily created when the alkaline solution is extracted. Another factor is the polarity of solvents and extracted compound (organic compounds that are composed of main hydrocarbons have a hydrophobic character; i.e., they dissolve better in nonpolar solvents). Therefore, in the extraction process, modifiers are often added—mainly to improve certain properties, such as solubility, viscosity, hydrodynamics, kinetics and an anti- or synergic agent that affect the change of partition coefficients and/or selectivity. The most popular are both aliphatic (kerosene) and aromatic (i.e. solvesso) hydrocarbons. As synergistic agents, TBP and TOPO are used; however, as modifiers alcohols C8–C12 or phenols C9 can be applied.

The main environmental threats associated with the extraction and processing of rare earth are related to the contamination of radioactive water containing radionuclides such as thorium and uranium as well as heavy metals, acids and fluorides. The air pollution is associated with the presence of the above-mentioned radionuclides, heavy metal ions and HF, HCl, SO₂, etc. There are estimates that around 20,000 tons of rare earth oxides have been illegally extracted and smuggled out of China. Most of these mines probably did not meet any emission standards [44]. In this case both acidic method REO are roasted at 673 and 723 K in concentrated sulphuric acid to remove fluoride and CO₂, after filtration, REEs were

leached using $(\text{NH}_4)\text{HCO}_3$ and HCl (to obtain the REE chlorides concentrate) and the alkaline method affect the environment.

For separation and refining of REO, extraction mainly based on 2-ethylhexyl hydrogen-2-ethylhexylphosphonate and HCl has been adopted followed by precipitation using $(\text{NH}_4)\text{HCO}_3$ or oxalic acid forming $(\text{RE}_2(\text{C}_2\text{O}_4)_3 \text{ or } \text{RE}_2(\text{CO}_2)_3)$. In the next step, these were heated and REOs formed by oxidation. LREEs have been extracted by molten salt electrolysis based on chloride or oxide. In the case of bastnasite, the ore was crushed and separated by both gravity and magnetic ways as well as the gravity one for the next step of flotation separation where 70% mixture of REO was obtained. In Sichuan, bastnasite is treated with the oxidizing roasting-hydrochloric leaching process. The roast is carried out at 873 K to remove CO_2 . The REE concentrates are leached in hydrochloric acid, precipitated by sodium hydroxide solution and leached in hydrochloric acid.

Besides the REE mining, the most important sources of REEs in soils are phosphate fertilizers produced from the natural phosphates. Therefore, the attempts to find solutions for the more efficient use, end-of-life recycling or reusing of rare earth, as well as potential substitutes, need to be intensified. Rare earth recycling is still in early stage and is connected with recycling of phosphors, permanent NdFeB magnets, industrial residues, nickel–metal hydride batteries and various other rare-earth-containing products. However, only phosphors and batteries can be recycled on an industrial scale. Therefore, taking the above into account there is the need to develop a new hydrometallurgical technology for the recovery of these valuable elements or their compounds from spent electronic equipment such as nickel–metal hydride batteries (NiMH), computer hard drives or electric motors and generators of hybrid cars. On the global level, the Waste of Electrical and Electronic Equipment (WEEE) is estimated to be around 50 mln tons per year. In Europe, the amount of generated WEEE is about 12 mln tons per year. Therefore, the recycling market for rare earth in Europe has great potential as the EU is a significant consumer of rare-earth-containing products. Among firms which initiated the projects for recycling of electronic devices such as phones and laptops, the Umicore in Belgium and the Saubermacher in Austria should be mentioned [45, 46].

8.3 Rare Earth Element Recovery from Nickel–Metal Hydride Batteries

The use of REE alloys in the nickel–metal hydride (NiMH) batteries is based, among others, on their hydrogen storage properties as hydrogen storage alloys. For example, LaNi_5 used as the negative electrode material in NiMH when transforming into LaNi_5H_6 is able to absorb large amounts of hydrogen; the density of hydrogen is higher than in liquid hydrogen (1 m³ contains 88 kg of hydrogen). Hydrogen uptake takes place at room temperature whereas dehydrogenation at temperatures up to 100 °C.

Hydrogen storage alloys based on LaNi_5 are expensive because of the requirement of high-purity lanthanum and nickel. Therefore, lanthanum has been partly replaced by mischmetal (a mixture of rare earth elements such as Ce, La, Nd, Pr and in smaller quantities of Sm, Tb and Y). It has been used as a deoxidizing and desulphurizing agent of steel.

The recycling of NiMH accumulators has been based on their conversion into a stainless steel (as a cheap source of nickel) [47]. Due to limited supplies from China, a method for recovery of nickel, cobalt and rare earth metals from NiMH batteries has been developed. Acids such as HCl , H_2SO_4 or HNO_3 were used for this purpose. The most favourable results were obtained with a 4 M HCl solution [48]. From the REE leaching solutions, they were precipitated in the form of phosphates. The technology for the precipitation of double sulphates with the use of Na_2SO_4 has also been developed [49]. Zhang et al. reported a hydrometallurgical process for the separation and recovery of nickel, cobalt and rare earth metals from NiMH batteries [50, 51].

Li et al. [52] formulated a flow sheet for a hydrometallurgical procedure including leaching in 3 M H_2SO_4 , solvent extraction, evaporation and crystallization to recover nickel, cobalt and rare earth from NiMH batteries. The recovery of rare earth elements such as La(III) and Nd(III) from spent nickel–metal hydride (NiMH) batteries by a novel synthetic adsorbent was described in a paper by Gasser and Aly [53]. The layered double hydroxides (LDHs), also known as hydrotalcite (HT)-like materials, were used. They belong to a class of synthetic two-dimensional nanostructured anionic clays. The batch-type experiments were conducted to investigate capacity and uptake of REEs by Mg–Fe-LDH- cyanex-272 using separate nucleation and ageing steps. The effects of some parameters, such as contact time, system pH and adsorbent weight, were investigated.

This process has been tested to separate La(III) and Nd(III) from the NiMH battery using H_2SO_4 as the leaching agent. The stripping of pure La(III) from the solid phase was performed using 0.01 M HCl at 298 K. La(III) and Nd(III) were removed from the filtrate in the form of oxalates, which were calcined at 773 K. After analysing the resulting mixture, it was shown that the neodymium precipitation percentage was higher than 97% and that of lanthanum was lower than 0.8%. The rare earth was obtained as a chloride solution with an overall recovery of 97.8%. Several other studies described the dissolution of rare earth from NiMH batteries by leaching with H_2SO_4 or HCl .

As leaching and precipitating agents used were 2 M HCl and 2 M NaOH solutions, respectively, at room temperature. After calcination at 1273 K, crystalline phases such as NiO , CeO_2 and LaCoO_3 were obtained [54]. The nickel was extracted with a solution of ammonia. After heating, nickel hydroxide was obtained which was converted into an oxide during calcination process. The precipitate containing the remaining CeO_2 and LaCoO_3 was digested in HCl at room temperature. At this stage, LaCoO_3 passed into the solution and CeO_2 remained in the sludge. Provazi et al. [55] studied the recycling of various metals, including cerium and lanthanum, from a mixture obtained from different types of batteries. After grinding to remove volatile metals such as cadmium, zinc and mercury,

the whole matter was heated at 1273 K for 4 h in an inert atmosphere. At this stage, manganese oxides were reduced to MnO and the whole material was leached with sulphuric acid. An attempt was made to separate metals in the leaching solution by selective precipitation and solvent extraction. The extraction with cyanex 272 proved to be the most effective method. Larsson et al. [56] used a similar methodology.

The industrial-scale pilot plant has been operating in Hoboken near Antwerp (Belgium) since 2011. The assumed capacity of the installation is 7,000 tons which are approximately 150 tons of hybrid batteries for electric vehicles or 250 mln batteries for mobile phones. Nickel–metal hydride and lithium-ion batteries have also been recycled. The batteries were placed in a vertical shaft furnace, along with a small amount of coke and slag. From the bottom of the shaft furnace, air enriched with oxygen was supplied. This process required a relatively small amount of energy as the significant energy released during organic electrolyte combustion. Valuable metals from a Ni–Co–Cu–Fe alloy such as Ca, Al, Si and Fe as well as Li and REEs were found in the slag in the form of oxides. These oxide slags can be processed to recover lithium and to manufacture rare earth metal concentrates which can then be used as raw materials in the Solvay REE separation plant (formally Rhodia) in La Rochelle (France).

The recycling process combines the capabilities of Umicore's proprietary ultra-high temperature (UHT) battery recycling process in Antwerp (Hoboken) with the Solvay rare earth refining competences. Rhodia is an international chemical company and a major player in the automotive, electronics, flavours and fragrances, health, personal and home care markets, consumer goods and industrial markets. Umicore is a global material technology group that focuses on application areas where its expertise in materials science, chemistry and metallurgy makes a real difference. Its activities are centred on catalysis, energy materials, performance materials and recycling. After the separation of the nickel and iron from the rare earth, Umicore processed the rare earth into a high-grade concentrate that can be refined and formulated into rare earth materials. The recycling process can be applied to different kinds of NiMH batteries, ranging from portable applications of rechargeable AA (double-A) and AAA (triple-A) batteries used in cordless phones, toys and games to those used in hybrid electric vehicles. Recently, Honda Motor Co., Ltd. and the Japan Metals & Chemicals Co., Ltd. announced to set up a recycling plant to extract REEs from used nickel–metal hydride batteries collected from the Honda hybrid vehicles at Honda dealers inside and outside of Japan. However, the recycling technology and process have not been disclosed. In 2016, Becker et al. [57] developed a hydrometallurgical process for recovery of components from electrode fractions separated from spent NiMH and Li-ion batteries. As a result, collective concentrates of Ni–Co oxides, as well as lanthanide oxides, were obtained. This technology was run in a pilot scale in waste treatment plant at Gorzow Wielkopolski (Poland). Most of the presented above technologies produce a mixture of lanthanides in the metallic form (as a mischmetal) or in the form of their oxides.

8.4 Rare Earth Element Recovery from Permanent Magnets

According to Molycorp in the case of the permanent magnets during their production, the following steps were distinguished: RE mining and concentration, separation of ores into oxides, refining of oxides to metals, forming metals into magnet alloy powders (75–80% in China and 20–25% in Japan) and NdFeB magnet manufacturing (75–80% in China, 17–25% in Japan and 3–5% in Europe). Main rare earth magnet applications are presented in Fig. 8.5.

Bulk permanent magnets are indispensable components of numerous consumer and industrial products for energy conversion. The escalation of rare earth costs presents an opportunity for new magnets with an energy product of 100–200 kJ/m³, intermediate between ferrite (<38 kJ/m³) and NdFeB (>200 kJ/m³), provided that the costs of raw materials and manufacturing kept low [58]. NdFeB magnets are comprised of a Nd₂Fe₁₄B matrix phase, surrounded by a neodymium-rich boundary phase, with small admixtures of Pr, Ga, Tb, Dy and others such as Co, V, Ti, Zr, Mo, Nb. However, the boundary phase contains Cu, Al or Ga. Dy is added to magnets to increase their thermal stability against demagnetization. Sintered NdFeB magnets (also known as Neo magnets, neodymium magnets or NIB) are the most powerful and advanced permanent magnets. These are characterized by high remanence, improved coercive force and better energy. The NdFeB magnets have some limitations due to their poor corrosion resistance. However, they can be easily formed into various sizes and different shapes like discs, rings, blocks and segments. The second type of magnets is based upon samarium–cobalt alloys (SmCo₅ or Sm₂Co₁₇) which contain admixtures of different transition metals, such as Fe, Zr and Cu (even though they are without protective coatings) [6]. Therefore, the recovery is only relevant for large magnets which can be directly reused after cutting by applying hydrometallurgical and pyrometallurgical processes. Demand

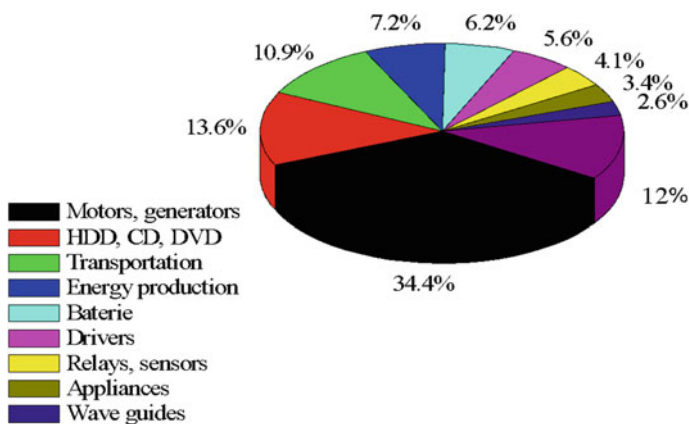


Fig. 8.5 Main rare earth magnet applications (own elaboration based on [58])

for REEs in magnets is predicted to grow by 6–8%. Much of this growth will be related to continuing demand for the use in consumer electronic equipment, wind turbines, motors in electric vehicles, the growth of neo magnets to perform at elevated temperatures. Firms like Hitachi, Showa Denko and Mitsubishi Materials are all searching ways of recycling REEs from discarded hard disc drives and other appliances [34]. The Hitachi approach to recover NdFeB magnets from HDDs and compressors of air conditioners is based on a combination of vibration, demagnetization and manual collection. Another recently developed technology by the University of Birmingham uses hydrogen at atmospheric pressure to separate the sintered REE magnets from the computer HDDs, leading to hydrogenated NdFeB powder.

8.5 Separation of High-Purity Rare Earth Elements

Lanthanide separation and preconcentration of high-purity compounds are the most difficult problems in inorganic chemistry and technology. For separation of lanthanide ions, it is possible to use chemical separation, fractional crystallization, solvent extraction or ion exchange processes. The rare earth elements can be successfully separated and recovered from the sulphurous acid solution using the organophosphorus compounds as extraction agents, e.g. di-2-ethylhexyl phosphoric acid or 2-ethylhexyl phosphonic acid monoethylhexyl ester of 99.9% purity. In the case of recovery and separation of thorium and rare earth elements from acidic aqueous solutions (together with a large concentration of ferric iron), the process comprises a mixture of dialkyl substituted orthophosphoric acid and the second component containing a phosphonyl group, thereby extracting thorium and other rare earth metal elements preferentially. Rare earth elements can also be successfully separated and recovered from sulphuric acid solutions.

As radioactive lanthanide isotopes are important products of the fission of ^{235}U , historically the ion exchange development of the technique followed the Manhattan project. Ion exchange separation of rare earth elements was initiated by Spedding and Powell. In the separation process of rare earth elements (III), the polystyrenesulphonic cation exchangers have been the most often used and rare earth cations exchanged with H^+ , NH_4^+ or other cations derived from the ion exchange phase. Charge, size and degree of hydration of the exchanged ions are the most important factors affecting their affinity for the cation exchanger. In the case of ions with the same charge, the affinity depends on their size and degree of hydration. In the lanthanide(III) group with the increasing atomic number, there is a decrease of the ionic radius but no significant differences in their affinity for the polystyrene cation exchangers were found. For this reason, the results obtained for individual rare earth elements using HCl , HBr , HNO_3 and H_2SO_4 were not promising. Only HCl and HNO_3 can be used to separate Ln(III) from the ions that occur in higher oxidation states. Similarly, it creates the possibility of separating Ce(IV) from other rare earth elements using HNO_3 . Some removal improvement of REEs can be

obtained using mineral acid solutions containing organic solvents such as methanol, ethanol, 1-propanol or acetone which significantly affects the process efficiency. Ion exchange methods involve three techniques: leaching, elution and frontal analysis. The elution technique with the use of complexing agents is usually used on an industrial scale. In this process, the order of elution of individual REEs depends on the values of stability constants of complex formation. These stability constants generally increase from light to heavy REEs. In the case of cation complexation of cations by anionic ligands, the cation exchanger prefers the cation forming the composite anion with the lowest average number of ligands and a number of analogous complexes that create the weakest complexes [33].

8.5.1 Separations of Rare Earth Elements of High Purity Using Cation Exchangers

In the case of REE separation with cation exchangers, the complexing agents used as eluents include aminopolycarboxylic acids (EDTA, NTA, HEDTA, DTPA, CDTA), carboxylic acids (acetic acid, malonic acid, maleic acid, phthalic acid), hydroxylic acids (α -hydroxyisobutyric acid, citric acid, lactic acid), keto acids (pyruvic acid), aldehyde acids (glyoxilic acid), thioacids (thiodiglycolic acid), phosphonic (1-hydroxyethane-1,1-diphosphonic) and aminophosphonic acids. However, there is a lack of the universal eluent. Therefore, the position of yttrium in the elution sequence of rare earth elements in the cation exchange systems with organic eluents is of interest; for example, yttrium(III) elutes between Dy(III)-Tb(III) with EDTA, near Nd(III) with DTPA, near Pr(III) with HEDTA, near Eu(III) with citrate at 283–293 K and Dy(III)-Ho(III) with citrate at 360–373 K, near Ho(III)-Dy(III) with lactate, near Dy(III)-Ho(III) with thiocyanate and between Sm(III)-Nd(III) with acetate. Therefore, it can be stated that the affinity for the cation exchanger and the kind of the complexing agent affected the separation process. However, the elution process depends on the stability constants (they increase from LREEs to HREEs). Among the eluents used in the process of cation exchange separation of rare earth elements, EDTA and NTA were most useful for industrial application [8, 59, 60].

8.5.2 Separations of Rare Earth Elements of High Purity Using Anion Exchangers

The ion exchange of rare earth elements on anion exchangers with organic chelating ligands has been fully investigated. However, the papers on this subject appearing in recent years indicate the particular application of anion exchangers in this field, giving new, previously unknown possibilities of their application. Anion

exchangers previously used to separate thorium(IV) and uranium(IV,VI) from lanthanides(III) solutions of mineral acids and studies of the chromatographic separation of rare earth elements (III) using anion exchangers were mainly related to isotopes of these elements and were mostly analytical, or physicochemical. In the separation process of rare earth complexes(III), the most practical importance among polystyrene-based anion exchangers was found in strongly basic, gel anion exchangers with quaternary ammonium groups. It was proved that affinity series of rare earth element(III) complexes with the aminopolycarboxylic acids for anion exchangers of various types were atypical and nonmonotonic. Application of the frontal analysis technique allowed to separate Y(III) from Ho(III);Dy(III),Er(III) and Yb(III) from Ho(III)-Er(III) using IDA (iminodiacetic acid) as well as Sm(III) from Ho(III)-Y(III); Nd(III) from Y(III); Y(III) from Ho(III)-Er(III)-Dy(III) and Yb(III) from Ho(III)-Er(III) using HEDTA ((2-hydroxyethyl) ethylenediaminetriacetic acid). In addition, based on the known affinity series of rare earth elements(III) complexes with DCTA (trans-1,2-cyclohexanodiaminotetraacetic acid) for the anion exchanger Dowex 1 $\times$ 4 the applicability of anion exchangers of polyacrylic skeleton for separation of the pairs Y(III)-Nd(III) and Y(III)-Sm(III) was shown. Also the studies to determine the effect of the addition of the polar organic solvent (methanol, ethanol, 1-propanol, 2-propanol and acetone) on separation of rare earth element(III) complexes with EDTA particularly of Y(III) from Nd(III) and Y(III) from Sm(III) were carried out [61–64]. The affinity of complexes of these elements for anion exchangers is associated with the differences in the structure of complexes being formed and physicochemical properties of anion exchangers. Moreover, it does not depend on the value of their stability constants as in the case of cation exchange of rare earth elements(III). This creates unique possibilities of separating this group of elements.

8.5.3 Separations of Rare Earth Elements of High Purity Using Chelating Ion Exchangers

Contrary to the cation and anion exchangers, chelating ion exchangers have varying degrees of affinity and selectivity with respect to rare earth elements(III). Their properties depend mainly on the nature of the functional group and less on the bead size and other physicochemical properties. The sorption selectivity particularly affects the relative position of functional groups, their spatial configuration, etc., while the less important are the properties of the matrix. Ion exchange capacity of ion exchange resins depends on the content of these groups and the pH of the solution. A negative feature is their low rate of sorption. For the separation of rare earth elements(III) and their purification from U(IV,VI), Th(IV), Fe(III), Cr(III), Cu(II), Ni(II), Co(II), Mn(II), the chelating ion exchangers with the following functional groups: phosphinic—PO(OH), phosphonic —PO(OH)₂, phosphate—OPO

(OH)₂, iminodiacetate—CH₂N(CH₂COOH)₂, iminodiacetate and aminoacetate—N-CH₂COOH, aminophosphonic—CH₂NHCH₂PO(OH)₂, carboxylic—COOH, etc. were used [33, 59, 60, 65, 66].

The chelating and selective ion exchangers were examined by Hubicki et al. [67] to separate microquantities of Sc(III) from Y(III), La(III) or lanthanides(III) by frontal analysis. The phosphonic, aminophosphonic and cellulose-phosphate ion exchangers proved to be the most effective. These ion exchangers can be used for selective separation of Sc(III) from Y(III), La(III) and Ln(III) from their salt solutions of concentrations up to 500 g/dm³ and acidity to 6 M HCl due to great stability of the complexes of scandium(III) with phosphonic and aminophosphonic acids. The phenol phosphonic acid precipitates Sc(III) in the presence of such complexing agents as citric and tartaric acids as opposed to other rare earth elements. The phosphonic ion exchanger can be used not only for selective separation of Sc(III) but also for its purification from many cations (6 M HCl solution does not elute Sc(III) by gradient elution with 0.5–6 M acid). In contrast to the phosphonic, aminophosphonic and cellulose phosphate ion exchangers the significant effect of concentration of the purified rare earth element salt on their separation from Sc(III) can be seen in the case of zirconium phosphate Bio-Rad ZPH.

Good results were also obtained using chelating ion exchangers of amino acid type in the purification of rare earth element salts from Sc(III) due to the differences in stability constants of Sc(III), Y(III), La(III) and RE(III) complexes with iminodiacetic acid. The iminodiacetic chelating ions proved to be particularly useful for the separation of Y(III) concentrates from HREE especially Yb(III) as well as preparation of La(III) of high purity. Similarly, it was used with advantage in the separation of samarium from europium by the redox chromatographic method and for the separation of Y(III) from Nd(III) using the chelating ion exchangers of amino acid type and the dilute HNO₃ solution as an eluent [68]. It was stated that the sequence of elution of Nd(III) and Y(III) for all the examined ion exchangers was not in agreement with the stability constant values of the complexes of Nd(III) and Y(III) with iminodiacetate as well as *N*-benzyl-iminodiacetate acids.

8.6 Current Technologies

There are many descriptions in the literature regarding the processing of rare earth metal raw materials, but over the last three decades, the state of knowledge has not increased significantly, which would modify the chemical technology of their separation. In previous years and at present, the development of extraction methods for separation of REE proceeded simultaneously to the ion exchange method which is the most successful to obtain these elements with a high degree of purity, as the final product of the concentrates obtained in the extraction process.

In 2005, Grirem Advanced Materials Co., Ltd. developed an environmentally friendly hydrometallurgical separation process. A non-saponification solvent extraction process based on hydrochloric acid and sulphuric acid was developed to

separate Nd(III) and Sm(III). In 2008, the separation method of quadrivalent cerium, thorium and fluorine as well as to a small extent trivalent cerium from sulphate solution was introduced with the synergistic extraction stage based on P507 (2-ethylhexyl 2-ethylhexyl phosphate) or P204 (di(2-ethylhexyl)phosphoric acid). Cerium, thorium, fluorine and iron were extracted into an organic phase.

In the literature, descriptions of new extractants are available. For example, sec-nonylphenoxy acetic acid (CA-100) was developed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The studies indicated that this extractant employed on a commercial scale has several advantages including stable composition, easy preparation, stronger acidity and low solubility in the aqueous phase [69]. The only disadvantages were: limitation of the extraction system for separation of yttrium over other HREE (low separation factors), two steps for yttrium separation from the impurities after removing the light and middle lanthanides. These can be overcome in heavy lanthanides in the CA-100-EDTA systems. The separation factors of yttrium with respect to Yb, Tm or Er increased with an increase of pH, and the maximum separation was at $[CA-100] > 0.04$ mol/l and $[EDTA]:[HRE] = 1:2$. Because of both EDTA and other complexing agents (DTPA, e.g. diethylenetriaminepentaacetic acid and HEDTA, e.g. *N*-hydroxyethylethylenediaminetriacetic acid) form 1:1 complex with rare earth elements, only free (not complexed) rare earth ions take part in the extraction.

A new approach is the molecular recognition technology (MRT) using SuperLig[™]. This is an excellent method for improving metal recovery, recycling and end product fabrication processes during metal life cycles with significant operating advantages and environmental gains over traditional procedures. The SuperLig[®] system consists of a solid support particle, silica gel, to which a metal-selective ligand 18-crown-6 is attached. Therefore, the MRT system is based on green chemistry principles. In this case, minimal waste is generated (chemicals are used only for washing and elution of columns). No organic solvents are used. Moreover, energy requirements are minimal. First of all high selectivity of the SuperLig[®] products makes separation and recovery of REE possible from the leach solutions at >99% purity level, and subsequent separation of individual REE at >99% levels [70].

To develop sustainable and efficient separation technology for HREEs, the extraction of Lu(III) and neighbouring HREEs using EHEHP type acid-base coupling bifunctional ionic liquid (ABC-BIL) was presented by Dong et al. [71]. Due to low volatility and combustibility, wide liquid range, thermal stability, adjustable functional group and high conductivity, ILs have been found suitable for solvent extraction of REEs [72, 73]. Among bifunctional ILs such as tricaprylmethylammonium sec-octylphenoxy acetates ([A366][CA-12]), tricaprylmethylammonium sec-nonylphenoxy acetates ([A336][CA-100]) in chloride medium were studied [74]. The results indicated that the bifunctional ILs exhibited by the higher efficiencies than the conventional CA-12, CA-100, TBP or P350 extractants. It was also proved that ILs with bis(2-ethylhexyl)phosphate anion can also be applied [75].

Current and future approach to the separation of REEs should include economic aspects for their recovery: low carbon footprint, closed loop for most critical elements, possibility to close the loop for other strategic elements. It is obvious that the

new solvents can help with better separation of REEs to obtain good selectivity. The introduction of more friendly solvents (limitation of the use of petroleum derivative solvents), as well as new synergistic formulations and reduction of salt effluent generation, is also a great challenge. Perhaps applying ionic liquids on the commercial scale and development of new technologies others than solvent extraction will be new approaches in the near future.

Equally important are more environmentally friendly mining and processing operations for new mines and collaboration with China to improve mining operations, extended producer responsibility, more efficient use of REEs in applications or substitution as well as the development of recycling processes for rare-earth-containing products. For example, recycling of NdFeB magnets to recover Nd and Dy means that less primary ores have to be mined to ensure supply of Nd and Dy. Less mining means less overproduction of cerium and samarium. Moreover, recycling of Eu, Tb and Y from lamp phosphors helps to maintain the balance of HREEs.

8.7 Conclusions

Separation of individual REEs on an industrial scale is very complex. Obtaining REEs of high purity requires purification of their concentrates. This is usually achieved by precipitation of REEs as double sulphates $\text{NaLn}(\text{SO}_4)_2$ or oxalates $\text{Ln}_2(\text{C}_2\text{O}_4)_3$ as well as extraction and/or ion exchange method application. The details connected with the general characteristics, occurrence, physicochemical properties, application and production of REEs in the world as well as their separations by the solvent extraction and ion exchange processes were described in the paper. It should be also mentioned that their separation together with the spectral, magnetic and coordinative properties of REEs is essential for their further applications.

References

1. Gueroult R, Rax JM, Fisch NJ (2018) Opportunities for plasma separation techniques in rare earth elements recycling. *J Clean Prod* 182:1060–1069
2. Klinger JM (2018) Rare earth elements: Development, sustainability and policy issues. *Extr Ind Soc* 5:1–7
3. Chakhmouradian AR, Wall F (2012) Rare earth elements: Minerals, mines, magnets (and more). *Elements* 8:333–340
4. Brown TJ, Shaw RA, Bide T, Petavratzi E, Raycraft ER, Walters AS (2013) World mineral production 2007–2011, British Geological Survey
5. Anielak AM (2000) Chemiczne i fizykochemiczne oczyszczanie ścieków. Wydawnictwo Naukowe PWN Warszawa (in Polish)
6. Binnemans K, Jones PT, Blanpain B, Van Gerven T, Yang Y, Walton A, Buchert M (2013) Recycling of rare earths: A critical review. *J Clean Prod* 51:1–22

7. Innocenzi V, De Michelis I, Ferella F, Veglio F (2016) Rare earths from secondary sources: profitability study. *Adv Environ Res* 5:125–140
8. Jha MK, Kumari A, Panda R, Rajesh Kumar J, Yoo K, Lee JY (2016) Review on hydrometallurgical recovery of rare earth metals. *Hydrometallurgy* 165:2–26
9. Kanazawa Y, Kamitani M (2006) Rare earth minerals and resources in the world. *J Alloys Compd* 408–412:1339–1343
10. Castor SB, Hedrick JB (2006) Rare Earth Elements. *Soc Mining, Metall Explor* 769–792
11. Aide MT, Aide C (2012) Rare earth elements: their importance in understanding Soil Genesis. *ISRN Soil Sci* 12:1–11
12. Charalampides G, Vatalis KI, Apostoplos B, Ploutarch-Nikolas B (2015) Rare Earth Elements: Industrial Applications and Economic Dependency of Europe. *Procedia Econ Financ* 24:126–135
13. Porowski A, Kaczor-Kurzawa D (2016) Pierwiastki ziem rzadkich (REE) w wodach termalnych: występowanie, pochodzenie, znaczenie i perspektywy badań w Polsce. *Tech Poszuk Geol Geoterm Zrównoważony Rozw* 1:89–102 (in Polish)
14. Dutta T, Kim KH, Uchimiya M, Eilhann EK, Jeon BH, Deep A, Yun ST (2016) Global demand for rare earth resources and strategies for green mining. *Environ Res* 150:182–190
15. Humphries M (2013) Rare Earth Elements: The Global Supply Chain. *Congr Res Serv* 27
16. Rydel P, Nowak M (2015) Review of the major minerals of rare earth elements—gold of the 21st century. *Przegląd Geol* 63:348–362
17. Jeżowska-Trzebiatowska B, Kopacz S, Mikulski T (1976) Pierwiastki rzadkie część I Występowanie i technologia. Państwowe Wydawnictwo Naukowe, Warszawa
18. Haxel GB, Hedrick JB, Orris GJ (2002) Rare earth elements—critical resources for high technology. *United States Geol Surv Fact Sheet* 87:4
19. Charewicz W (1990) Pierwiastki ziem rzadkich: surowce, technologie, zastosowania: opracowanie zbiorowe. Wydawnictwa Naukowo-Techniczne, Warszawa (in Polish)
20. Kabata-Pendias A, Mukherjee AB (2007) Trace elements from Soil to Human. Springer, Berlin
21. Henderson P (1984) General geochemical properties and abundances of the rare earth elements. *Rare Earth Element Geochemistry*. Elsevier, London, pp 1–32
22. Goering PL, Fisher BR, Fowler BA (1991) The Lanthanides. In: *Metals and their compounds in the environment: occurrence, analysis, and biological relevance*. pp 959–970
23. Jarosinski A (2016) Możliwości pozyskiwania metali ziem rzadkich w Polsce. *Zesz Nauk Inst Gospod Surowcami Miner i Energią Pol Akad Nauk* 75–88
24. Davris P, Balomenos E, Taxiarchou M, Pnias D, Paspaliaris I (2017) Current and Alternative Routes in the Production of Rare Earth Elements. *BHM Bergund Hüttenmännische Monatshefte* 162:245–251
25. Deng M, Xu C, Song W, Tang H, Liu Y, Zhang Q, Zhou Y, Feng M, Wei C (2017) REE mineralization in the Bayan Obo deposit, China: Evidence from mineral paragenesis. *Ore Geol Rev* 91:100–109
26. Alonso W, Sherman E, Wallington AM, Everson TJ, Field MP, Roth FF, Kirchain RE (2012) Evaluating Rare Earth Element Availability: A Case with Revolutionary Demand from Clean Technologies. *Environ Sci Technol* 46:3406–3414
27. Alonso E, Sherman AM, Wallington TJ, Everson MP, Field FR, Roth R, Kirchain RE (2012) Evaluating rare earth element availability: A case with revolutionary demand from clean technologies. *Environ Sci Technol* 46:3406–3414
28. Klinger JM (2015) A historical geography of rare earth elements: From discovery to the atomic age. *Extr Ind Soc* 2:572–580
29. Bielański A (2002) Podstawy chemii nieorganicznej. Wydawnictwo Naukowe PWN, Warszawa (in Polish)
30. Cotton S (2006) Lanthanide and Actinide Chemistry. Chichester
31. Huang C (2010) Rare Earth Coordination Chemistry Fundamentals and Applications. John Wiley & Sons, Asia
32. Cotton SA, Raithby PR (2017) Systematics and surprises in lanthanide coordination chemistry. *Coord Chem Rev* 340:220–231

33. Kołodyńska D, Hubicki Z (2012) Investigation of sorption and separation of the lanthanides on the ion exchangers of various types. In: Ion Exchange Technologies A. Kilislioglu (ed) ISBN 980-953-307-139-3, str. 101-154, <http://dx.doi.org/10.5772/50857>
34. Massari S, Ruberti M (2013) Rare earth elements as critical raw materials: Focus on international markets and future strategies. *Resour Policy* 38:36–43
35. Akah A (2017) Application of rare earths in fluid catalytic cracking: A review. *J Rare Earths* 35:941–956
36. Gschneidner KA (2009) The rare earth crisis -the supply demand. Situation for 2010–2015. *Mater Matters* 6
37. Zhou B, Li Z, Chen C (2017) Global potential of rare earth resources and rare earth demand from clean technologies. *Minerals* 7:1–14
38. Gonzalez V, Vignati DAL, Leyval C, Giamberini L (2014) Environmental fate and ecotoxicity of lanthanides: Are they a uniform group beyond chemistry? *Environ Int* 71:148–157
39. Gambogi J (2015) U.S. Geological Survey, Mineral Commodity Summaries
40. Gambogi J (2017) U.S. Geological Survey, Mineral Commodity Summaries
41. Bütikofer R (2015) Erecon: Strengthening the European rare earth supply-chain, Challenges and policy options
42. Sozański A (1981) Industrial methods for separation of thorium from rare earth elements. *Prace Naukowe Instytutu Chemii Nieorganicznej i Pierwiotków Rzadkich Politechniki Wrocławskiej*, Wrocław
43. Leveque A (2014) Extraction and separation of Rare Earths, EREAN Summer School Leuven University, 19 August 2014
44. Schüler D, Buchert M, Liu R, Dittrich S, Merz C (2011), Study on Rare Earths and Their Recycling, Final Report for The Greens/EFA Group in the European Parliament
45. Umicore (2014) Rechargeable Batteries (storing energy). Retrieved from <http://www.umicore.com/en/cleanTechnologies/batteries/>. Accessed 20 Apr 2018
46. Saubermacher (2014) Leistungen: Entsorgungslösungen. Retrieved from <http://www.saubermacher.at/de/leistungen/#elektroaltgeraeteentsorgung>. Accessed 24 Apr 2018
47. Müller T, Friedrich B (2006) Development of a recycling process for nickel-metal hydride batteries. *J Power Sources* 158:1498–1509
48. Lyman JW, Palmer GR (1995) Hydrometallurgical treatment of nickel-metal hydride battery electrodes. In: In Third International Symposium on Recycling of Metals and Engineered Materials. November 12–15. Point Clear, Alabama (USA) 131–144
49. Yoshida T, Ono H, Shirai R (1995) Recycling of used Ni-MH rechargeable batteries. *Miner Met Mater Soc* 145–152
50. Zhang P, Yokoyama T, Itabashi O, Wakui Y, Suzuki TM, Inoue K (1998) Hydrometallurgical process for recovery of metal values from spent nickel-metal hydride secondary batteries. *J Power Sources* 50:61–75
51. Zhang P, Yokoyama T, Itabashi O, Wakui Y, Suzuki TM, Inoue K (1999) Recovery of metal values from spent nickel-metal hydride rechargeable batteries. *J Power Sources* 77:116–122
52. Li L, Xu S, Ju Z, Wu F (2009) Recovery of Ni, Co and rare earths from spent Ni-metal hydride batteries and preparation of spherical Ni(OH)₂. *Hydrometallurgy* 100:41–46
53. Gasser MS, Aly MI (2013) Separation and recovery of rare earth elements from spent nickel-metal-hydride batteries using synthetic adsorbent. *Int J Miner Process* 121:31–38
54. Kanamori T, Matsuda M, Miyake M (2009) Recovery of rare metal compounds from nickel-metal hydride battery waste and their application to CH₄ dry reforming catalyst. *J Hazard Mater* 169:240–245
55. Provazi K, Campos BA, Espinosa DCR, Tenório JAS (2011) Metal separation from mixed types of batteries using selective precipitation and liquid-liquid extraction techniques. *Waste Manag* 31:59–64
56. Larsson K, Ekberg C, Odegaard-Jensen A (2011) Metal separation after selective dissolution of nickel metal hydride batteries. 19th International Solvent Extraction Conference (ISEC2011), 3-7 October 2011. Santiago, Chili, pp 38–45

57. Becker K, Chmielarz A, Szołomicki Z, Gotfryd L, Piwonońska J, Pietek G, Pokora M (2016) Hydrometalurgiczny recykling akumulatorów Ni-MH i Li-ion. *Rudy i Met Nieżelazne Recykling* 61(6):235–243 (in Polish)
58. Coey JMD (2012) Permanent magnets: Plugging the gap. *Scr Mater* 67:524–529. <https://doi.org/10.1016/j.scriptamat.2012.04.036>
59. Hubicka H, Drobek D (2000) Studies on separation of intermediate and heavy lanthanide complexes with iminodiacetic acid on anion-exchangers. *Chem Environ Res* 9:245–257
60. Hubicka H, Kołodyńska D (2000) Study on separation of lanthanum from praseodymium complexes with IMDA by gel and macroporous anion-exchangers. *J Rare Earths* 18:90–96
61. Hubicka H, Kołodyńska D (2004) Separation of rare earth element complexes with trans-1,2-diaminocyclohexane-N, N, N', N'-tetraacetic acid on the polyacrylate anion-exchangers. *Hydrometallurgy* 71:343–350
62. Hubicka H, Kołodyńska D (2005) Effects of polar organic solvent on the separation of the Y(edta)/Nd(edta)⁻ complexes on polyacrylic anion exchangers. *J Rare Earths* 23:124–128
63. Hubicka H, Kołodyńska D (2008) Application of monodisperse anion exchangers in sorption and separation of Y³⁺ from Nd³⁺ complexes with DCTA. *J Rare Earths* 26:619–625
64. Kołodyńska D, Hubicka H, Hubicki Z (2008) Sorption of heavy metal ions from aqueous solutions in the presence of EDTA on monodisperse anion exchangers. *Desalination* 227:150–166
65. Hubicka H, Kołodyńska D (2004) Studies of applicability of strongly and weakly basic polystyrene and polyacrylate anion exchangers for separation of Y(edta)⁻ from Sm(edta)⁻ complexes. *Chem Environ Res* 13:73–85
66. Hubicka H, Kołodyńska D (2004) Separation of rare-earth element complexes with trans-1,2-diaminocyclohexane-N, N, N', N'-tetraacetic acid on polyacrylate anion exchangers. *Hydrometallurgy* 71:343–350
67. Hubicki Z (1990) Studies on selective separation of Sc(III) from rare earth elements on selective ion exchangers. *Hydrometallurgy* 23:319–331
68. Hubicka H, Hubicki Z (1992) Studies on separation of pair Y(III)-Nd(III) on chelating ion exchangers of aminoacid type using aminopolyacetic acids as eluents. *Hung J Ind Chem* 20:249–254
69. Wang YG, Xiong Y, Meng SL, Li DQ (2004) Separation of yttrium from heavy lanthanide by CA-100 using the complexing agent. *Talanta* 63:239–243
70. Izatt SR, McKenzie JS, Izatt NE, Bruening RL, Krakowiak KE, Izatt RM (2016) Molecular recognition technology: a green chemistry. Process for separation of individual rare earth metals, White Pap Sep Rare Earth Elem
71. Dong Y, Sun X, Wang Y, Chai Y (2015) The development of an extraction strategy based on EHEHP-type functional ionic liquid for heavy rare earth element separation. *Hydrometallurgy* 157:256–260
72. Quinn JE, Soldenhoff KH, Stevens GW (2017) Solvent extraction of rare earths using a bifunctional ionic liquid. Part 1: Interaction with acidic solutions. *Hydrometallurgy* 169:306–313
73. Quinn JE, Soldenhoff KH, Stevens GW (2017) Solvent extraction of rare earth elements using a bifunctional ionic liquid. Part 2: Separation of rare earth elements. *Hydroamtealrgy* 169:621–629
74. Wang W, Yang HL, Cui HM, Zhang DL, Liu Y, Chen J (2011) Application of bifunctional ionic liquid extractants [A336][CA-12] and [A336][CA-100] to the lanthanum extraction and separation from rare earths in the chloride medium. *Ind Eng Chem Res* 50:7534–7541
75. Rout A, Kotlarska J, Dehaen W, Binnemans K (2013) Liquid–liquid extraction of neodymium (III) by dialkylphosphate ionic liquids from acidic medium: the importance of the ionic liquid cation. *Phys Chem Chem Phys* 15:16533–16541